

CHARACTERIZATION OF EL-BAHARIYA CLAY FOR CERAMIC INDUSTRY

EL BAHARÎYA KİLLERİNİN SERAMİK SANAYİİ İÇİN DEĞERLENDİRİLMESİ

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ÖZET

Bu çalışmanın amacı seramik sanayi için ekonomik ve teknik olarak uygun genel kaynaklar sağlamaktır. Bu amaç için seçilen El-Bahariya Killelerinden on örnek alınmış ve bu örneklerin kimyasal, mineralojik, ısıl ve reolojik analizleri yapılmıştır. Çalışmalar yalnızca bir örneğin seramik sanayisi için gerekli olan ekonomik ve tetnik şartları sağladığını göstermiştir.

ABSTRACT

The aim of the present research study is to propose local raw material which meets the economic and technical requirements for ceramic industry. El-Bahariya clay deposits were chosen for this purpose. Ten samples have been chosen randomly to perform the chemical, mineralogical, thermal, and rheological analysis.

Analysis of results obtained and ore reserve calculations show that only one sample could be technically and economically used in ceramic industry.

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1. INTRODUCTION

It is customary to define a ceramic product as an article made of clay with or without the addition of other materials, shaped in plastic stage dried and then fired. Importance of the raw material characterization in ceramic industry is not questionable and this is due to the fact that there is strong relationship between raw material composition and their industrial behavior (GRIM, 1962; KONTA, 1979; MANDOUR , 1989). Many studies were made on El-Bahariya region but most of them were pointed toward the mineralogy of the soils and other material in the region (EISSA, 1976; KHALIL, 1980; AWADALLAH, 1984, WASSEF, 1983; KHALIFA, 1984; KABIL, 1985; PHILIP, 1987). The present study is aiming to substitute entirely or partially El-Bahariya clay, for those of Aswan clay which will have clear impacts on the production costs.

Therefore a group of different analysis such as the grain size distribution, X-ray diffraction, oxides and soluble salts content **and** rheological experimentation **were** carried out. This group of analysis in its **total gave a proper** characterization of **the** clays.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1. Location And Sampling Techniques

The Bahariya is a large natural and oval - shaped depression existing in the northern part of the western Desert of Egypt. The investigated area lies between latitudes 27°48" north and 28°28" north and between longitude 28°33" east and 29°11" east. It is a depression of about 95 km. long and 45 km wide, with area about 1800 km², which is called El-gedida iron mine as shown in figure (1).

2.1.1 Mine Description

The iron ore formation in El-Gedida mine is covered by an overburden layer which contains mainly weathering products of ore associated with sand and gravel. The sandstone bed forms 41.2% of the total overburden, while clay represents 29%. The rest consists of 27.6% alluvium and 2.2% quartzite.

El-Gedida iron mine has been divided into 9 blocks according to the amount of iron oxide contents as shown in figure (2). Only four blocks have been found to contain sufficient amount of clay. These are block 1, block 3, block 4 and block 9.

2.1.2 Sampling Technique

Sampling has been carried out using vertical channel method. Each sample represents the whole face and includes all clay deposit. Locations of different samples are shown in figure (2). Collected samples can be described as follow:

- A* Samples obtained from block(1) could be separated into three types of clays according to their colours, green, yellow, and dark brown. These samples will be defined as B3, B4, BS and B6.
- B* Samples of block 3 have also different colours, green, brown, red and yellow. However, it is very difficult to separate them. The sample will be defined as B7.
- O Samples obtained from the end of block (3) and the beginning of block (4) are green clay (B8), yellowish white clay (B9 and BIO).
- L> Samples obtained from the upper position of bench face of block (9) have pale green colour (B1), while samples obtained from the lower position have dark green colour (B2).

The visual description of all samples has been presented in table (1).

Table (1). Visual Description Of Collected Samples

Sample No.	Sample Location	Visual Description	
		Color clay	Color sand
B1	Block (9) upper	Pale Brown	Dark Gray Brown
B2	Block (9) lower	Light Yellowish Brown	Clay Brown
B3	Block (1)	Very Pale Brown	Pale Brown
B4	Block (1)	Yellowish Brown	Dark Yellowish Brown
B5	Block (1)	Very Dark Gray	Black
B6	Block (1)	Black	Very Dark Brown
B7	Block (3)	Yellowish Brown	Dark Yellowish Brown
B8	Between Block (3) and (4)	Light Olive Brown	Olive Brown
B9	Between Block (3) and (4)	Very Pale Brown	Yellowish Brown
B10	Between Block (3) and (4)	Very Pale Brown	Yellowish Brown
B11	Between Block (3) and (4)	Yellow	Darkish Yellow

Table (2). Grain Size Distribution Of El-Bahariya Samples

Sample No.	Grain Size Distribution, %				
	Coarse Sand (150-600 μm)	Fine Sand (60-150 μm)	Silt (4.75-60 μm)	Clay (<4.75 μm)	CaCO ₃
B1	54.3	32.8	4.5	17	0.4
B2	30.9	22.1	3.8	37	1.3
B3	31.4	28.1	16.8	22.3	0.1
B4	18.2	34.4	7	40.3	1.2
B5	16.9	19.9	11.3	36.9	1.4
B6	15.3	43.9	18.9	26.3	0.9
B7	17.1	32.3	9.1	41	0.7
B8	10	9.0	0.2	80.8	0.0
B9	4.2	22.1	20.8	51.5	9.3
B10	8.7	14.0	4.5	76.8	0.0



Figure (1). Location Map Of El-Bahariya Mine.



Figure (2). Location Map Of The Different Blocks.

2.2 Grain Size Analysis

The grain size distribution has been determined using Andreasen pipette method. The analysis was carried out with a suspension containing from 1 to 3% by volume solids. The cylinder was filled to a given mark with the well-shaken suspension. The pipette-holding stopper is inserted. Samples (10 ml.) are withdrawn at given times and transferred to glass evaporating dishes and solid content is found by evaporation and drying at 110°C (SINGER, 1987).

2.3 Determination of pH and Soluble Salts Content

The samples were air dried, crushed and sieved through a 2mm. Sieve as primary preparation for analysis to determine the following:

- A* Ph of saturated paste by using Orion portable pH meter mold SA 210.
- B* total salinity by measuring the electric conductivity of a paste.
- C* Calcium and magnesium by titration with versant (EDTA) using ammonium purpurate as indicator for calcium and eriochrome black as indicator for calcium plus magnesium (VOGEL, 1961).
- I> Sodium and potassium by flame photometry (VOGEL, 1961).
- E* Carbonate and bicarbonate by titration using phenolphthalin as indicator for carbonate and methyl orange as indicator for bicarbonate.
- F> Sulfate by precipitation using barium chloride.
- G~ Chloride by using Mohres method.

2.4 X-Ray Analysis

X-ray diffraction analysis was carried out on clay fraction less than 2 μ in diameter using Philips PW 1140/90 X-ray apparatus cu-k.alpha radiation . nickel filter .Clay sample were prepared on glass slides.Four slides has been prepared for each sample. The four slides were prepared as described elsewhere (JENKINS, 1985). they are :

- A- air dried Mg-saturated slide,
- B* glycol solvated Mg-saturated slide,
- G air dried K-saturated slide,
- D- k-saturated slide heated for 4 hours at 550°C.

Interpretation of the diffraction patterns is based on the presence of diffraction peaks of each crystalline species in the sample. The intensity and sharpness of the peaks are affected by the concentration of the crystalline species, fineness of the crystals, crystal imperfections and the presence of amorphous materials.

The criteria for identification of the clay and accessory minerals are the following:

- A« Kaolinite, gives a strong reflections at angles corresponding to 7.16 \AA^0 and 3.57 \AA^0 in the Mg-saturated air dried samples which remain constant in the other treatments and disappear upon heating at 550°C for four hours.
- B« Montmorillonite (Smectite) exhibits a basal reflection (001) at about $14.0\text{-}14.5 \text{ \AA}^0$ for Mg-saturated and air dried sample which expands to 17.8 \AA^0 by adding glycol solution and shifts to 10.0 \AA^0 after K-saturation and heating at 550°C for four hours.
- C- Illite (Hydrous mica) gives diffraction peak at angles corresponding to $9.96\text{-}10.28 \text{ \AA}^0$ in the Mg-saturated air dried sample. There is change in peak position by different treatments.
- I» Chlorites is detected by the presence of $14\text{-}14.7 \text{ \AA}^0$ peak (first order) and $7.07\text{-}7.18 \text{ \AA}^0$ (second order) in all treatments. The presence of $4.72\text{-}4.9 \text{ \AA}^0$ peak (third order) further confirms its presence.
- E» Sepiolite is identified by the presence of diffraction peaks at angles corresponding to $12.05\text{-}12.3$, $7.7\text{-}7.4$, $4.49\text{-}4.5$, $4.29\text{-}4.31$, $3.73\text{-}3.75$, $3.33\text{-}3.67$ and $2.66\text{-}2.69 \text{ \AA}^0$ in all treatments.
- F» Quartz, usually gives two fairly strong peaks at angles corresponding to 3.35 and 4.26 \AA^0 which are stable peaks throughout the different treatments.

2.5 Chemical Analysis

SiO_2 , Al_2O_3 , Fe^{2+} , TiO_2 , CaO and MgO concentrations have been determined as described by Vogel, 1961.

2.6 Determination Of Methylene Blue Index (Mbi)

The method depends on the addition of a standard solution of methylene blue to a clay in aqueous suspension until its cation exchange capacity is satisfied. This is indicated by leaving the suspension to settle and checking the supernatant liquid which will be coloured.

$\text{MBI} = \text{Vol. taken} \times \text{molarity of MB} \times 100 / \text{weight taken}$

$\text{MBI} = \text{c.e.c (cation exchange capacity) - surface area}$

2.7 Determination Of Plasticity

The pfefferkorn test makes use of the amount of water needed for a powder shaped in the form of a cylinder, left to deform to a certain value of its original height (1/3)

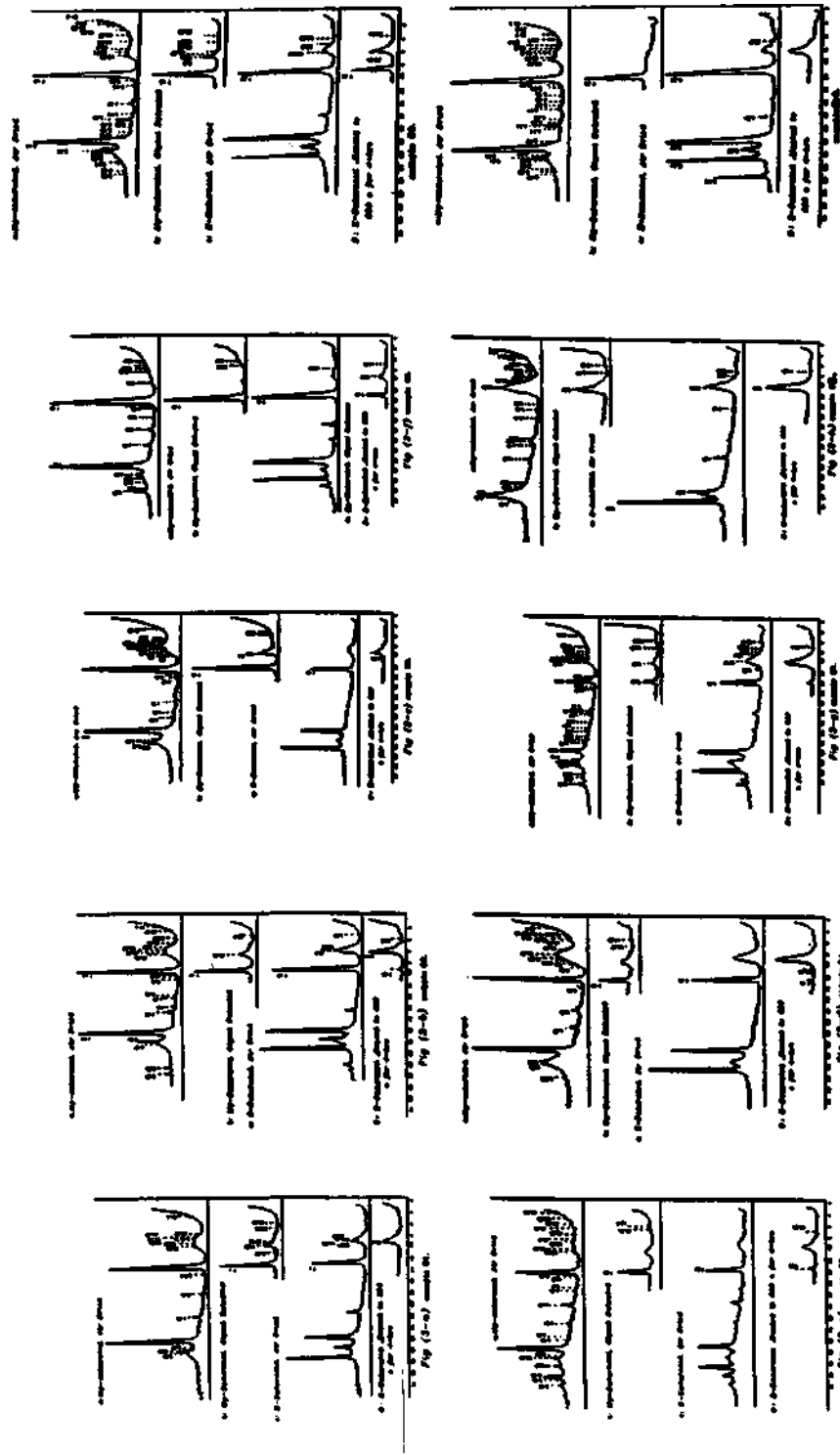


Figure (3). X-Ray Diffraction Pattern Of El-Bahariya Clay Samples (Continued).

under a standard load released from a fixed distance as a measure for the plasticity coefficient. The greater the amount of water needed the more plastic the material. Results are plotted representing the relation between the amount of water added and the ratio of deformed height.

2.8 Modulus Of Rupture

Specimens in the form of rectangles 1*1*7 cm were moulded under a force of 30 KN processed by the semi-dry press method. The amount of water added was between 6 to 7 %. Specimens were subjected to test just after firing at 1050°C for sample B9. The average of five specimens was taken. Test was carried out using an Instron, the rate of loading was 0.5 mm/min. Modulus of rupture is calculated from the following equation:

$$MOR=3LD/2bd$$

L: breaking load

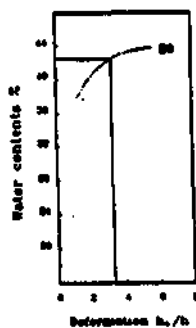
b: breadth of the rectangular specimen

D: span between supports in cm.

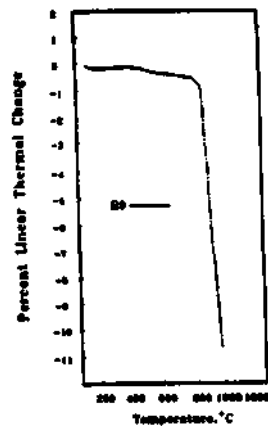
d: depth of the rectangular specimen

2.9 Determinations Of Thermal Behavior

Specimens in the form of rectangles 1*1*7 cm were processed by the semi-dry-press method under force of 10 KN. Specimens were left to dry at 110°C for 24 hours. Length of the respective rectangles was measured L_0 . Specimens were mounted in the dilatometer (Orton). Heating up with a constant rate was carried out up to 100°C. The percentage of linear change was directly plotted on the graph(FRCU, 1991).



Figure(4). Plasticity Coefficient Of El-Bahariya Clay Sample.



Figure(5). Thermal Behaviour Of El-Bahariya Clay Sample.

3- Results And Discussion

The grain size distribution of the collected samples given in table (2) can be divided into two main categories, the first include samples of clay fraction less than 50% (samples B1 to B8), where the dominant grain size of samples fall in the range of coarse and fine sand. The second category which include samples of clay fraction over 50%, samples B9 and B10.

A special case can be noticed in sample B7 where the percentage of CaCO₃ rise upto 8.3% which may be unacceptable in ceramic industry, therefore it could be excluded.

Figure (3) shows diffraction patterns of clay minerals separated from El-Bahariya clay. From these patterns the predominant clay minerals can be estimated as shown in table (3). Its obvious that kaolinite is the dominant clay mineral in all collected samples except for sample B8 where illite is the dominant. Therefore sample B8 could be excluded.

Table (4) gives the soluble salts analysis of the ten samples. It can be seen that the sodium chloride is the dominant soluble salt in most of the samples specially samples B1 and B2. The samples also contain calcium and/or magnesium sulphate. However, the concentration of the sulphate is much less than that of sodium chloride in all samples. Soluble salts analysis and electrical conductivity measurements indicate that samples B1, B2 and B3 contain the highest concentration of salts in decreasing order.

Samples B1 and B2 have similar pH which shows slight acidity while for the rest of the samples the pH range between 7.6 to 7.9.

Table (5) gives the oxide analysis of the samples. It is clear that the first eight samples contain large amounts of Fe₂O₃ especially samples B5 and B6 (more than 50% Fe₂O₃) which might cause large problems in ceramic industry and therefore these samples may be excluded.

Table (3). X-Ray Analysis Of Clays Separated From El-Bahariya Samples.

Sample No.	X-Ray Analysis								
	I.S.	Non-montmorillonite	Illite	Smectite	Vermiculite	Chlorite	Polygonizable	Quartz	Feldspar
B1	Few	Trace	Dom.	Few	-	Trace	Trace	Few	Trace
B2	Few	Trace	Dom.	Mod.	-	Trace	Few	Few	Trace
B3	Few	Few	Comm.	Few	-	Trace	Few	Comm.	Trace
B4	Mod.	Trace	Comm.	Mod.	Few	Trace	Few	Few	Trace
B5	Few	Trace	Dom.	Few	Few	Trace	Few	Few	Trace
B6	Few	Trace	Comm.	Trace	-	Trace	Trace	Few	Trace
B7	Few	Trace	Dom.	Few	Trace	Trace	Trace	Mod.	Trace
B8	Few	Trace	Trace	Dom.	-	Trace	-	Few	Trace
B9	Few	Trace	Dom.	Trace	-	Trace	Trace	Few	Trace
B10	Trace	Trace	Dom.	Trace	-	Trace	Trace	Trace	Trace

Above: -
Trace: 0-3%
Few: 3-15%

Medium (Mod): 15-25%
Common (Comm.): 25-40%
Dominant (Dom.): > 40%

Table (4). Soluble Salts Analysis Of El-Bahariya Samples

Sample No.	pH	E.C.	Soluble ions, meq./lit						
			Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	Cl ⁻	SO ₄ ²⁻
B1	6.9	20.57	8.52	29	330	2.7	0.6	324	45.6
B2	6.8	12.88	7.39	15.4	160	2.3	0.6	178	14.5
B3	7.6	9.17	55.9	14	62	1.3	0.8	68	32.4
B4	7.8	9.38	17.6	10.1	58	1.3	1.0	56	30
B5	7.7	5.57	15.9	6.4	34	1.0	1.0	32	24.3
B6	7.7	6.31	9.1	11	47	0.7	0.8	42	25
B7	7.9	7.85	25	21.2	35	1.8	1.0	34	47.9
B8	7.85	4.21	3.41	2.6	35	1.1	1.0	40	1.1
B9	7.75	12.16	7.95	13.8	122	2.2	1.0	126	19
B10	7.6	8.79	8.52	2.4	92	1.8	1.0	90	13.6

E.C. is the electric conductivity.

Table (5). Oxide Analysis Of El-Bahariya Samples In Weight Percent.

Sample No.	LO.L.	SiO ₂	Al ₂ O ₃ +TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	CoO	ZnO	BaO
B1	-	56.3	15.6	11.7	2.3	2.8	3.3	4.5	-	1.3	-	0.4
B2	10	37.3	17.8	25.6	2.26	2.8	0.15	2.9	0.022	0.010	0.002	-
B3	16	49.2	16	15.53	0.96	1.25	0.32	1.02	0.30	0.10	0.017	-
B4	11.6	47.6	14.2	22.27	1.12	2.09	0.16	0.76	0.97	0.16	0.024	-
B5	9.63	22.8	9.98	34.34	0.35	0.5	0.32	0.19	1.99	0.009	0.006	-
B6	9.84	28.3	8.308	37.3	0.68	0.78	0.35	0.31	4.52	0.001	0.031	-
B7	13.99	30.4	4.20	17.04	4.09	1.75	0.17	0.65	1.29	0.014	0.010	-
B8	98.92	51.3	12.41	18.03	0.55	1.36	0.15	1.30	0.039	0.006	0.024	-
B9	12	43	34	8.5	0.3	0.9	0.3	0.4	-	0.3	-	-
B10	13.95	44.1	11.21	8.50	0.35	0.92	0.21	0.47	0.013	0.006	0.01	-

Table (6). Rejected Clay Samples.

Sample No.	Reason Of Rejection
B1	high concentration of soluble salts and Fe ₂ O ₃
B2	high concentration of soluble salts and high Fe ₂ O ₃
B3	High Fe ₂ O ₃ %
B4	High Fe ₂ O ₃ %
B5	High Fe ₂ O ₃ %
B6	High Fe ₂ O ₃ %
B7	High Fe ₂ O ₃ % and CaCO ₃ %
B8	High Fe ₂ O ₃ % , High Illite concentration

Table (7). Unfired And Fired Properties Of Clay Sample B9.

MBN	Coeff- icient of Plas- ticity	MDR		Deflect- -ion	Water	Temp- erature Of Firing	Water Absor- -ption	Modulus Of Rupture	Linear Thermal Expansion
		Green	Dried						
0.0079	42.6	12.22	42.83	1.1	100	950	0.38	304.1	8.72

Alumina is very important in the ceramic industry, sample B9 posses the highest alumina content among the other clay samples. Table (6) gives a summary of all rejected clay samples. From this table a primary decision could be taken. Samples B9 and BIO are the most preferable for ceramic industry because of the high percentage kaolinite which is the backbone of traditional ceramics and also for the low Fe_2O_3 content in comparison with the other samples. However the clay from which sample BIO has been taken is not well distributed in the mine. This leaves only sample B9 which has high clay content and at the same time the reserve estimation gives encouraging results.

3.1 Thermal, Mechanical And Rheological Behavior Of Sample B9

Table (7) shows the unfired properties of sample B9. Methylene Blue Index (MBI) is considerably high which is an indication of the high surface energy and reactivity of this sample. The modulus of rupture (MOR) for both green and dried conditions are within acceptable range.

From figure (4) it can be seen that this sample has high coefficient of plasticity, this result is confirmed by the large amount of water content and deflocculant (sodium tri-poly phosphate) needed to form a slip. High plasticity might cause large problems if the dry method is used in ceramic industry.

The results of thermal behavior is demonstrated in figure (5). The curve starts with a contraction from 100°C upwards. The contraction was gradual and nearly flattened with two troughs occurring at 200°C and 600°C with values 0.4 and 0.6% respectively, followed by an abrupt contraction at 800°C. The total contraction was about 10.9%. From the linear thermal expansion measured for the fired specimens it was found that it was about $8.72 \times 10^{-6} / ^\circ C$ and the softening temperature was 880°C.

From table (7) it can be seen that sample B9 has low porosity (water absorption 0.38%) and high modulus of rupture (304 Kg/Cm) which makes it suitable for ceramic industry.

4. CONCLUSION

- 1* The clay samples of El-Bahariya are characterized by relatively a high content of Fe_2O_3 , because it lies among the iron bearing quarry in the area. The clay content ranges between 20 and 75% but about 50% in most of the samples. The main

clay mineral is kaolinite with quartz as minor consistent. The clay contains soluble salts in the form of chlorides, sulphates and bicarbonates.

- 2« From the previous analysis and calculation of the deposit reserve, only one sample B9 could be technically and economically used in ceramic industry.
- 3« Its maximum firing temperature is 880°C.
- 4* Based on the obtained analysis, it was possible to set up a program for detailed industrial experimentation using this sample. This program was carried out and will be discussed in detail in future publication.

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