Identification and simultaneous optimisation of Tunisian clay properties: Preliminary study for the ceramic products

Salah Mahmoudi[1]*, Ezzeddine Srasra[2], Fouad Zargouni[3]

[1]**Department of Earth Sciences, Faculty of Sciences of Gabes, 6072, Zrig, Gabes, (TUNISIA)**
[2]**Materials Center, Technopolis of Borj Cedria, BP95, 2050, Hammam Lif, (TUNISIA)**
[3]**Department of geology, Faculty of Sciences of Tunis, 1060 Belvédère, Tunis, (TUNISIA)**
E-mail : salahmahmoudii@yahoo.fr

ABSTRACT

The relationship between composition and physical parameters such as specific surface area, cationic exchange capacity and plasticity is studied with the aim of developing regression models that would permit the prediction of clay properties. These models could be useful for mineralogists and industrial applications. Nineteen representative clay samples were collected from Jebel Ressas in north-eastern Tunisia. Mineralogical data show that clay samples cover a very large variety of minerals. The main clay mineral is illite (50–60 wt.%), secondary minerals including quartz, calcite and minor amounts of Na–feldspar. This study reveals that the average amount of silica (SiO_2) and alumina (Al_2O_3) are 51.9 and 19.6 wt.%., respectively. The contents of lime (CaO) and iron (Fe_2O_3) vary between 4 and 8 wt.% whereas the amount of alkalis ($Na_2O + K_2O$) is on average 4.1 wt.%. The grain size data indicates a significant amount of silt fraction, and the fraction < 2 µm varies between 23 and 35 wt.%. Values for plasticity index range from 16 to 28 wt.%. The cation exchange capacity and the specific surface values are 34.1 – 45.7meq/100g of air–dried clay and 302 – 374 m²/g, respectively. Lastly, regression models are used to correlate the properties with the mineralogical and chemical compositions. The significance and the validity of models were confirmed by statistical analysis and verification experiments. The regression models can be used to select the clay properties (plasticity index, cation exchange capacity and specific surface) in relation with clay minerals proportions and the finer fraction amounts.

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KEYWORDS

Clay characterization;
Regression models;
Physical properties;
Atterberg limits.

INTRODUCTION

Clay materials are secondary sedimentary products found in many parts of the world. They occur essentially in geological formations of Mesozoic and Cenozoic era. They have been an important natural raw material, and have a large variety of uses in geology, agriculture, construction, engineering, process industries and environmental applications. In particular, clays are widely used in the manufacture of many traditional ceramics. Each ceramic body-product requires clays having particular and appropriate compositions. In order to have the best quality of the end product, we must identify the raw material and know the relationship be-

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tween mineralogical and physical parameters.

Our study area includes Jebel Ressas in north-eastern Tunisia; the clay sediments are composed of Aptian clays alternating with occasional sandstone units (Figure 1). The average thickness of useful clays is 380 m. The geology of the study area and its surroundings have been reported by[33,3,10,21,11]. This work is integrated within the research program dealing with the characteristics (mineralogical, chemical and physical properties ceramic) of the raw materials located in the region proximal to the ceramic factories (30–40 km from Tunis, the Tunisian capital).

Many studies[32,2,27,20,28,1,24,13,9] show that the plasticity is greatly related to the amounts of clay minerals and finer fraction in the clays. On the other hand, the argillaceous rocks are characterized by a specific surface and cation exchange capacity, which vary when the proportions of clay minerals and finer fraction vary[25,4] centred on the establishment of a mathematical model between mineralogical–granulometric analyses and physical parameters. No study has been established for simultaneous optimisation of the Tunisian clay

properties up-to-date. The mineralogical and physical properties of Aptian clays taken from Jebel Ressas were measured to assess its suitability as raw materials for traditional ceramics.

MATERIALS AND METHODS

Nineteen samples were taken from the study area. In order to ensure a representative sample, no less than 5 kg of clay was collected from Jebel Ressas in north-eastern Tunisia, every 20 m-along a line. The raw materials were initially dried at 105 °C until a constant weight was achieved, and they were powdered for 30 min. To prepare the oriented aggregates, the clay-size fraction was purified by classical methods. In fact, the raw material was completely decarbonated by adding a small amount of 1 N HCl, and treated with H_2O_2 to eliminate organic matter. The material was washed five times with 1 N NaCl, excess salt being removed by dialysis. The fraction $< 2\mu m$ was separated in a centrifuge, and the suspension was dried at 60 °C[14,31,21].

The mineralogical analyses of samples were carried out by X–ray diffraction (XRD) analysis with a Philips X'Pert diffractmeter using CuKα radiation (1.5418 Å). Diffraction data were collected in the range from 2° to 70°. The accelerating voltage and filament current were maintained at 40 kV and 40 mA, respectively.

The concentrations of major elements of the raw materials were determined with atomic absorption spectroscopy, after tri–acid digestion of each sample in mixtures of $HCl – H_2SO_4 – HNO_3$. Loss on ignition (LOI) was measured from total weight after ignition at 1000 °C for 2 h. The experimental error is $\pm 2\%$.

The cation exchange capacity (CEC) is measured using the standard acetate ammonium procedure[23]. Each cation was measured in meq/100g and after the sum of exchangeable bases was determined.

Specific surface area was determined with methylene blue index method. A suspension of 10 g of powdered clay and 100 mL of distilled water was prepared and mixed with a methylene blue solution (10g/L). One drop of this suspension is then placed upon filter paper and the value for the specific surface is derived from the quantity of adsorbed methylene blue[12]. It is used to classify the argillaceous fraction activity and to detect expandable clay minerals like smectite.
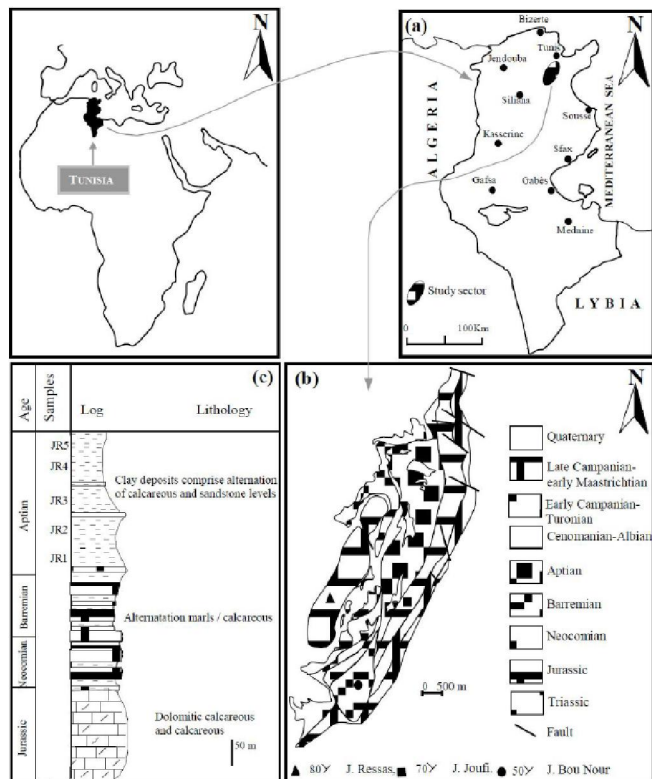

Figure 1 : (a) The geographic; (b) geological situation of the study sector (Turki, 1988); (c) synthetic lithostratigraphic log of J. Ressas

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TABLE 1 : The mineralogical and chemical analyses of studied clays. Cm: Clay minerals; Qz: Quartz; Cc: Calcite; Fel: Feldspar

	Chemical compositions (%)										Mineralogical compositions (%)			
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	LOI	Cm	Qz	Cc	*Fel*
JR1	53.4	18.6	6.1	5.4	1.8	0.9	3.1	0.4	0.3	9.2	48	23	18	*11*
JR2	50.1	20.1	5.5	7.2	1.5	0.8	3.2	0.3	0.3	10.7	42	28	23	*07*
JR3	52.1	18.4	6.1	8.2	1.3	0.9	3.8	0.2	0.2	7.8	57	21	15	*07*
JR4	49.2	19.2	7.6	6.6	1.2	0.5	3.0	0.4	0.5	11.1	53	18	20	*09*
JR5	48.4	19.1	6.7	7.5	1.0	0.7	3.9	0.6	0.3	11.2	51	23	20	*06*
JR6	54.2	17.4	5.8	6.9	0.9	0.6	3.3	0.4	0.2	9.4	60	19	15	*6*
JR7	55.8	17.2	5.1	6.9	0.7	0.6	2.9	0.2	0.3	9.7	65	15	12	*08*
JR8	48.6	18.7	7.4	7.7	0.6	0.3	3.3	0.2	0.2	12.3	51	18	18	*13*
JR9	47.8	21.3	7.6	6.9	0.7	0.8	3.5	0.3	0.3	10.4	55	20	17	*08*
JR10	52.1	20.8	5.8	7.4	0.4	0.6	3.2	0.2	0.4	8.3	49	17	26	*08*
JR11	54.8	23.5	6.2	4.6	0.5	0.8	2.5	0.1	0.6	6.3	50	20	20	*10*
JR12	55.6	18.6	5.6	7.9	0.2	0.4	4.0	0.2	0.6	6.2	47	24	18	*11*
JR13	51.7	20.6	6.7	5.8	0.4	0.6	3.2	0.4	0.3	9.8	45	24	20	*11*
JR14	51.1	20.8	5.4	6.8	0.3	0.9	3.7	0.3	0.3	9.9	42	24	20	*14*
JR15	48.9	22.5	6.3	5.9	0.4	0.8	3.8	0.5	0.4	9.7	40	27	20	*13*
JR16	47.5	19.8	7.3	6.4	0.8	0.9	3.8	0.6	0.3	11.7	44	30	18	*08*
JR17	52.5	19.2	4.2	7.2	1.3	0.8	3.7	0.3	0.5	9.5	44	27	20	*09*
JR18	56.6	19.8	5.5	4.2	1.2	0.6	3.8	0.5	0.5	6.7	48	22	18	*12*
JR19	55.9	20.5	4.1	5.1	1.9	0.7	3.4	0.5	0.3	6.9	45	24	23	08

The Atterberg Limits include liquid limit (LL), plastic limit (PL) and plastic index (PI), where PI =LL"PL[27,1,36,24]. These parameters were determined by the Casagrande method (Casagrande; 1948), in accordance with the French Standard NF P 94-051.

For the fraction inferior to 63 mm, the grain-size distribution was determined by a Micromeritics 5000 sedigraph.

RESULTS AND DISCUSSION

Clay characterization

The X–ray diffraction analysis of the total samples (TABLE 1) indicates the dominance of clay minerals (40–65 wt.%), moderate presence of quartz and calcite (15–30 wt.% and 15–26 wt.%, respectively) and minor amounts of feldspars (6–14 wt.%). The purified fraction shows illitic clays with moderate amounts of kaolinite and minor proportions of interstratified illite/smectite (Figure 2). These illitic compositions are suitable for traditional ceramic and similar to those reported in the literature[5,12,29,35].
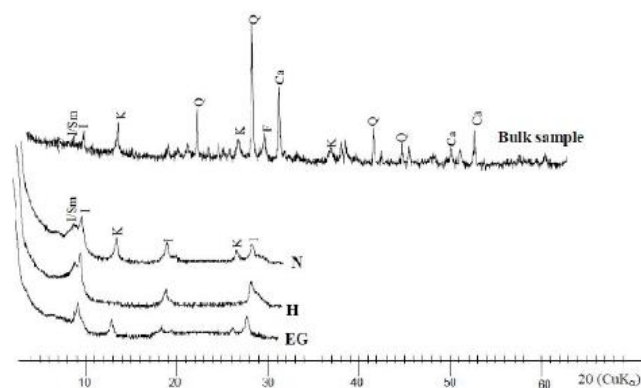

Figure 2 : XRD patterns of bulk sample and fine fraction of studied sample; N: Normal; EG: saturated with ethylene glycol; H: heated at 550°C; Q: quartz; Ca: calcite; F: feldspars; I: illite; K: kaolinite and I/Sm: interstratified illite/ smectite

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The results of the concentrations of major elements are reported in TABLE 1. SiO_2 content is between 47.5 and 56.6 wt.%, with an average value of 51.9 wt.%. The wt.% of Al_2O_3 varies between 17.2 and 23.5 wt.%, with an average value of 19.6 wt.%. The average ratio for SiO_2/Al_2O_3 concentration is: 2.64, indicates that the clays are mixed 1/1 with 2/1 dioctahedral phyllosilicates. On the other hand, this value is slightly high with regards to the classic value which equals 2 due to the presence of free silica[25].The study samples also contain concentrations of Fe_2O_3 (average 6 wt.%), responsible for reddish colour of the fired products[17,19]. This means that the clays are suitable for traditional ceramic. These clays show that the average amount of alkalis ($Na_2O + K_2O$) is 4.1 wt.%, explaining why these samples mature at relatively low temperatures. The study samples appear to be chemically homogeneous, having nearly the same geochemical characteristics. On this side, we can consider that the studied sector constitute a mine of clays.

The granulometric analysis (TABLE 2) reveals that the fraction $< 2\mu m$ varies between 23 and 35 wt.% but the fraction $> 63\mu m$ is very minor (average 11 wt.%). The grain size data indicate a significant amount of silt material.

Atterberg limits for the study samples (TABLE 1) are liquid limit LL (40 ± 4 wt.%) and plastic index PI (22 ± 6 wt.%), which indicates that these clays belong to the domain of illitic clays (Figure 3), having moderate plastic properties according to the Holtz and Kovacs (1981) diagram. These parameters, plotted in the
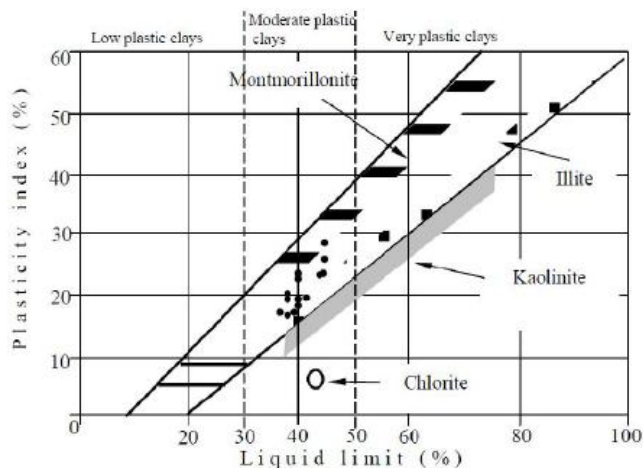

Figure 3 : Plot of the study clays on the Holtz and Kovacs diagram (Holtz and Kovacs, 1981)

Casagrande chart[16] indicate that these samples have optimum properties (Figure 4) and are suitable and encouraging for optimal behaviour in pressing (cohesion) and drying (negligible contraction) which are in agreement with the range defined in the literature for ceramic production[34]. The plasticity results agree with mineralogical results.
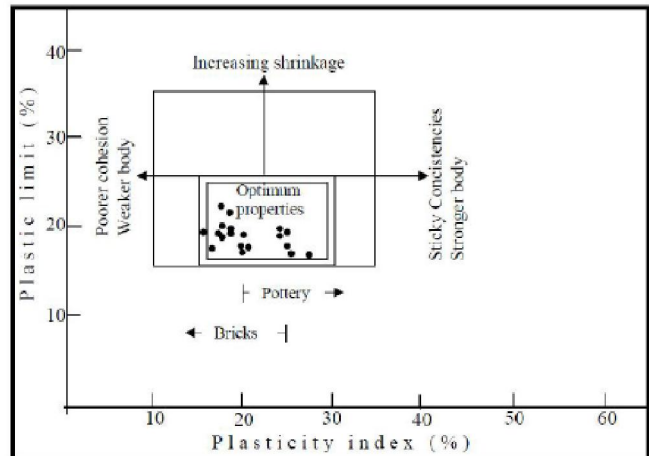

Figure 4 : Plot of study samples on the Casagrande chart (Casagrande, 1948)

The CEC and SS are listed in TABLE 2. The greatest value of CEC and SS are 45.7meq/100g of air–dried clay and 374 m^2/g, respectively and indicate the lack of expansible clay minerals such as smectite and vermiculite. These results are in agreement with the plasticity data.

Simultaneous optimisation of clay properties

Based on the data obtained (TABLE 1), regression equations can be thought for the properties analysed of each clay sample. The mathematical equations (1), (2) and (3) are expressed in their canonical form as second–degree polynomials, these Eqs. can relate each property with the clay minerals (c) and the finer (g) fraction ($< 2\mu m$). The mathematic model is valid, when the error ε (ε: difference between measured and calculated values) is uncorrelated and randomly distributed with a zero mean value and a common variance[7,26,8].

$$PI(c,g) = \sum_{i=0}^{n} \alpha_i \, c^i \, g^{n-1} \tag{1}$$

$$SS(c,g) = \sum_{i=0}^{n} \beta_i \, c^i \, g^{n-1} \tag{2}$$

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TABLE 2 : The geotechnical and physical parameters of studied clays. LL: liquid limit; PL: plastic limit; PI: plastic index; CEC: cation exchange capacity; SS: specific surface

	Plasticity (wt.%)			Microgranulometry (wt.%)						Physical analyses	
	LL	PL	PI	> 63 µm	50–63µm	50–20µm	10–20µm	10–2µm	<2 µm	CEC (meq/100 of air-dried clay)	SS (m²/g)
JR1	38	18	20	16.2	8.7	16.1	22	12	25	39.1	321
JR2	38	19	19	13.1	14.7	14	24.5	12.7	21	341	309
JR3	40	16	24	11.4	12.1	10.7	19	16.8	30	43.8	357
JR4	40	17	23	6.2	11.4	18	20	16.4	28	40.8	350
JR5	40	17	23	6.8	12.9	17	20	16.3	27	41.9	342
JR6	44	18	26	12	9.6	10	23.2	13.2	32	43.9	370
JR7	44	16	28	6.1	9.7	10.2	23	16	35	45.7	374
JR8	44	21	23	10.3	12.9	16.4	13.4	20	27	40.5	344
JR9	44	20	24	13.1	8.9	20.1	14	14.9	29	43.1	351
JR10	42	23	19	13.7	11.6	19.8	18.5	12.4	24	38.2	348
JR11	40	21	19	12.5	12.5	16.8	17	16.2	25	39.8	324
JR12	38	18	20	10.1	13.7	19.7	14.5	18	24	39.1	351
JR13	38	18	20	12.3	14.6	10	16.9	22.2	24	38.7	316
JR14	36	19	17	10.7	14.2	9.2	20	22.9	23	36.5	312
JR15	40	22	18	9.3	13.4	10	19.6	24.7	23	37.1	302
JR16	40	21	19	9.8	10.6	12	20.4	20.2	27	37.4	312
JR17	36	20	16	12.4	13.1	14.3	15.2	20	25	37.6	307
JR18	38	19	19	11	10.6	15.1	18.7	18.6	26	39.9	319
JR19	36	18	18	10.4	7.1	14.7	22.4	19.4	26	38.6	314

$$CEC\,(c,g) = \sum_{i=0}^{n} \lambda_i\, c^i\, g^{n-1} \tag{3}$$

where PI: Plastic Index; SS: Specific Surface; CEC: Cation Exchange Capacities; c is the wt. % of the clay minerals; g is the wt. % of the finer fraction ($<2\mu m$); $\alpha_i \in \mathbb{R}$; $\beta_i \in \mathbb{R}$; $\lambda_i \in \mathbb{R}$ and $i \in [0\ 2]$.

The experimental results were used to calculate the coefficients of the regression equations relating the PI, SS and CEC with the proportion of c and g in the raw materials. The calculations were carried out with MATLAB 7.5.0.

$$PI\,(c,g) = -\,0.004\,c^2 + 0.0329\,g^2 + 0.0031\,cg + 0.6693\,c - 1.78\,g + 17.2602 \tag{4}$$

$$SS\,(c,g) = 0.0071\,c^2 - 0.0993\,g^2 + 0.0121\,cg + 3.5718\,c + 1.7661\,g + 146.6228 \tag{5}$$

$$CEC\,(c,g) = 0.0369\,c^2 - 0.1442\,g^2 - 0.0029\,cg - 3.0367\,c + 7.656\,g + 2.1575 \tag{6}$$

The Eqs. (4), (5) and (6) are the final results and the values obtained from these mathematical models show that PI, SS and CEC are 16.95–28.91 w.% 300.07–376.48 m²/g and 36.71–45.39 meq/100g, respectively. The significance and the validity of the mathematical models can also be evaluated by comparing the experimental and the calculated error (TABLE 3). The margin of error between the calculated and the measured values is less than 7.9 w.%. Indeed, the calculated values reveal that these clays are characterised by a moderate plasticity, having low CEC and SS. This suggests that the developed model is valid,

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TABLE 3 : The errors between measured and calculated values. PI: wt.%; CEC: meq/100 of air-dried clay; SS: m2/g; Error: wt.%

|	PI measured	PI calculated	Error	CEC measured	CEC calculated	Error	SS measured	SS calculated	Error
JR1	20	19.9531	0.23	39.1	39.2085	0.27	321	331.0376	*3.12*
JR2	19	18.1779	4.32	34.1	34.3337	0.68	309	313.1318	*1.33*
JR3	24	23.9253	0.31	43.8	43.8947	0.21	357	357.5873	*0.16*
JR4	23	22.0511	4.12	40.8	41.8761	2.63	350	345.4281	*1.3*
JR5	23	21.1833	7.89	41.9	40.8596	2.48	342	339.2084	*0.81*
JR6	26	25.6998	1.15	43.9	44.5587	1.5	370	364.5548	*1.47*
JR7	28	28.9197	3.28	45.7	45.3920	0.67	374	376.4858	*0.66*
JR8	23	21.1833	7.89	40.5	40.8596	0.88	344	339.2084	*1.39*
JR9	24	22.9651	4.31	43.1	42.8878	0.49	351	351.5544	*0.15*
JR10	19	20.3279	6.98	38.2	39.2305	2.69	348	338.1073	*2.84*
JR11	19	20.6627	8.75	39.8	40.2225	1.06	324	340.1778	*4.99*
JR12	20	19.6085	1.95	39.1	38.3583	1.89	351	329.0197	*6.26*
JR13	20	18.8571	5.71	38.7	37.7813	2.37	316	319.9889	*1.26*
JR14	17	17.7735	4.54	36.5	36.7125	0.58	312	319.9889	*2.56*
JR15	18	16.9483	5.84	37.1	36.8677	0.62	302	300.0774	*0.63*
JR16	19	18.5723	2.25	37.4	38.1261	1.94	312	307.1974	*1.53*
JR17	16	19.9531	2.47	37.6	38.0661	1.23	307	312.9276	*1.93*
JR18	19	19.9998	5.26	39.9	39.3711	1.32	319	328.3202	*2.92*
JR19	*18*	*18.8661*	*4.81*	*38.6*	*38.4123*	*0.48*	*314*	*314.6801*	0.21
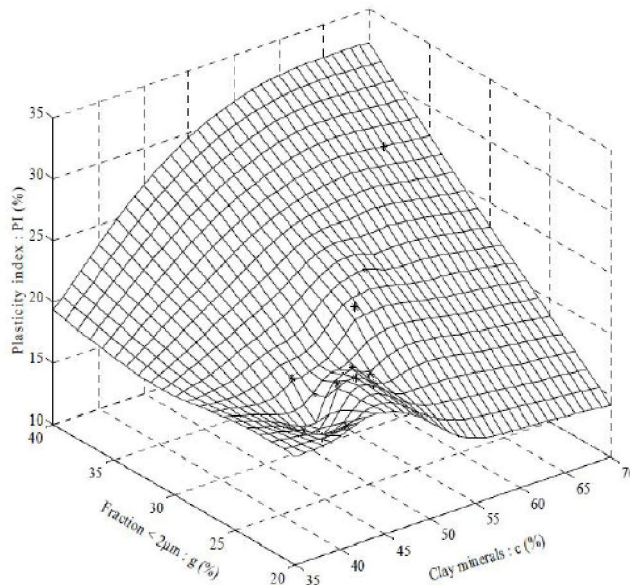
Figure 5 : Response surface plot of PI as function as the amounts of clay minerals and finer fraction
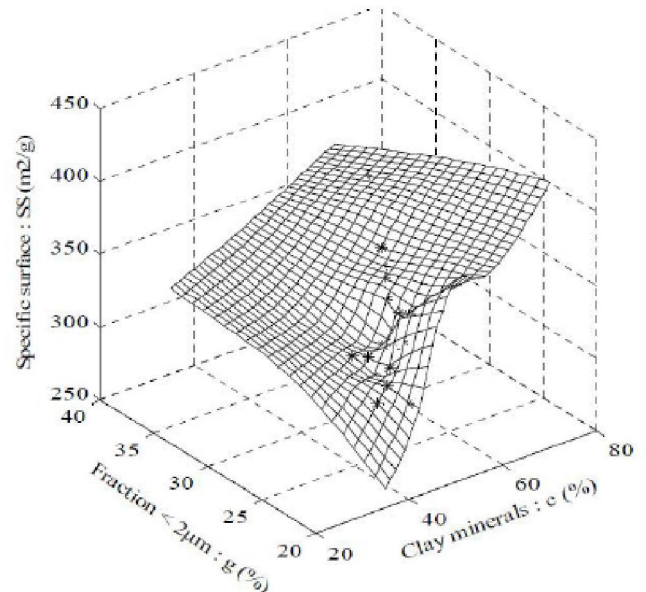

Figure 6 : Response surface plot of SS as function as the amounts of clay minerals and finer fraction
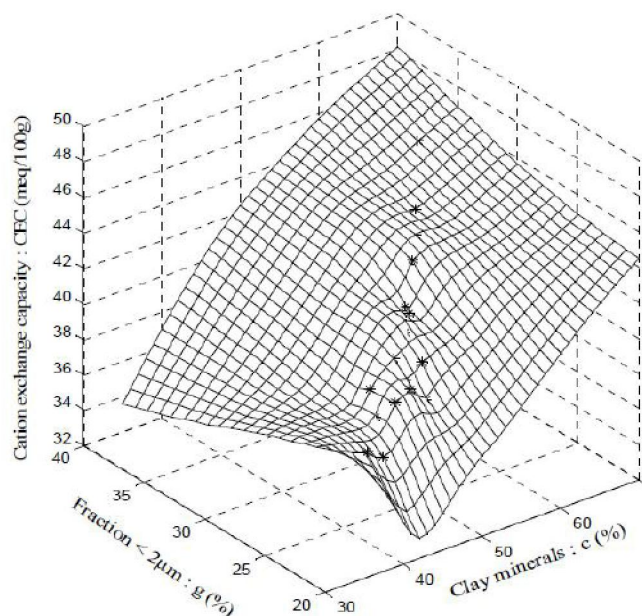
Figure 7 : Response surface plot of CEC as function as the amounts of clay minerals and finer fraction

as the predicted values are consistent with the results obtained from experimental results and the regression equations are considered statistically significant.

Figures 5, 6 and 7 show the response surface plots for PI, SS and CEC, respectively. The 3D surface plots are the graphical representation of the Eqs. (4), (5) and (6) and allow for easy and rapid predictive estimate over the entire properties under investigation. Figures 4, 5 and 6 show that PI, SS and CEC increase with the increase of (c) and (g) amounts. Another way of visualizing the effect that changes in clay properties (c and g) might have on the PI, SS and CEC and prove the interpretation of the statistical results through the use of response plots. In this way, the effect of each property can be visualized.

CONCLUSION

This study presented the compositions and the properties of Tunisian clays based on chemical analysis, X–ray diffraction, microgranulometry, Atterberg Limits, CEC and SS. The major oxides in the samples are SiO_2 and Al_2O_3, indicative of the dominance of clay minerals. The dominant minerals are illite, kaolinite, quartz, calcite, with accessory phase of illite/smectite interstratified minerals and Na–feldspar. Particle size distribution shows that the most clays are clayey silts. Although, the sampled raw materials are not highly plastic

(PI = 22 ± 6 wt.%), their chemical and mineralogical compositions suggest that they could have potential as raw materials for ceramic uses. The CEC and SS values were $34.1 – 45.7$ meq/100g of air–dried clay and $302 – 374$ m^2/g, respectively, confirming that these clays are not swelling clays.

Regression models were calculated, correlating the physical properties with the compositions. It appears that the clay characterization, in conjunction with regressions models could be instructive for mineralogists and specialists in geotechnical and industrial applications.

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