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Utilization of black shales in earthenware recipes

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Abstract

Black shales associated with coal seams in Gabal Maghara (Sinai) Egypt, together with other two samples, by-product of the coal beneficiation process namely mudcake and discard were investigated to assess their application in ceramic products. The rheological property and the firing characteristic were also studied. The samples contain appreciable amount of organic matter that proved by IR to be a mixture of aliphatic and aromatic groups. The content of clayey materials ranged between 89 and 94%. The loss on ignition in the mudcake was about 39.79%. The mudcake gave a porosity of about 50% an attempt to produce bricks or pipe for irrigation were carried out.

Keywords: Carbonaceous clay; Organic matter; Bricks; Rheology

1. Introduction

Carbonaceous or organic matter could be found associated with clays, (e.g. ball clays, bituminous clays, fire clay, plastic clay, loam clay, etc.) and shales (e.g. black shale). It may be disseminated in large masses, minute grains or films covering the clay particles surface. The bonding between clay mineral and organic matter is achieved through the role of the organic polyvalent compound with cation such as Ca^{2+}, Fe^{2+} and Al^{3+} [1]. These organic compounds are responsible for the cohesion of clay particles producing clay–organic complexes with larger particle size. This is achieved either by sharing of inter crystalline ionic forces between clay particles or by the bridging cation of polyvalent organic matter [2,3].

Organic matter is sometimes added to clays to improve the thermal insulation capacity of the structural ceramics and to reduce the energy consumption [4,5]. The presence of this organic matter in ceramic formulations improves the rheological properties of the processed mass. It decreases the viscosity of the slip raising its fluidity for casting. Also, it increases the plasticity of the batch for paste forming [2,6,7] and mechanical properties for green and fired bodies [8]. Organic matter may be added to increase the porosity of the fired bodies, e.g. bricks [9].

Carbonaceous clays found its application in ceramics products [5,10–14]. Caligaris et al. [5] reported that, coal tailings could be used for brick making without any other clayey additions. The presence of remnant coal enhances sintering at a relatively low temperature resulting in considerable energy saving. Abdel Monem [10] utilized mudcake carbonaceous clay a by product from coal beneficiation for the manufacture of building bricks after blending with another source of clayey materials. Ibrahim et al. [11] reported the possible application of carbonaceous clay as raw materials for whiteware products only after getting rid of coloring oxides (iron compounds), soluble salts and gypsum by washing the clay samples with 0.02N HCl. Molyavko et al. [12] recorded that, the addition of 20% by product beneficiation of carbonaceous clay increased the strength and cold resistance of the bricks. Stanasita et al. [13] investigated three sorts of Romanian coal bearing mine waste, which are suitable as raw materials for bricks and blocks. El-Didamony et al. [14] added that Wadi El-Hai clays could be substitute by 20–50% carbonaceous shale in building bricks with reasonable properties.

The present work deals with the study of mineralogical and rheological properties as well as firing characteristics of Gabal Maghara black shales associated with coal seams

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there and the by products of beneficiation of coal to assess their suitability for use in ceramic products.

2. Materials and methods

Black shales among the stratigraphic succession with the main coal seams in Gebel Maghara (Sinai) Egypt, were studied together with two other samples by product of the coal beneficiation process namely; mudcake and discard. Representative samples about 10 kg from each sample were collected. The samples were crushed, quartered and storied. Specimens of 100 g were taken from each sample were ground to pass-200 mesh sieve to carry out following tests: chemical analysis by XRF using a Philips X-ray PW, 1370. The major and trace elements were determined. The thermal behavior of the three samples was determined by DTA and TG. The chemical bonding was identified by IR spectra using Perkin Elemer IR-spectrophotometer. The main crystalline phases were determined by the X-ray diffraction (XRD) using Philips equipment type PW, 1710 provided with a copper Target and Ni filter.

A semi-quantitative determination of mullite, quartz and cristobalite phases was carried out using CaF_2 as an internal standard according to the method described by Khandelwwel and Cook [15].

The main size fractions of the investigated samples were determined by sedimentation method [16]. Workability of the samples was estimated in terms of plasticity coefficient from the measurements by Pfefferkorn equipment [16]. Methylene blue index was used to determine the surface area [16]. Rheological properties of the prepared slip were determined. Viscosity was measured by Brook-field rotational viscometer with the appropriate electrolyte added. Density of the slip was calculated from the weight of a known volume. The firing properties were determined for the processed specimens discs 25 mm diameter and 3 mm thickness, discs: 50 mm diameter and 2 mm thickness and bars 1.0 cm × 1.0 cm × 7.0 cm were fabricated by the semi-dry press method under a pressure of 40 MPa to measure physical, chromaticity and mechanical properties, respectively. The specimens were dried for 48 h in air followed by 72 h at 110 °C. Then fired under a controlled firing schedule comprising heating up at a rate of 1 °C/min up to 500 °C in an oxidizing atmosphere with air flowing with a rate of 10 m/s (in order to avoid the destruction of the specimens as a result of the sudden combustion of the organic matter). Temperature was raised further of at rate 10 °C/min to maximum between 1000 and 1200 °C with 50 °C interval and soaking time of one hour at each firing temperature. Physical properties in terms of bulks density, water absorption and apparent porosity were determined according to the ASTM specification Nos. $C_{373–72}$, $C_{326–56}$ and $C_{372–56}$, respectively. Modulus of rupture of fired samples was measured using an instron machine type 1128 at a loading rate of 5 mm/min. The color of specimens fired at 1200 °C was measured using type "Hunter lab" equipment, color difference meter model D_{25}-A-2. Fusion temperature was determined for cone specimens and the pyrometeric cone equivalent according to the Egyptian standard No. 1950-91 and ISO standard No. 1146. Mix composition (1:1 wt.%) mudcake and Aswan clay was used to produce briquettes by the stiff mud processing. A representative 10 kg sample was aged in water for 28 h. The plasticity of the mixture was tested by Pfefferkorn method [16]. Massive briquette with the dimension 5 cm × 5 cm × 2 cm was formed by extrusion process using a laboratory auger machine type "Händle." The specimens were dried in air for a week then for another week at 100 °C. The same firing schedule described above was applied. The firing characteristics of the processed specimens were determined.

The mudcake specimens fired at 1200 °C were utilized to carry out a test for water permeation. Specimens were glued on a mouth of glass bottles filled with water colored by methylene blue. The bottles were placed up side down in a flowerpot. The mouth of glass lying in the dry-sieve mud.

3. Result and discussion

As revealed from the XRD patterns shown in Fig. 1, the main clay mineral in clay samples is kaolinite with minor amount of illite, while the accessory minerals detected were quartz, goethite, pyrite and halite. The content of clay mineral, i.e. kaolinite and illite was calculated from the XRD patterns of the oriented clay fraction as shown in Table 1. IR absorption spectrogram of Fig. 2 exhibits the characteristic

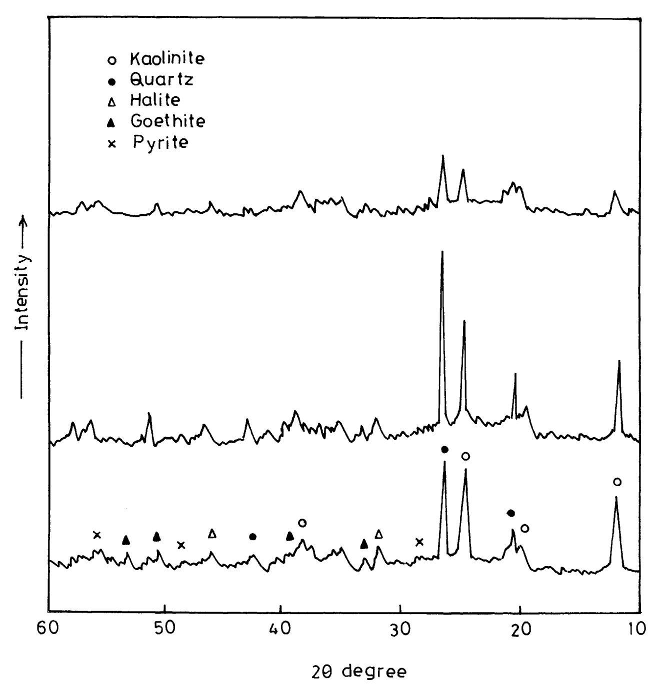

Fig. 1. X-ray diffraction patterns of bulk samples.

Table 1
Semi-quantitative XRD analysis of samples

Sample	Kaolinite (%)	Illite (%)
Mine	89.28	10.71
Discard	94.46	5.53
Mudcake	94.13	5.86

absorption bands of clay samples, which correspond to the mode of vibration of the constituting groups. The absorption bands corresponding to OH group adsorbed or lattice water occur at 3500–3700 and 900–1100 cm^{-1}, while the O–Si–O group occurs at 470–800 cm^{-1}. The organic groups detected were a mixture of benzene rings and aliphatic acid chains. All samples showed a mixture of aliphatic and aromatic groups matters, the aliphatic (lignitic) group (CH_3 and CH_2) are represented by the bands at 1445, 2856 and 2962 cm^{-1}, while anthracitic group presented by benzene rings (C_6H_6) displayed by the band at 1630 cm^{-1} [17].

Thermal behavior of the studied specimens was determined in terms of DTA and TG results. Figs. 3 and 4 show an endothermic effect occurring at 100–200 °C accompanied by a loss in weight ranging between 1.66 and 2.9 wt.%, this is related to the loss of adsorbed water. A second endothermic peak occurring at 400–800 °C is attributed to the dehydroxy-

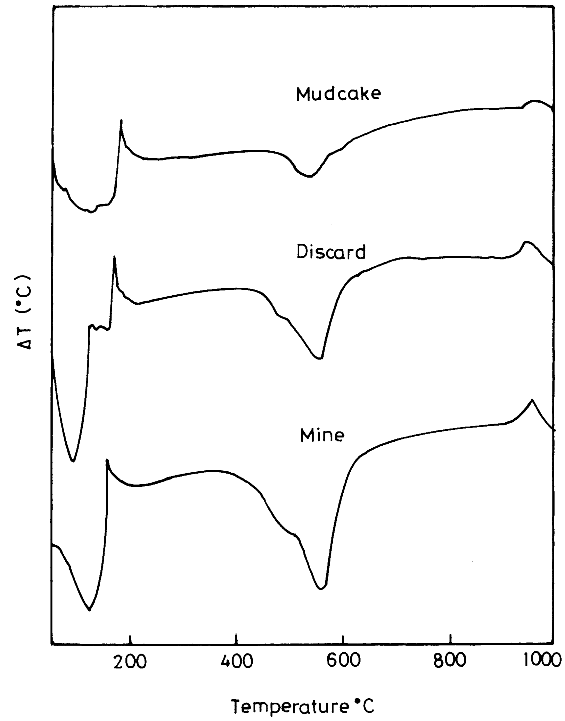

Fig. 3. DTA curves of the clay samples.

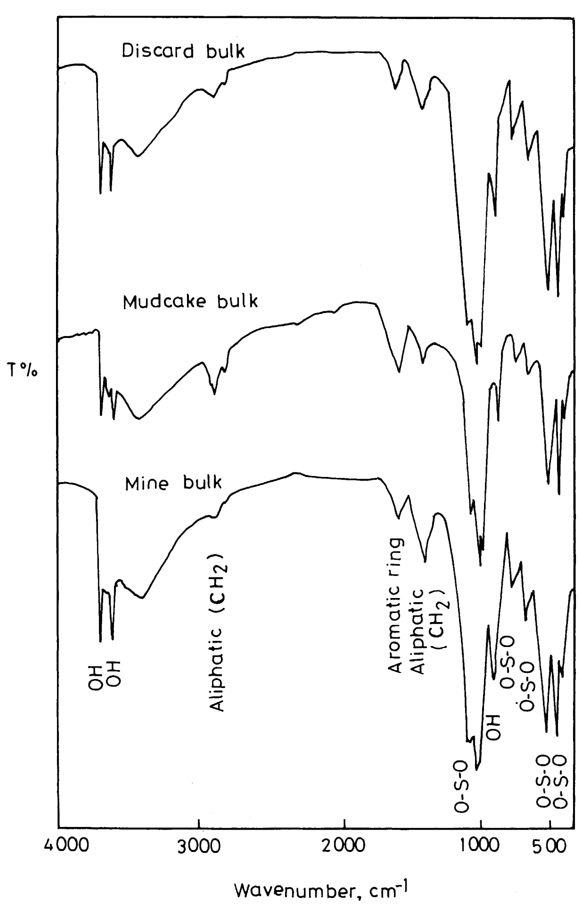

Fig. 2. Infrared spectra of clay samples.

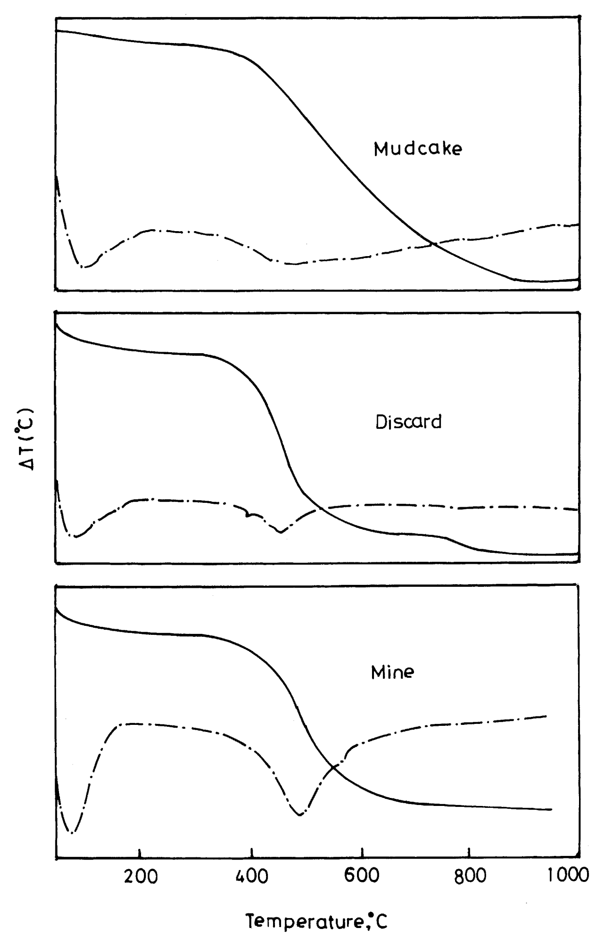

Fig. 4. TG curves of clay samples.

Table 2
Chemical analysis of clay samples

Constituents (wt.%)	Mine	Discard	Mudcake
SiO_2	46.17	49.5	32.72
Al_2O_3	24.95	22.87	16.76
Fe_2O_3	7.08	6.60	4.38
TiO_2	2.21	2.14	1.65
CaO	0.41	0.6	0.61
MgO	1.60	1.64	1.80
Na_2O	1.55	1.65	1.87
K_2O	0.96	1.08	0.80
MnO	0.14	0.12	0.05
Loss on ignition	14.69	16.52	39.78
Free silica	16.82	22	13
SO_4	1.37	5.16	5.01
Cl	0.042	0.052	0.15
S	0.46	1.72	1.67

lation of the clay minerals as well as the organic matter [18]. This reaction is accompanied by a loss in weight ranging between 15.59 and 31.59 wt.% depending on the content of the organic matter. Between 948 and 966 °C an exothermic peak has been noticed in all samples attributed to the crystallization of spinel. TG curves shown in Fig. 4 the loss in weight of 7.47 wt.% occurs between 750 and 1000 °C. This is attributed to the destruction of illite and minor amount of carbonates.

The main constituting elements as well as the trace elements for the three samples are demonstrated in Tables 2 and 3. It is evident that carbonaceous clay samples under investigation are classed as low-grade clays [19], they contain low Al_2O_3 content varying between 16.76 and 24.95%, and an appreciable amount of coloring oxides $Fe_2O_3 + TiO_2$ ranging between 6.03 and 9.29%. Mudcake sample displayed considerably high ignition loss (39.78%) as compared with mine and discard samples (14.69 and 16.52%). This means that this sample contains the highest percentage of organic matter. Table 3 shows that the mine and discard samples are enriched in V, Ba, and Zn, CO, Ni, Rb, Th, U and MO than the mudcake sample.

Table 4 summarizes the results of particle size analysis and rheological properties of the bulk clay samples. Table 1 shows that, the mine sample contains a relatively high proportion of illite and low content of kaolinite as compared with discard and mudcake. While the results of the particle size analysis show that the mine and discard samples are formed mainly of silt (60 and 64%) and clay particles (30 and 26%) with a limited amount of sand grains (10%), whereas, the coarse sand fraction is concentrated in mudcake sample (40%). Accordingly, the results of specific surface area and plasticity coefficient were affected. Mine and discard samples showed higher values of MBI (0.00396 and 0.0034 meq./g) compared with (0.0021 meq./g) for mudcake sample.

Table 3
Chemical analysis of some trace elements of clay samples

Element	Mine (ppm)	Discard (ppm)	Mudcake (ppm)
V	157.998	131.078	74.41
Ba	353.759	341.343	250.2
Co	32.9	33.76	14.06
Ni	64.546	50.084	35.58
Rb	46.372	47.383	12.70
Th	16.475	14.513	7.707
U	19.345	16.532	6.258
Zn	136.605	220.341	74.83
Mo	11.948	6.989	3.438

Table 4
Rheological properties of carbonaceous clay samples

Property	Mine	Discard	Mudcake
Particle-size analysis (μm)			
Sand > 63	10	10	40
Silt < 63-2	60	64	41
Clay < 2	30	26	17
MBI (meq./g)	0.00396	0.0034	0.0021
Coefficient plasticity	21.0	21.5	22.5
Electrolyte (%)	0.3	0.15	0.1
Viscosity (CP)	80	45	45
Density of slip (g/cm^3)	1.21	1.43	1.85

Rheological properties were affected by both the degree of fineness and the amount of organic matter present, as demonstrated in Table 4. Fig. 5 illustrates the plasticity curves of the studied clay samples. The water content corresponding to the deformation ratio $L_o/L = 3.3$ is considered as the water of workability. The results indicate that, the three samples have plasticity coefficient in the same range (21–22.5%), the organic matter contribute to the plasticity of the samples. As explained by Füchtbauer and Müller [20], the organic matter has large charged molecules, which affect positively on the movement of particles over one another and consequently raises the plasticity coefficient.

The viscosity of the formed slips and the behavior on standing "thixotropy": are demonstrated in Fig. 6. There too,

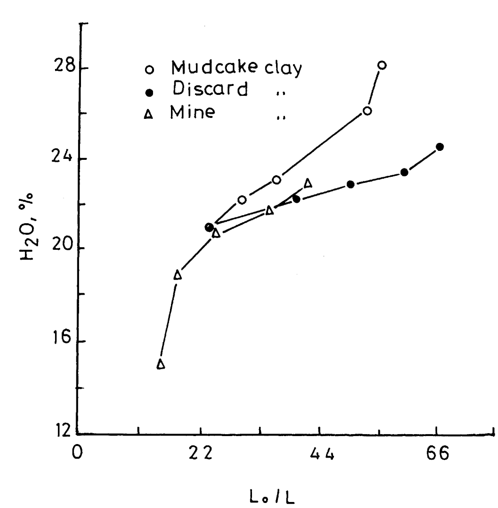

Fig. 5. Plasticity of the mine, discard and mudcake samples.

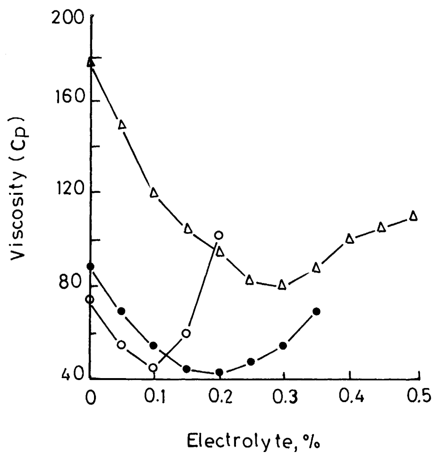

Fig. 6. Effect of electrolyte content on viscosity of slips.

the content of organic matter [21] affected the content of electrolyte added (0.3, 0.15, 0.15) to the slip and as a result the viscosity values (80, 45, 45) for mine, discard and mudcake, respectively. Both the clay content and organic matter affect thixotropic behavior of the slip. Fig. 7 shows that, mudcake sample show a dilatent behavior (dispersion of particles) on standing due to its relatively low clay content and high organic matter. Meanwhile the discard and mine samples show the thixotropic behavior (flocculation) on standing [22]. Table 4 shows that, the mudcake gave a slip with specific gravity 1.85 g/cm^3 compared with (1.21 and 1.43 g/cm^3) for discard, and mine, respectively. This is related to the higher solid content of the slip.

The effect of organic matter present in the investigated samples on the densification properties in terms of bulk density and water absorption of the specimens fired between 1000 and 1200 °C is shown in Fig. 8 and Table 5. It is evident that the mine and discard samples fired at 1200 °C gave the highest bulk density (2.14 and 2.03 g/cm^3) with the lowest values of water absorption (7.48 and 10.39%) and apparent porosity (16.0 and 21.09%). The mudcake gave the highest values of water absorption 60.60% and apparent porosity 52.12%. This sample contains the highest proportions of organic matter. The fired body is, therefore, characterized by the development of high proportion of pore space.

Table 5
Physical and mechanical properties as well as crystalline phases of fired bodies at 1200 °C

Property	Mine	Discard	Mudcake
Linear shrinkage (%)	9.71	10.57	12.3
Bulk density (g/cm^3)	2.14	2.03	0.86
Water absorption (%)	7.48	10.39	60.60
Apparent porosity (%)	16	21.09	52.12
MOR (N/mm^2)	23.46	16.62	1.47
Crystalline phases (wt.%)			
Mullite	28	27.5	23.2
Cristobalite	8.5	2.5	5.5
Quartz	4.5	6.5	6.0
Augite	Detected	Detected	Detected
Magnetite	Detected	Detected	Detected
Hematite	Detected	Detected	Detected

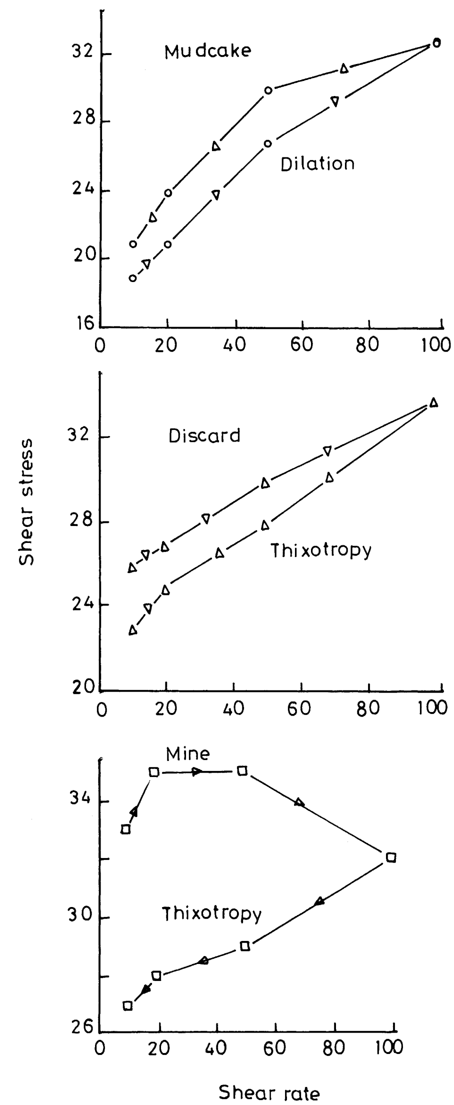

Fig. 7. Rheological behavior of the prepared slips for mine, discard and mudcake samples.

Table 5 and Fig. 9 show the main crystalline phases present in the bodies at 1200 °C were mullit, cristobalite and quartz relics. Magnetite (FeO, Fe_2O_3), hematite (Fe_2O_3) and augite phases were also detected. The goethite present in the raw samples was converted into magnetite, while the oxidation of pyrite (FeS_2) lead to the formation of hematite on firing in the stream of air.

The high porosity of the fired bodies affected the bending strength Table 5. The highest values of MOR were obtained by mine sample (23.46 N/mm^2), whereas the mudcake with maximum porosity of 52% showed the lowest MOR.

The chromaticity of the fired clay samples are given in Table 6 and plotted on the CIE diagram. From these data, it

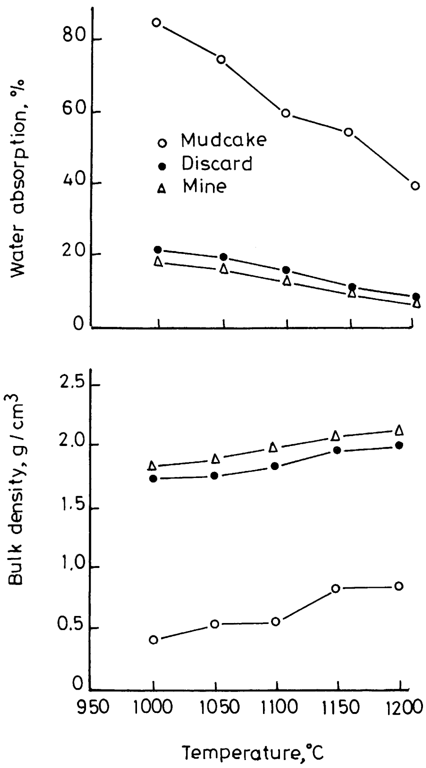

Fig. 8. Bulk density and water absorption of fired bodies.

is evident that, the colors of the studied samples lie in the region of yellow side CIE diagram. The presence of relatively high amount of coloring oxides Fe_2O_5 and TiO_2 ranges between (6 and 9.29%) in the fired samples are responsible for

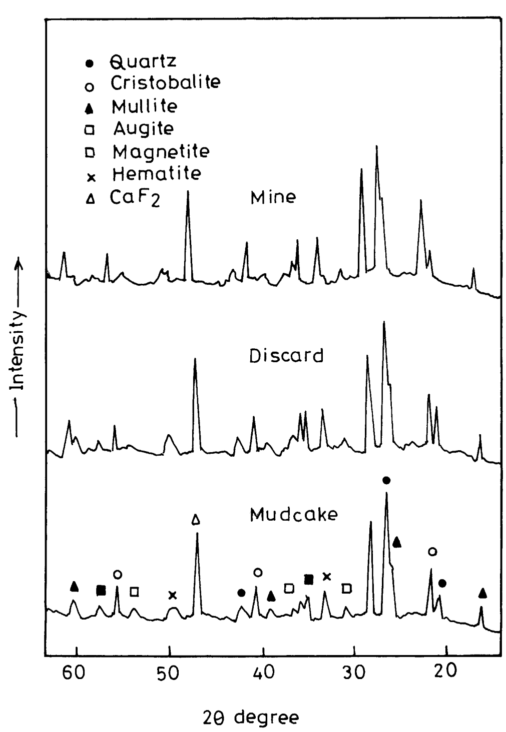

Fig. 9. XRD patterns of fired bodies at 1200 °C.

Table 6
Color "chromaticity" coordinates of the fired bodies

Sample	*X*	*Y*	*Z*	*x*	*y*	Remarks
Mine	21.65	20.75	13.4	0.388	0.372	Yellow
Discard	24.4	32.15	15.75	0.384	0.369	Yellow
Mudcake	32.4	32.30	19.65	0.388	0.381	Yellow

Table 7
Fusion temperature of the fired bodies

Sample	Refractoriness	
	Cone no.	Temperature (°C)
Mine	19	1520
Discard	19	1520
Mudcake	16	1460

their coloration. The mine and discard samples gave dark buff color, while the mudcake shows a light buff color, this is related to the presence of high amounts of carbonaceous material and the lower content of iron oxide.

All samples show lower fusion temperature Table 7 than the pure kaolinite (>1700 °C). Due to the low Al_2O_3 content ranging between (16.76 and 24.95%) compared with 37% for pure kaolinite and the presence of high amounts of fluxing oxide ranges between (11 and 13%).

The physical and mechanical properties of the fired massive briquettes prepared from the mixture of Aswan clay and mudcake (1:1 wt.%) are displayed in Table 8. It is clear that significant improvement in properties of massive briquettes was felt as compared with mudcake specimens. The increase in the content of clayey materials raised the coefficient of plasticity to 28.65%. The firing properties were also affected. Better densification was achieved as it is evident from the results bulk density (1.70 g/cm^3) water absorption (9.13%) and apparent porosity (15.52%), MOR was improved from 1.47 to 5.4 N/mm^2. This is probably

Table 8
Physical and mechanical properties as well as crystalline phases of massive briquettes at 1200 °C

Property	Mudcake sample	Briquettes of batch composition from mudcake and Aswan clay by (1:1 wt.%)
Coefficient plasticity	22.5	28.65
Bulk density (g/cm^3)	0.86	1.7
Water absorption (%)	60.60	9.13
Apparent porosity	52.12	15.52
MOR (N/mm^2)	1.47	5.40
Crystalline phases		
Quartz		Detected
Mullite		Detected
Augite		Detected
Magnetite		Detected
Hematite		Detected

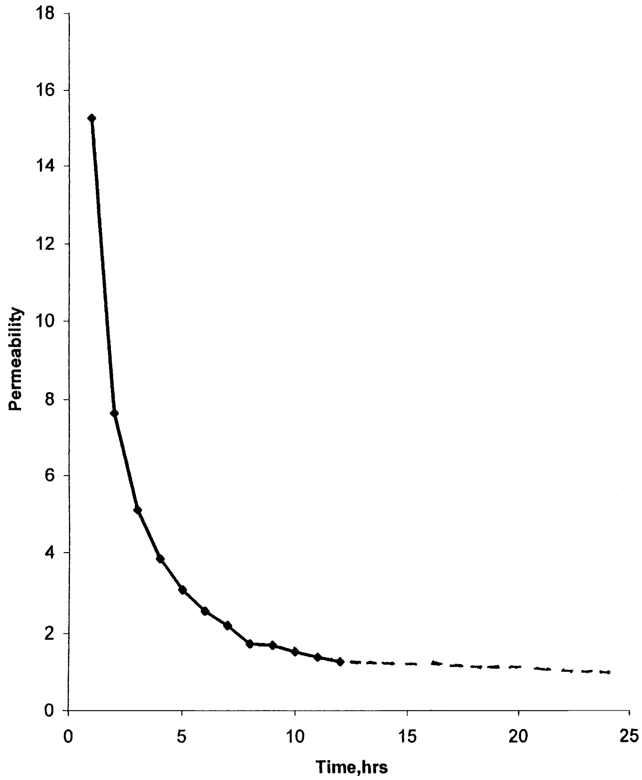

Fig. 10. Permeability of fired bodies from mudcake sample.

due to the relative decrease of organic matter present as well as open-pores structure of the fired briquettes is appreciably closed by the liquid phase developed during firing. The crystalline phases detected were almost the same Table 8.

The rate of permeation was followed on a period of three days. The results of permeation obtained were determinated in Fig. 10.

4. Conclusion

– The carbonaceous clay sample associated with the coal seams at Maghera (Sinai) Punsoula is characterized by the fine particle size mainly silt and clay. The presence of accessory minerals as quartz, goethite, pyrite beside kaolinite and illite clay minerals.
– The by products of coal beneficiation discard and mudcake show concentration of the coarse particles sand and silt.
– The organic matter is concentrated in the form of aliphatic and aromatic.
– Relatively high porosity 52% and low MOR 1.47 N/mm^2 characterized mudcake specimens.
– The utilization of mudcake in irrigating pipes for agricultural use was demonstrated by the rate of permeation 1.39 at 12 h.
– Also, mudcake can be added up to 50% to another clay (e.g. Aswan clay) to produce building bricks both hollow and massive as well as light weight bricks.

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