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Refractory Aspects of Some Iraqi Fire-Clays

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ABSTRACT. The physical and technical properties of clay materials from different localities in Iraq were investigated for making fire-clay refractories. Medium-heat duty fire-clay bricks could be produced using suitable grog/raw clay ratios. To achieve high strength, good volume stability, and suitable density and porosity, the bricks should be pressed under 250 kg/cm^2 and fired to at least 1300°C. The role of the relatively more plastic clays as a binder was also studied and was found to improve the sintering properties and to decrease the firing temperatures of the finished bricks.

The development of heavy and light industries in Iraq has resulted in an increase in the consumption of refractory bricks of various types, especially fire-clay bricks which are commonly used in the lining of almost all types of industrial furnaces. The annual consumption of refractories in Iraq is expected to reach 80,000 tons, of which about 49,000 tons are fire-clay refractory bricks (30 - 42% Al_2O_3). As there are no production lines for fire-clay bricks from domestic materials, large quantities are either imported or manufactured from imported raw materials. Therefore, investigations leading to the manufacture of such refractories from indigenous clay minerals are of paramount importance to the national economy.

Although clay materials occur in workable deposits in Iraq and can be easily mined by simple quarrying methods, only limited information is available about their characteristics and their profitability for refractory brick-making (Al-Taie and Hamid 1975). Therefore, a reassessment of domestic raw clays has been undertaken to determine if such materials could be utilized economically for the refractories industry in Iraq.

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Materials and Methods

Four types of raw clays obtained from different localities in the Gaara area, which lies in the Eastern Desert of Iraq, were selected for this study. These raw clays are Dewekhla clay (D), Samhat clay (S), Tel Afief clay (T), and Bir Mlusi clay (B). For each locality, five core samples were blended in the field. Representative sample of 300 kg were delivered from each locality. The size of the lumps was first reduced by a jaw crusher. A process of quartering was carried out several times till obtaining a sample of 500 g. The quartered samples were ground and used for the study of the different characteristics of the raw clays. The main crushed samples were used for the preparation of the sample briquettes.

The investigated clays are almost white in colour, compact and consolidated and have a soapy feeling. They are also readily slaked in water.

The chemical constitution of these clays was determined applying standard methods. The free silica content was determined separately (Trostel and Wynne 1950). The results were reproducible to the extent of 0.05%.

The particle size distribution was investigated by the hydrometer method as specified in the ASTM D 422-54 T for grain size analysis of soils.

Plasticity measurements were carried out using the Pfefferkorn apparatus and the results are given in Fig. 1. This method is based on the extent of the

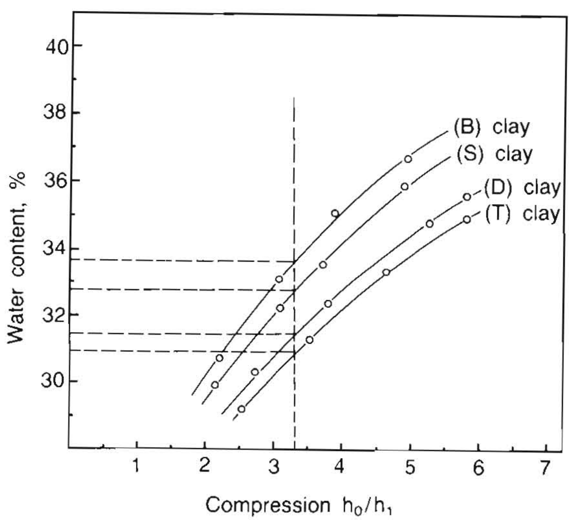

Fig. 1. The plasticity curves of the investigated raw clays.
h_0 = Initial height of the test sample.
h_1 = Height of the test sample after compression.

compression which a moulded clay cylinder suffers at different water content by one blow of a dropping stamp. The coefficient of plasticity determined denotes the percentage of the water content at which the moulded clay cylinder attains a compression of 30% of its initial height. This property was also investigated by means of the Atterburg apparatus, following the procedure laid down in the ASTM D 423-54 T and D 424-54T.

The dry modulus of rupture test is likely to indicate the bonding strength of the clay particles after forming into shapes. The procedure adopted for the determination of this property was similar to that of the ASTM C 689-71 T.

The pyrometric cone equivalent (PCE) was determined according to the method given in the British standard specification 1902 (1967).

The results of the proceeding investigations are recorded in Table 1.

Table 1. Chemical constitution and physical properties of the investigated clays

Property	Dewekhla clay (D)	Samhat clay (S)	Tel-Afief clay (T)	Bir-Mlusi clay (B)
1. Chemical analysis, wt.%				
Free SiO_2	8.64	10.60	12.52	11.19
Combined SiO_2	40.34	41.73	40.42	40.20
Total SiO_2	48.98	52.33	52.94	51.39
Al_2O_3	33.41	32.15	32.58	32.63
Fe_2O_3	1.24	1.42	0.73	1.04
TiO_2	1.07	0.91	0.85	1.00
CaO	0.28	0.28	0.14	0.21
MgO	0.27	0.19	0.07	0.24
K_2O	0.35	0.69	0.14	0.51
Na_2O	0.44	0.23	0.56	0.31
Loss on ignition	13.65	11.50	11.90	12.40
SO_3	0.34	0.34	0.39	0.33
2. Al_2O_3:SiO_2 ratio	1:2.49	1:2.76	1:2.76	1:2.67
3. Plasticity measurements by Atterburg apparatus				
Liquid limit, %	42.04	42.00	38.26	41.20
Plastic limit, %	26.08	23.53	24.02	22.50
Plasticity Index, %	15.96	18.47	14.18	18.70
(by Pfefferkorn apparatus)				
Plasticity coefficient	31.50	32.80	31.00	33.70
4. Dry modulus of rupture, kg/cm^2	10.50	12.00	9.50	13.00
5. Particle size distribution, wt. %				
Coarser than 20 micron	13	11	17	10
Between 20-2 micron	29	27	28	26
Finer than 2 micron	58	62	55	64
6. PCE, SK No.	←	29 – 30	→	
°C	←	1630 – 1650	→	

The mineral constitution of the investigated clays was determined by a combination of differential thermal analysis (DTA) and X-ray diffraction methods.

The DTA technique was carried out up to 1000°C, with a constant heating rate of 10°C/min. The DTA curves are shown in Fig. 2. X-ray analysis was carried out

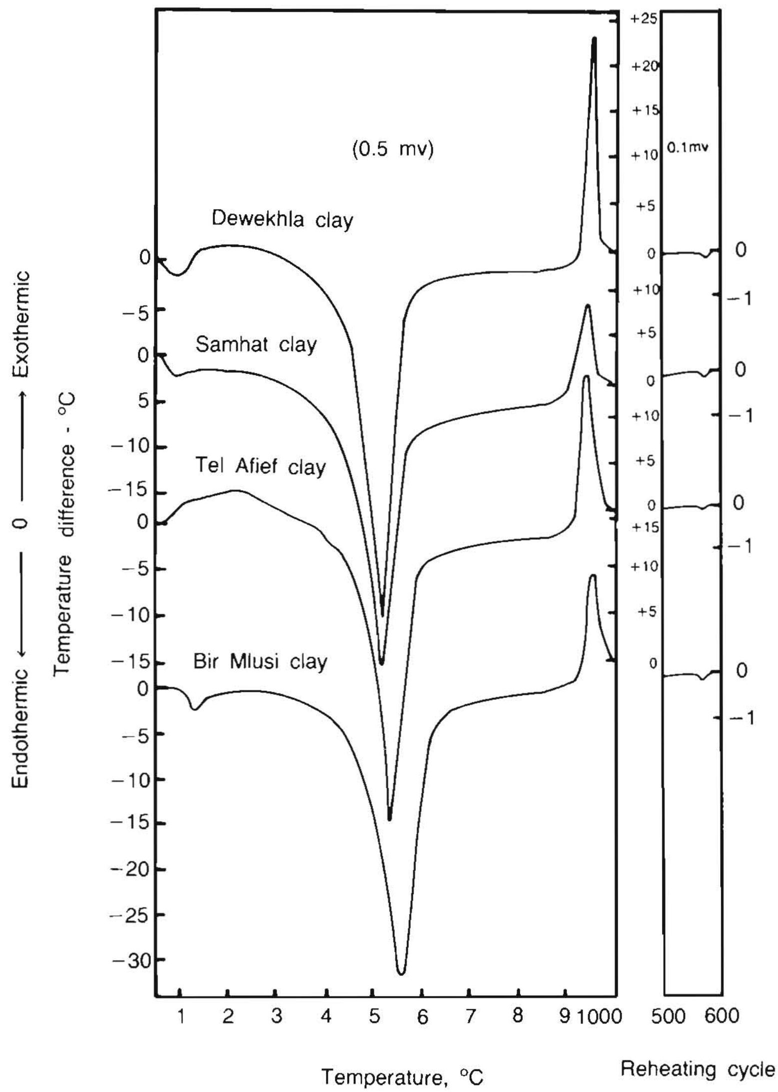

Fig. 2. Differential thermal analysis curves of the investigated clays

using a Siemens X-ray Diffractometer type 500-D. The results obtained are shown in Fig. 3.

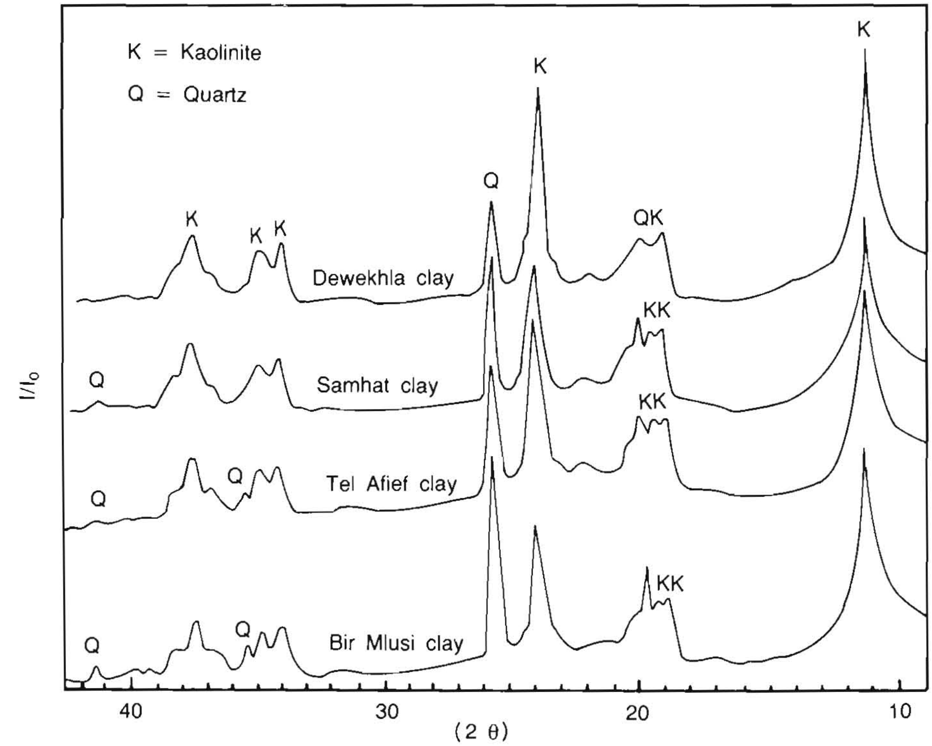

Fig. 3. X-ray diffraction patterns of the investigated clays.

The sintering parameters of the clays investigated were determined for hand moulded samples (50 mm diameter and ≃ 50 mm height) prepared from the finely ground clays (−0.25 mm sieve) and mixed with about 10% water. The process of sintering in these clays could be deduced from the curves delineating the variation in apparent porosity and cold crushing strength with firing temperature, Fig. 4.

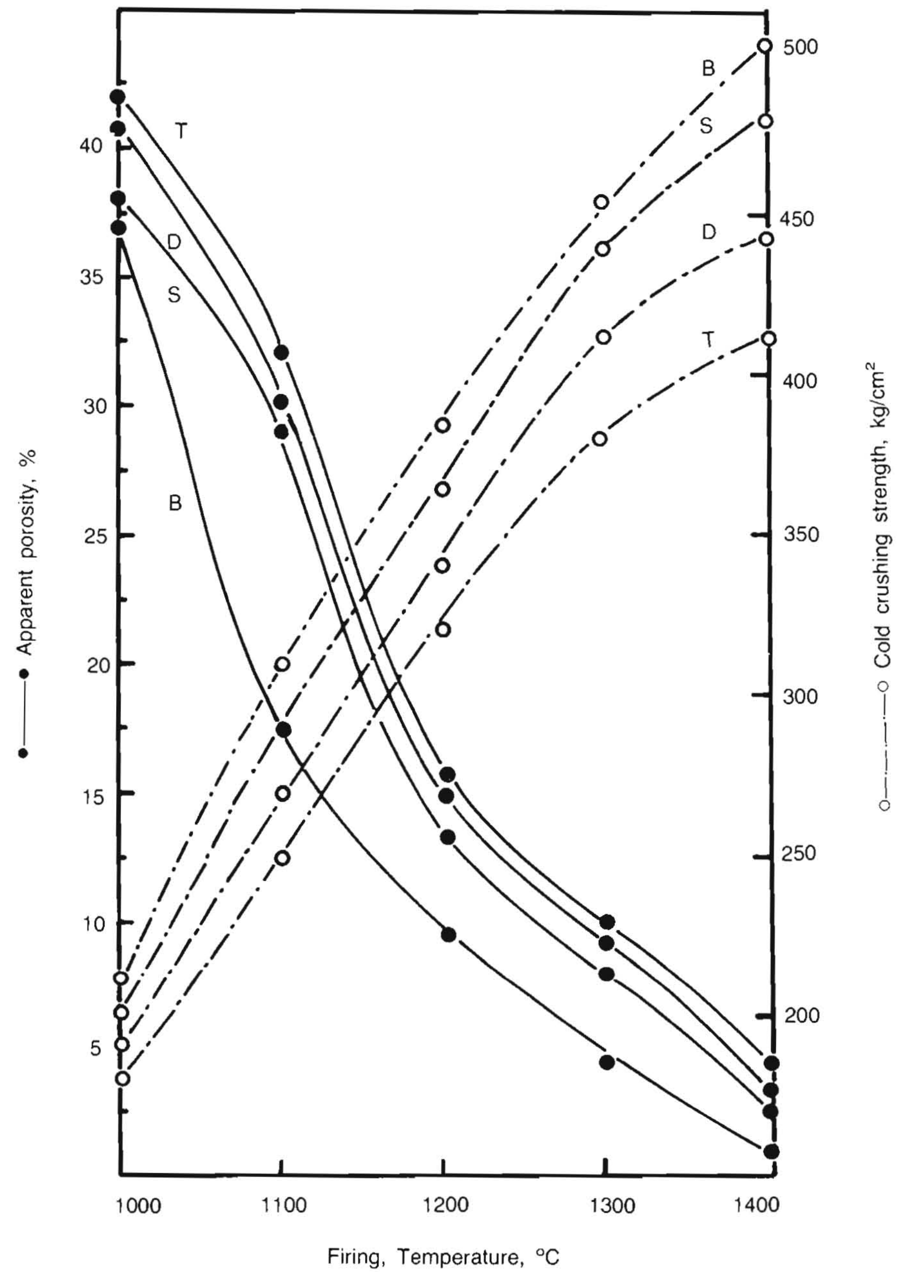

Fig. 4. Variation in porosity and strength ot raw clays as function of firing temperatures

Representative samples from each raw clay were selected for the preparation of grog. Grog was generally made by calcining the clay lumps for 2 hr at 1350°C, followed by crushing and grinding into two grain sizes of (2.0–0.25 mm sieve) and (< 0.25 mm sieve) and their packing densities were determined. Optimum grain size combinations for grog and raw clay were found through a series of packing density determinations. A mixture of 65% graded grog and 35% finely ground raw clay was the optimum proportion. Thus, a mixture of the following graddings was used for the preparation of the bricks:

2.0 – 0.5	0.5 – 0.25	– 0.25	mm diameter
45% grog	10% grog	+ 10% grog 35% raw clay	wt. %

The sintering parameters of the prepared grogs are given in Table 2.

Table 2. Sintering parameters of the grogs fired at 1350°C

Source of grog	Bulk density g/cm^3	Apparent porosity %	Water absorption %
Dewekhla clay (D)	2.43	4.85	2.28
Samhat clay (S)	2.50	2.25	1.06
Tel Afief Clay (T)	2.42	5.09	2.34
Bir Mlusi Clay (B)	2.49	2.29	1.07

Batches from each raw clay were mixed with the corresponding grog and were processed in the form of briquettes (50 mm in diameter and ≃ 50 mm in height), by the semi-dry method using moulding pressures of 250 kg/cm^2 and 500 kg/cm^2. The moulded samples were carefully dried at 110°C for 24 hr, followed by firing at temperatures ranging between 1300 - 1450°C. The rate of heating was 10°C/min up to 1000°C, then 3-5°C/min from 1000 to 1450°C. The soaking time was 2 hr at each firing temperature. The physical properties of the fired samples were determined following the British standard specifications 1902 (1967), and the results are given in Table 3. The technological properties of the selected samples were also determined according to B.S.S. 1902 (1967), and the results are given in Table 4. The results obtained in Tables 3 and 4 were within the permissible limits of error of each property.

Table 3. Physical properties of the fire-bricks produced from the investigated clays

Sample No.	Composition of the mixes, wt%		Moulding pressure kg/cm²	1300°C			1350°C			1400°C			1450°C		
	Grog	Raw clay		B.d. g/cm³	App. por. %	Water abs. %	B.d. g/cm³	App. por. %	Water abs. %	B.d. g/cm³	App. por. %	Water abs. %	B.d. g/cm³	App. por. %	Water abs. %
1	65 D	35 D	250	2.18	25.77	12.58	2.18	25.22	12.31	2.18	24.33	11.88	2.20	23.59	11.49
2	65 D	35 D	500	2.23	21.99	10.33	2.23	21.59	10.11	2.25	21.41	9.96	2.26	19.93	8.01
3	65 S	35 S	250	2.25	20.48	9.99	2.26	17.84	8.44	2.28	14.89	7.44	2.29	12.84	6.27
4	65 S	35 S	500	2.29	17.58	7.96	2.30	14.74	6.72	2.31	11.44	5.60	2.33	10.92	5.33
5	65 T	35 T	250	2.14	21.49	10.29	2.15	21.00	10.24	2.15	20.10	9.81	2.16	19.44	8.90
6	65 T	35 T	500	2.16	20.46	9.43	2.17	19.86	9.10	2.18	18.66	9.01	2.20	17.11	7.76
7	65 B	35 B	250	2.19	20.43	9.76	2.22	19.29	9.10	2.24	17.62	8.11	2.26	14.52	7.70
8	65 B	35 B	500	2.26	18.02	8.85	2.28	16.91	7.87	2.29	14.67	6.56	2.30	12.50	5.60
9	65 D	35 B	250	2.22	18.54	8.41	2.25	17.90	8.07	2.26	17.26	7.73	2.27	15.13	6.98
10	65 D	35 B	500	2.24	16.68	7.41	2.27	15.92	7.01	2.28	15.09	6.65	2.30	13.90	6.41
11	65 T	35 B	250	2.20	18.09	8.83	2.22	17.07	8.10	2.23	16.00	7.81	2.26	13.54	5.92
12	65 T	35 B	500	2.24	17.44	7.79	2.26	16.63	7.34	2.27	15.28	6.83	2.30	12.27	5.32

B.d. = Bulk density, App. por. = Apparent porosity, Water abs. = absorption.

Table 4. Technological properties of the selected fire-clay brick samples

Sampe No.	1	2	3	5	7	9	11	Commercial Type
Moulding Pressure, kg/cm²	**250**	**500**	**250**	**250**	**250**	**250**	**250**	
Firing temperature, °C	**1450**	**1350**	**1350**	**1350**	**1350**	**1300**	**1300**	
Properties								
Total linear shrinkage, %	0.81	0.97	1.07	0.64	0.93	0.97	0.97	–
Bulk density, g/cm³	2.20	2.23	2.30	2.15	2.22	2.22	2.21	1.97
Apparent porosity, %	23.59	21.64	17.89	21.05	19.28	18.50	18.09	22.10
Water absorption, %	11.48	9.55	8.55	10.27	9.10	8.40	8.25	–
Cold crushing strength, kg/cm²	250	300	400	280	350	410	420	246
Permanent linear change, % (2 hr at 1410°C)	Nil	−0.10	−0.10	−0.10	−0.10	−0.24	−0.27	−0.35
Thermal shock resistance in water, (Heating - cooling cycles)	+15	+15	+15	+15	+15	+15	+15	–
Refractories, SK No.	← 31 – 32 →							31
°C	← 1670 – 1690 →							1670

The effectiveness of the more plastic clay as a binder for the grog of other clays was also studied and the results are presented in Fig. 5.

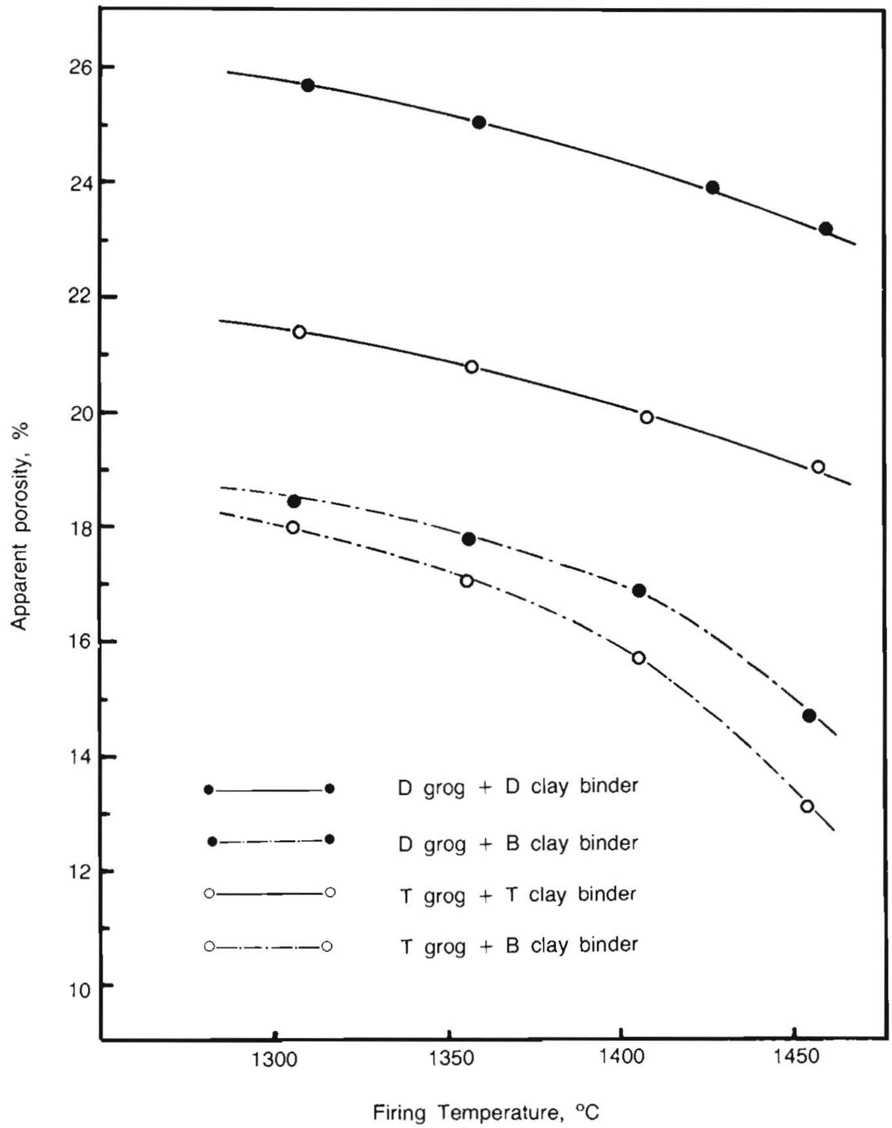

Fig. 5. The effect of using plastic clay (B) as binder for (D) and (T) clays.

The mineralogical constitution of selected fired sample briquettes was determined by the X-ray method and the results are shown in Fig. 6.

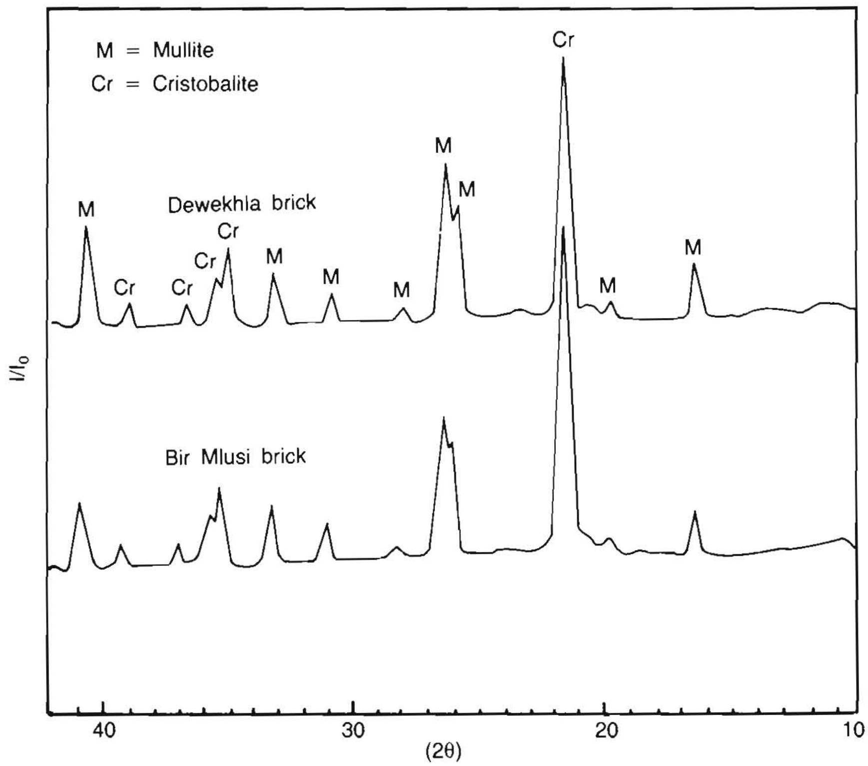

Fig. 6. X-ray diffraction patterns of the selected fired bricks

Discussion

The investigated clays are relatively pure, containing only small amounts of Fe_2O_3. The low levels of CaO and MgO indicate that carbonate contents are negligible. Alkalis and alkali earths are advantageously small, Table 1.

The alumina-to-silica ratio of the investigated clays lies between 1:2.49 and 1:2.76 which does not differ much from that of a pure kaolinite (1:2.0). This suggests that the dominating clay mineral is within the kaolinite group which reflects the refractory nature on such clays. Further, the alumina-to-silica ratio in the investigated clays is consistent with the refractoriness of the samples as determined from P.C.E. values.

The main endothermic and exothermic peaks as depicited by DTA, Fig. 2, indicate that in general, the investigated clays are kaolinitic in nature. The main endothermic peak for the tested clays lies between 550 - 570°C, which is associated with the loss of the lattice water of the kaolinite mineral. The exothermic peak for these clays lies between 960 - 980°C, and is due to the formation of γ-alumina. These two peaks are characteristic of the kaolinite mineral (De Keyser 1959). However, (D) and (T) clays display large and sharp exothermic peaks at a comparatively high temperature, showing that the kaolinite mineral in these clays is well crystallized. Smaller and broader exothermic peaks for (S) and (B) clays reveal poor crystallinity of the kaolinite mineral. The reversible peaks at 573°C indicate the presence of variable amounts of free quartz in the investigated clays.

The X-ray diffraction patterns, Fig. 3, are consistent with the DTA results and indicate that the kaolinite mineral is the main constituent of these clays. Nevertheless, free quartz is also detected.

The plasticity measurements indicated that the investigated clays are quite plastic. However, (S) and (B) clays, containing relatively higher amounts of particles $< 2\ \mu$, showed relatively higher plasticity coefficients as compared with (D) and (T) clays, Fig. 1. Consequently, the former clays showed relatively higher bonding strength, (Table 1) and better sintering parameters, (Fig. 4). Accordingly, the investigated clays showed a wide sintering range. They are adequately plastic and suitable for use as a binder. Moreover, they may be used for making grog.

Based on the above preliminary data, taking into consideration the physical and thermal characteristics of the investigated clays, a technical study was conducted on briquettes produced from different batches.

A combination of nonplastic grog and raw plastic clay is recommended for producing good quality fire-clay bricks. The lower the porosity of the used grog, the better are the properties of the finished bricks. It was found that a firing temperature of 1350°C is quite sufficient for producing dense grog, with the required low porosity, from the investigated clays, Table 2.

The extent of sintering in investigated brick samples is usually assessed from their densities, porosities, and strengths. Higher firing temperatures give higher degrees of sintering, which means a decrease in porosity and increase in density and strength. The sintering parameters of brick samples can also be improved by increasing the moulding pressure which leads to more compactness of the particles and less pore voids.

The results given in Table 3 indicate that fire-clay bricks of the medium heat-duty type (32-38% Al_2O_3) could be produced from the investigated raw clays (35%) mixed with their own grog (65%) after semi-dry moulding under a pressure of 250 kg/cm^2 and firing at a temperature not less than 1350°C.

For (D) clay, a higher firing temperature of 1450°C was found necessary for reducing the porosity of the bricks formed under a moulding pressure of 250 kg/cm^2. However, if the bricks were fired at a lower temperature of 1350°C (the normal firing temperature of the medium heat-duty fire-clay bricks) a high moulding pressure of 500 kg/cm^2 was needed.

The investigation of the effect of adding the relatively higher plastic (B) clays to the grog of the other clays (D) and (T), and forming under a moulding pressure of 250 kg/cm^2, indicated that the sintering parameters of the bricks produced were greatly improved even after firing at a relatively low temperature of 1300°C, Fig. 5.

The results given in Table 4 confirm that the technological properties of the produced briquettes, formed under the selected working conditions, adequately meet the requirements of the fire-clay bricks of the medium-heat duty type, (Chesters 1973).

According to the thermal equilibrium diagram of the binary system $Al_2O_3 - SiO_2$ (Aramaki and Roy 1962), any refractory brick made from natural clay is composed of a glassy matrix plus crystals of which mullite and cristobalite are two of the most important components. Indeed, X-ray diffraction patterns of the investigated fired briquettes, (Fig. 6), revealed that they consisted mainly of mullite ($3Al_2O_3$-$2SiO_2$) and cristobalite minerals. Such mineral constitution is characteristic of fire-clay bricks.

Conclusion

The investigated clays are kaolinitic in nature. They are recommended as a valuable source of raw materials for the manufacture of fire-clay refractory bricks. Through proper selection of grog-binder clay composition, suitable moulding pressure, and appropriate firing temperature, fire-clay bricks of the medium-heat-duty type could be produced. Using the relatively more plastic clay as binder was found to improve the sinterability and to decrease the firing temperature of the finished bricks.

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صلاحية بعض أنواع الطين الناري العراقي لإنتاج الحراريات

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مركز بحوث البناء ـ بغداد ـ العراق

يهدف هذا البحث إلى دراسة تركيب وصلاحية بعض أنواع من الطين الناري الموجود بكميات اقتصادية في العراق لإنتاج حراريات الطين الناري.

وقد تم دراسة الخواص الفيزيقية والحرارية لهذه الخامات وأيضاً تركيبها الكيميائي والمعدني وقد اثبتت النتائج ان الخامات المستخدمة ذات لدونة مناسبة وتتميز بدرجة عالية من النقاوة وتتحمل درجات حرارة عالية دون أن تنصهر وتتكون أساساً من معدن الكاؤلينيت بالإضافة إلى نسبة قليلة من معدن الكوارتز.

وقد أمكن تحديد صلاحية هذه الخامات لإنتاج حراريات الطين الناري بواسطة عمل خلطات مناسبة من الطين المحروق والطين الخام واستخدام حبيبات ذات حجوم مختلفة وتشكيل نماذج من الطوب بالطريقة الشبه جافة. وقد تمت دراسة تأثير الضغوط المختلفة ودرجات الحرق المناسبة على الخواص التكنولوجية للنماذج المحروقة.

وقد أثبتت النتائج صلاحية خامات الطين الناري العراقية لإنتاج حراريات الطين الناري ذات الأداء المتوسط ($32 - 38\%\ Al_2O_3$) وذلك بعد اختبار الخلطات المناسبة وتشكيلها تحت ظروف الضغط ودرجة حرارة الحرق المختارة. وهذه الأنواع من الحراريات تستخدم في تبطين معظم الأفران الصناعية ويتم استيرادها بالكامل من الخارج.

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(١) أستاذ الحراريات بالمركز القومي للبحوث بالدقي ـ القاهرة.