Pakistan Journal of Applied Sciences 3(2): 103-109, 2003

Improvement of Chemical and Thermal Properties of Fire-Clay Refractory Bricks

Abu-Hamatteh, Z. S. H. and Al-Taie, M.
Natural Resources and Chemical Engineering Department, Tafila Applied University College
Al-Balqa' Applied University, P.O. Box: (26) Tafila 66141, Jordan

Abstract: The current investigation examines the possibility of using locally available raw materials for the production of fire-clay refractory bricks. The basic raw material is kaolinite clay, which was used for the production of the grog (Chamotte) and as binder clay. The aim of this research work is to improve the chemical and thermal properties of fire clay bricks by adding different percentages of Al_2O_3 to the clay. This study describes the results of tests carried out in order to find the best granulometric composition of the chamotte, the proper chamotte binder ratio, the chemical resistance, gas permeability, thermal shock resistance and the most suitable processing conditions.

Key Words: Chamotte, Refractory Bricks, Kaolinite Clay, Fire Clay, Refractory Lining

Introduction

Refractory materials are used in industry whenever service temperatures in excess of 1000°C are applied. With few exceptions the softening temperatures of these materials are at least 1585°C (SK26).
The kilns and furnaces used in metallurgical, ceramics, cement, glass and other high temperature operations must be designed to withstand long exposures to high temperatures. The main purpose of the refractory lining with which the kilns are supplied is to confine the heat without excessive wear and loss in medicinal strength (Harders and Keinov, 1960).
Consequently, refractory materials must not only have temperature resistance and high softening points, but also a number of other properties such as mechanical, chemical, physical and thermal properties (Darroudi and Landy, 1987).
Chemical reactions between refractory and furnace charge, slag and molten glass and metals, as well as with dust and vapour generated in the kiln, are the main reasons for wear on refractory lining. They lead to a gradual dissolution of the lining. This is frequently combined with the infiltration of liquid phase (slag, glass and metal or reaction products) into the refractory with the result that the thermal properties, in particular the thermal shock resistance are altered (Konopicky, 1965).
Infiltration of foreign materials increases with the size of the pore spaces. Therefore, the DIN standard requires that fire-clay refractory bricks have a porosity of between 15 and 25%. The lower porosity limit is preferred for fine brick linings which are in contact with molten media where a fine texture with even wear characteristics is essential. In those cases where resistance against spalling is of importance, a somewhat higher porosity results in a better resistance against crack propagation (Didier, 1974).
Chemical resistance against flue gases and dust, which are liberated in the kilns, are other essential properties. Porosity is of great influence on gas permeability. The gas permeability can be changed appreciably by proper selection of moulding pressure and by granulometric variations of grog (burned clay).
The resistance against temperature change (thermal shock resistance) is one of the most important properties for the performance of the brick in practical applications when it is exposed to rapid changes in temperatures (Schmidt-Reinholz and Schmitz, 1986).
Temperature gradients and periodic changes in temperature are observed on many parts of metallurgical and glass melting furnaces, air heaters, heat regenerators and boiler units. In areas of high temperature gradients within the refractory work internal stresses are developed because of the difference in temperature on the hot and cold side. In the intermat stresses exceed the ultimate strength limit of the material, the structure of the material is weakened or destroyed through the formation of cracks which can eventually lead to a disintegration of the refractory bricks. Sensitivity to temperature changes is one of the main reasons for the failure of refractory linings (Darroudi and Landy, 1987).
Fire-clay refractory bricks (chamotte bricks) and produced by mixing crushed grog with sufficient binder clay to produce a mass which can be molded into bricks and which will retain their shape during subsequent drying and burning. The grog may consist of calcined fire clay, clacined kayanite (sillimanite-groups), calcined bauxite or other suitable non-plastic high temperature materials. In this work the grog had been prepared from calcined fire clay. It was mixed with plastic fire clay as a binder. The use of grog reduces the drying and fining shrinkage and makes it possible to dry the bricks quickly and without deformation of damage (Harders and Keinov, 1960).
The aim of this research work is to improve the chemical- and thermal properties of fire-clay bricks produced from local kaolinite as a type of clays by adding different percentages of Al_2O_3 to the clay.
Experimentation: The identification of the clay minerals used in this research work was carried out by using Differential Thermal Analyses (DTA). A fixed weight of the sample is packed into a silica glass crucible (Fig. 1), the other compartment using filled with an inter material which has no thermal reaction over the range of temperature of the test, the specimen holder, which is made of sintered alumina, fits into the lower half of a refractory block, the lid of which completes the cylindrical shape, thus enabling it to be used in a tubulary furnace. Thermocouples, which are usually chromed-alumel wire, are arranged in the specimen holder.
The suitability of clay for refractory work depends primarily on its sintering or softening point. In this respect, the chemical analysis is of great importance. Usually, refractory clays are classified by their alumina content, it must be ranged between (25 to 45%). The TiO_2 content in clay normally ranges between 1 and 4%.

The content of iron oxide (Fe_2O_3) which acts, as a flux should not exceed 2.5%. Earth alkalis, which also lower the melting points, are usually found in only small quantities. The total content of flux in refractory clays ($Na_2O + K_2O + CaO + MgO$) should not exceed 6%. Table 1 shows the chemical analysis of the clay used in our develop work. The results indicated that the clay used in this work is suitable for manufacture of fire-clay refractory bricks.

Table 1: The Chemical Analyses of the Clay

Compositions	Weight Percentage (%)
Al_2O_3	37.0
SiO_2	57.8
TiO_2	1.6
Fe_2O_3	1.45
CaO	0.7
K_2O	0.4

In addition to the chemical analysis the burning characteristics of clays depend upon the mineralogical composition which is usually determine by means of X-Ray Diffraction (XRD).
The XRD chart is shown in Fig. 2. The results indicate that the clay consists of 14% quartz and 86% kaolinite.
Another important property is the softening point of the clay during heating. Ceramists usually list the softening point in Pyrometric Cone Equivalent (PCE) which is designation of the standard cone which has a comparable softening point as a cone prepared from the material to the tested. In this investigation Seger Cone (SK) have been used. The investigated clay gave SK 30/31 (1680-1695^{0}C).
The softening point was also determined in the heating microscope. The instrument used was from Leitz/ Wetzlar. The heating microscope consists of an electric furnace with a service temperature of up to 1550^{0}C.
The specimen used in the instrument was made from regular raw material used in the preparation of the fire-clay refractory bricks by means special manually operated press. As shown in the photographic reproduction (Fig. 3), no deformation were observed in the sample up to temperature of 1500^{0}C. Slight changes in the dimensions are due to the firing shrinkage.
Preparation of fire- clay bricks as all clays are subjected to substantial volume changes during drying and burning. It is not possible to manufacture larger items from pure clay, which are dimensionally accurate and free from warpage and distortion. The clay is mixed with Chamotte (grog) in order to reduce the shrinkage. Chamotte (grog) is clay, which has been burnt until temperature of the chamotte was 1450^{0}C. Time of burning was 24 hours in a high temperature electrical furnace.
In most cases chamotte fractions are prepared by crushing and grinding in suitable crushes and mill aggregates. The crushed chamotte is usually divided into three fractions: coarse from 2.5-6.0 mm, 30%, medium 1.0-2.5 mm, 20% and fine 0-1.0 mm, 50%
The crushed Chamotte fractions were mixed and then combined with an optimum quantity of binder clay, in range of 50/50, 70/30 and 80/20 chamotte/ plastic clay and water to obtain moldable mix.
The binder clay was the same clay, which was still plastic, that means not burned. The Chamotte was mixed with varying quantities of plastic clay and water. The amount of water depends on the amount of plastic clay used as binder, it was ranged between 6 to 9%.
For the improving of the chemical- and thermal properties of the fire- clay basic suitable quantities of alumina (Al_2O_3) with some size distribution 20-75 mm 82% and 6-20 mm 18%
Were added to the Chamotte- clay mix. The content of (Al_2O_3) was varied in the range of 5-10%. The green sample was prepared by the semi- dry method using a hydraulic press and a molding pressure of 50n/mm^2. The sample had cylindrical shape (50-mm diameter and 50 mm height) for testing.
After molding and drying the bricks were burned at 1250, 1300, 1350, 1400 and 1450^{0}C. The fired bricks were investigated to their important chemical and thermal properties.
The chemical resistance of produced bricks is carried out according to konopcky. The sample is placed in refractory dish filled with crushed glass. The crushed glass covers one-third the height of the sample. The dish is placed in a furnace heated at 1400^{0}C for duration of one hour. After heating, the sample is removed vertically. After cooling, the coated end of the sample was cut sectionally. The chemical Resistance (R) is then given by:

$$R = \frac{a_{aft} \times 100}{a_{bef}}$$

a_{bef} = sectional area before the testing
a_{aft} = sectional area after the testing

From the equation is to be shown, that higher (R) indicates high chemical resistance.
The permeability of coarse- grain specimen is easily determined in the laboratory by means of opparatus known as the permometer. The principle of the test is to create airflow through the refractory sample by means of a pressure gradient a cross the specimen. The rate of gas flow can then be easily measured. Then by applying Darcy's equation, the coefficient of permeability can be calculated as follows:

$$Ds = \eta \frac{h}{A\Delta P} \times \frac{v}{t}$$

Where:
Ds = specific gas permeability
η = Gas viscosity
v= gas volume in (cm^3)
t= time in minutes
h= length of the specimen
ΔP = Pressure different

The apparatus used for the determination of the specific permeability in schematically is shown in Fig. 4.
The results are expressed in perms. A porous body has a permeability of 1 perm (Pm) if the gas flow through a sample 1-cm long with a cross- section of 1 cm^2 in 1 cm^3 per sec, the gas viscosity is 1 poise and pressure gradient across the length of the specimen is 1 dyne/cm^2. In practical applications the unit nanoperm is used.
Thermal shock resistance was determined according to DIN1068 using cylindrical specimen. The specimens were placed in a furnace of 15 minutes. Rapid quenching was accomplished by dipping in cold water. During the test, the specimen was checked after each cycle for cracks or other visible changes in its structure. When testing high quality refractory bricks, the test is rather time consuming. Frequently, actual failure of the specimen is reached only after a large number of cooling and heating cycles.

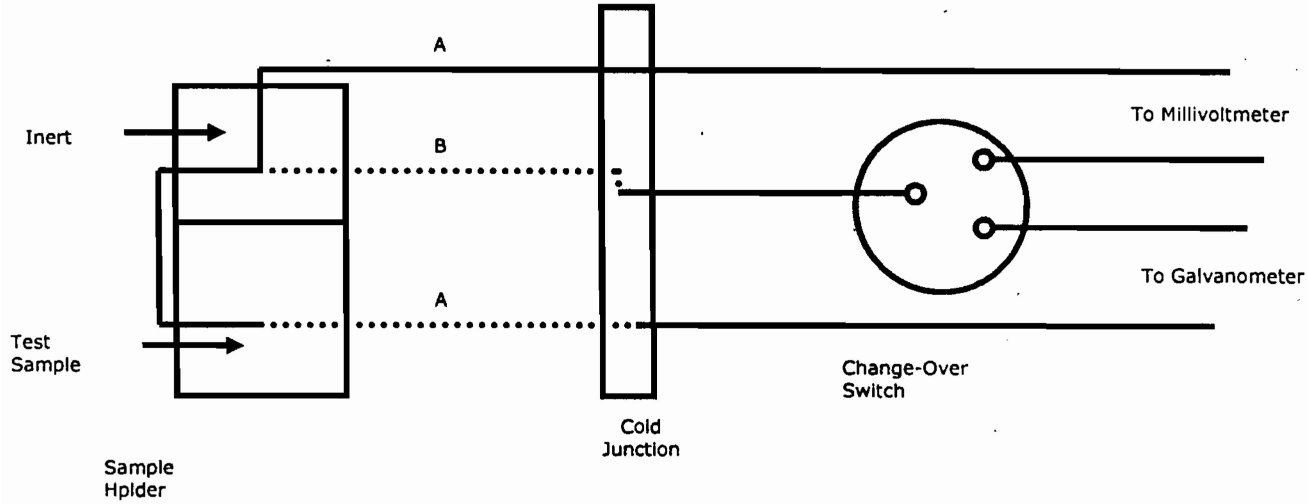

Fig. 1: Differential Thermal Analysis Apparatus, the Specimen Holder and the Thermocouple Arrangement

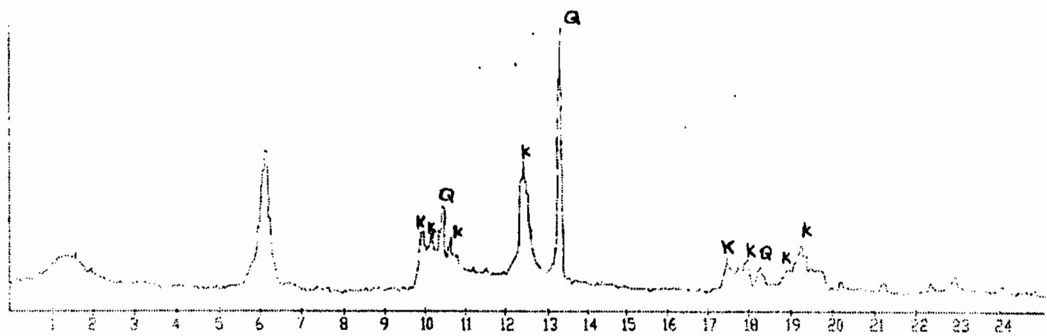

Fig. 2: X-Ray Analysis of the Examined Clay, where K= Kaolinite and Q= quartz

Results and Discussion

The fire- clay bricks produced in this research work had a yellow to brownish color. This is due to the low content of iron oxide in the clay. To burnt bricks. The burnt bricks had a bright and clean sound when hit with a small steel hammer. This is clear indication of the quality of burning. Well-burnt and faultless bricks produce clear metallic sound. The DTA curve (Fig. 5) indicated that the type of the clay is a kaolinite.

Infiltration of foreign material increases with size of the pore space. Therefore, the DIN standard required that Chamotte bricks have a porosity of between 15 and 25%. Fig. 6 shows that the porosity is reduced substantially with increasing firing temperature.

Table 2 shows that the chemical resistance decreases by increasing the Al_2O_3 content. According to these details, the chemical Resistance (R) must not be lower than 85%. The results obtained on our bricks fall within this limit.

Table 2: The Chemical Resistance of Produced Bricks

Time (hr) Immersion In the Molten Gear	Al_2O_3%	A aft Cm^2	A bef Cm^2	R %
1		18.93	19.95	94.9
2	5	18.93	19.87	95.25
3		18.78	19.82	94.75
1		18.55	19.71	94.1
2	10	18.47	19.71	93.7
3		17.79	19.82	89.75

When evaluating the potential attack of liquid slag on the refractory, information about pore sizes in as essential as data about the total pore space. Therefor, the determination of the gas permeability, which is related to pore diameters, has recently received greater attention. The results of the gas permeability measurements are shown in Table 3.

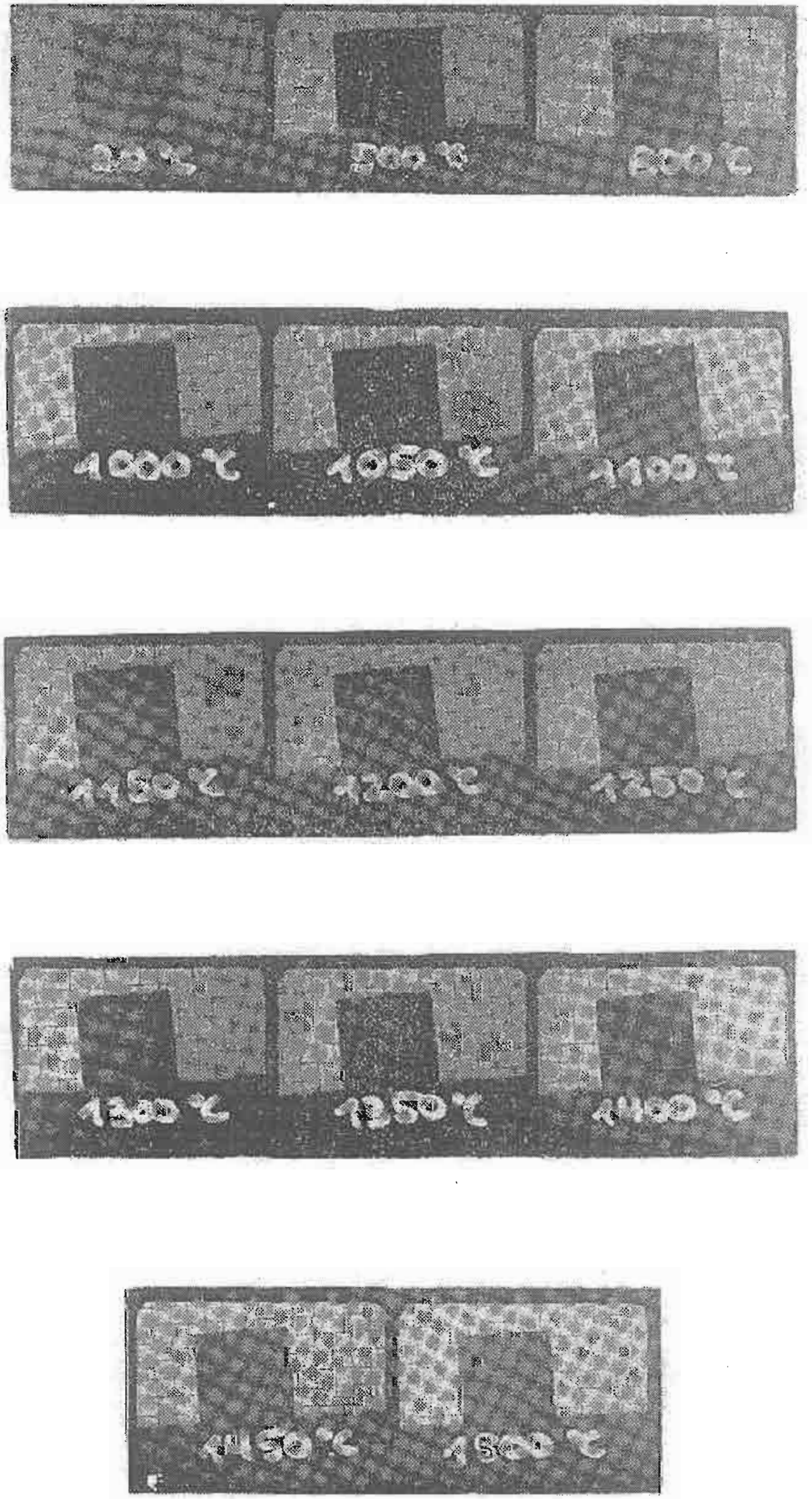

Fig. 3: Thermal Behavior of the Examined Clay in Heating Microscope

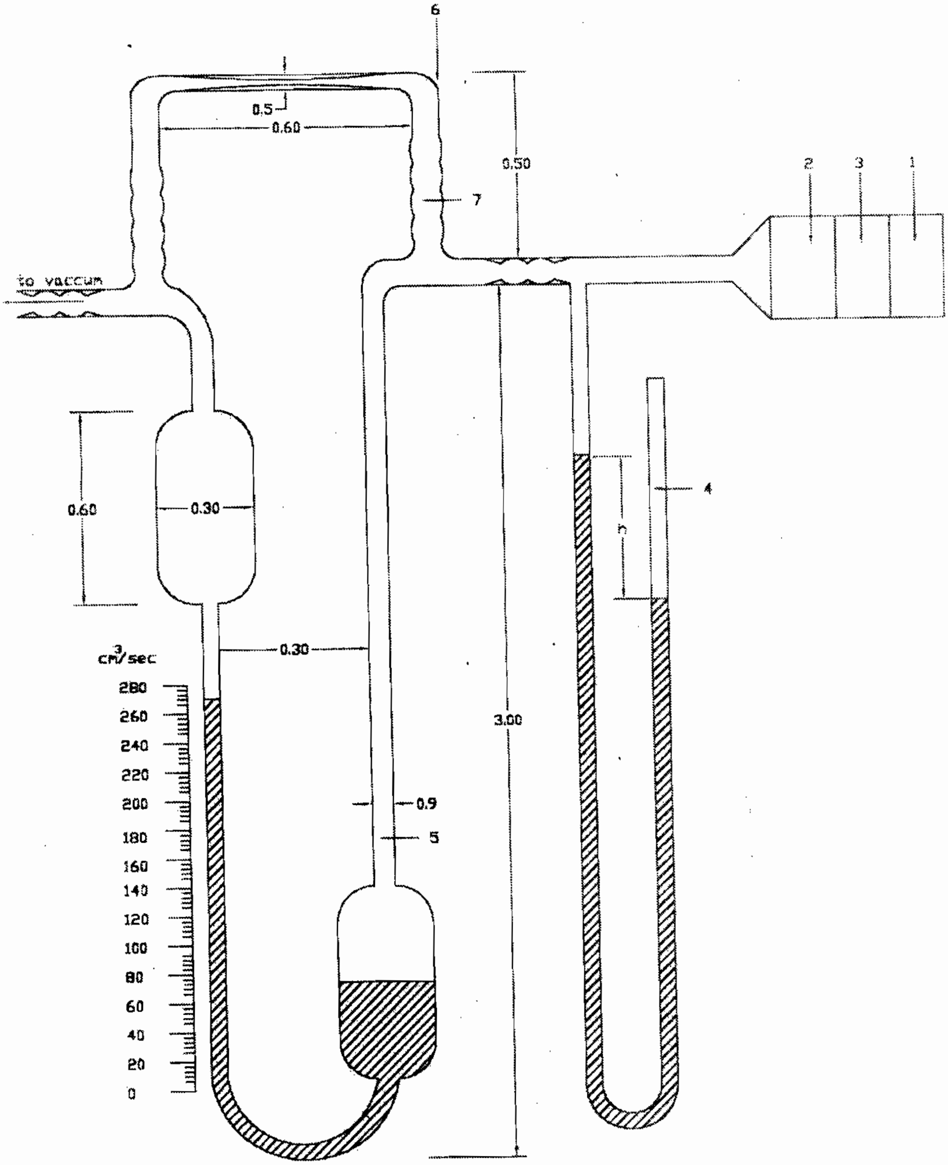

Fig. 4: Gas permometer where; (1) Specimen to be Tested, (2) Sample Holder, (3) Rubber Support for Fitting the Specimen, (4) Open Manometer, (5) Gas Flow Meter, (6) Capillary Tube and (7) Rubber Connections

Table 3: Gas Permeability of Chamotte Bricks

Firing Temp. ^{0}C	Chamotte/ Plastic Clay	Al_2O_3 %	Porosity %	Thermal Shock (Cycle)
	70/30	0	21	> 15
	75/20	5	19	> 21
	65/30	5	18	> 21
1400	55/40	5		> 12
	70/20	10	23.0	> 30
	60/30	10	22.0	> 23
	50/40	10	18.5	> 17

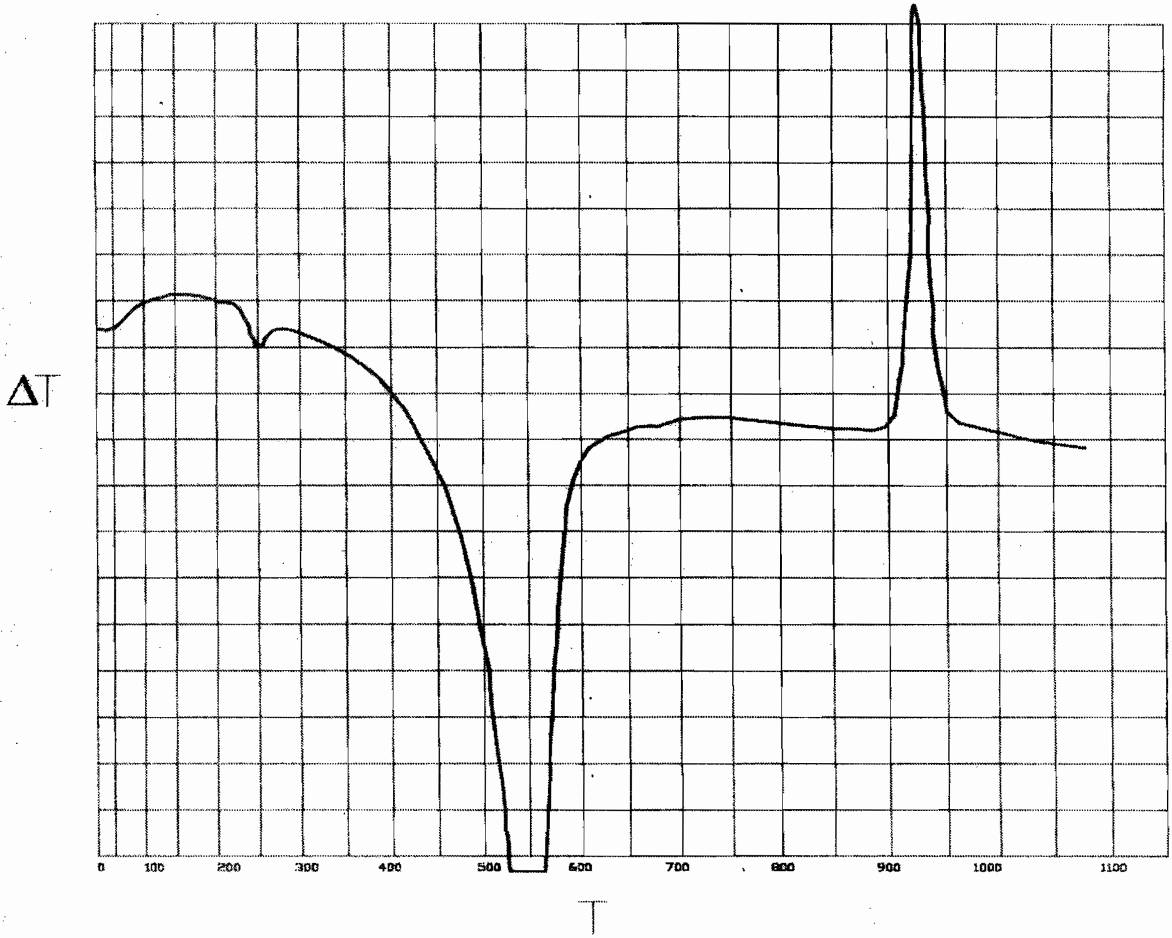

Fig. 5: The DTA Curve

Table 4: The Thermal Shock Resistance of Fire- Clay Bricks

Firing Temp. °C	Chamotte Fraction %		Chamotte/ Plastic Clay	Porosity %	Ds (npm)
1400	50% (0.0-1mm) 20% (1.0-2.5mm) 30% (2.5-6.0mm)		50/50	15.9	9.20
		1-	with 5% Al_2O_3	21.5	10.37
		2-	with 10% Al_2O_3	23.5	12.40
			70/30	14.4	15.96
		3-	with 5% Al_2O_3	19.0	16.21
			with 10% Al_2O_3	22.0	16.88

Lowest value (9.20 npm) has observed on mixes proposed with the Chamotte fractions 0-1 mm (50%), 1-2.5 mm (20%) and 2.5-6 mm (30%) with a Chamotte/ clay ratio of 50/50 and a firing temperature of 1400°C. The highest value was obtained with some Chamotte mix when a Chamotte/ clay ratio 70/30 with 10% Al_2O_3 was used. The reason for the different behavior is the higher porosity of the last mentioned mix. Frequency curves for the values of gas permeability determined on a large number of bricks have been published by Dortmund- Hoerder Hutten Union A. G. The frequency maximum for various types of Chamotte bricks is between 6 and 18 N Perm. The results obtained on our bricks are well with in their limits.

The resistance against temperature change (thermal shock resistance) in one of the most important properties for the performance of the brick in practical applications when it is exposed to rapid changes in temperatures. The resistance against temperature

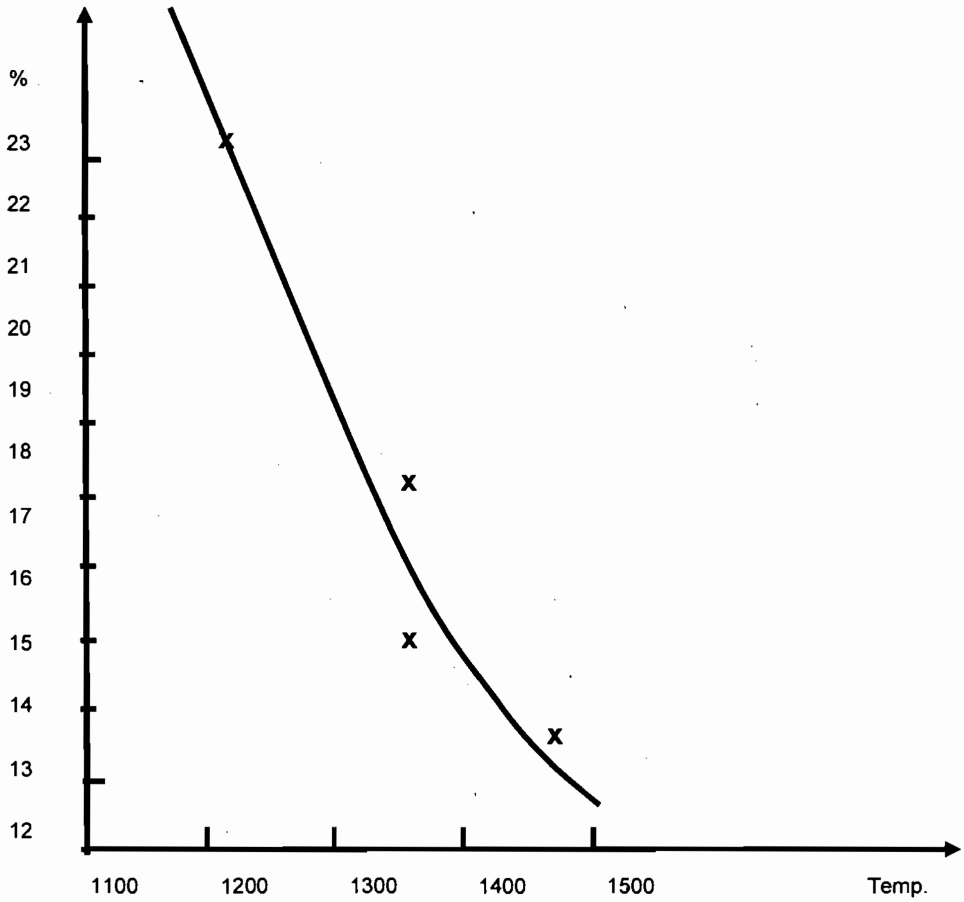

Fig. 6: Relationship Between the Porosity and the Firing Temperature

paper (heating to 900^{0}C and dipping into cold waters). Suitable bricks should with stand 15 cooling and heating cycles without damage in order to fulfill the requirements of the standard. Table (4) shows that all specimen met the above mentioned requirements. The higher value reached with higher porosity and higher content of Al_2O_3.

Conclusion

1. The fire-clay bricks produced in this research work had a yellow to brownish color.
2. The burnt bricks had a bright and clean sound when hit with a small steel hammer.
3. The DTA-curve indicated that the type of the clay is a kaolinite.
4. The chemical resistance of produced chamotte bricks decreases by increasing the Al_2O_3-content.
5. The gas permeability of produced chamotte bricks increases by increasing Al_2O_3 content.
6. The resistance against temperature change (thermal shock resistance) of the produced chamotte bricks increased with the increasing of Al_2O_3 content.

References

Darroudi and R. A. Landy, 1987. Effect of temperature and stressing rate on factor strength of high-Al_2O_3 refractors, the American Ceramic Society Bulletin, Vol. 66, No. 7:1139-1143.

DiDier Feuerfest Technik, 1974. Feuerfeste Baustoffe und ihre Eigenchaften.

Harders and Keinov, 1960. Feuerfestkunde, Springer-Verlag, Berlin, 364.

Konopicky, K., 1965. Vorganse in der grenzchicht Zwischen Feuerfesten Material und glas bzw. Schlacke, Westdeuscher-Verlas, Koln und opladen, 27.

Schmidt-Reinholz, Ch. and H. Schmitz, 1986. Physicalische und chemische Untersuchungs Verfahren in der Grob-Keramik, Sprechsaal, Vol. 119, No. 1:14-18.