

## STUDY OF MULLITE FORMATION IN FIRECLAY BRICKS

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Blends of high alumina clay from Choi, Attock and fireclay from Mianwali have been studied to produce bricks with improved characteristics. Improvement were followed by investigating mullite formation, thermal shock resistance, permanent linear change on reheating, crushing strength, porosity and bulk density.

**Key words:** Mullite, Fireclay, Bricks alumina refractories.

### Introduction

Mullite and high alumina refractories belong to one of the most important group of refractories. The chief advantages of a large proportion of mullite in refractory bricks are (i) increased refractoriness (ii) greater refractoriness under-load (iii) greater resistance to corrosion and (iv) increased spalling resistance. Besides these advantages mullite bricks generally have lower porosity and higher strength than other high alumina bricks because of inter-locking mullite crystals in the matrix. Since these refractories are resistant to iron oxide corrosion, so in steel manufacturing where refractories are liable to be corroded by slag containing high amount of iron oxide, mullite refractories are of great value.

Mullite is the main constituent of aluminosilicate refractories, which are being used in glass, cement, iron and steel industries. This is stable upto 1800°. In the field of ceramic technology, mullite containing bodies are generally prepared by firing one or more sillimanite group of minerals or kaolinite.

Formation of mullite is not only temperature dependent but also time dependent [1]. Impurities also effect the rate of mullite formation. The role of impurities or mineralisers for mullite formation in solid state reactions is well-known. Mineralisers for mullite formation have been investigated by many workers [2-6]. It has been found that elements of group II of the periodic table, increase the rate of mullite formation, with increasing atomic number. Elements of group III retard mullite formation. Cations like Mn, Ti, Zr and B have the intermediate positions. The results of various authors differ greatly from one another, e.g. Svirivenko *et al.* [7] had concluded for groups I and II elements that mineralising effect of a given change increased with decreasing radius. Skinner *et al.* [8] investigated the effect of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O on mullitization of Al<sub>2</sub>O<sub>3</sub> and quartz fired at 1200°. They found that alkali oxides do not aid mullite transformation, but even diminish the effect of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. Efficiency of the mineralisers to accelerate mullitisation depends to a large extent on their concentration and temperature.

Palmeri [9] arranged mineraliser in the following series:



Parmelee and Rodriguez [10] found that when concentration of TiO<sub>2</sub> is upto 1%, mullite formation is maximum. When the concentration of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> increased from 1-4%, the yield of mullite decreased in case of TiO<sub>2</sub> but increased in case of Fe<sub>2</sub>O<sub>3</sub>. Similarly upto 1% of MgO increases the yield of mullite. Mullite formation is maximum when K<sub>2</sub>O and Na<sub>2</sub>O concentration is 1% and the firing temperature is 1500-1600°.

Bricks presently available in the market may have high alumina content, but their physical properties are substandard because of inadequate compositions and improper firing. Mullite formation may be negligible or very small in the commercially available bricks.

We have tried to develop bricks with maximum possible mullite formation. For this purpose, we are studying blends of various clays. The present study investigates blends of high alumina clay from Choi, Attock and fireclay from Mianwali. We have tried to understand and interpret the effect of various impurities present in these clays. These studies will provide guidance for carrying out further studies of various other blends.

### Materials and Methods

High alumina clay abundantly available at Choi area, Dist. Campbellpur and fireclay of Mianwali were the only raw materials used for these investigation. Grog of Choi clay was produced by firing the clay at about 1575°. The fireclay was used in the raw state in the composition-blends. The chemical compositions of the clays are shown in Table 1.

*Preparation of high-alumina-clay grog.* The raw high-alumina-clay was pressed in the form of bricks of standard size with about 7-10% moisture with the help of a hydraulic press (200 ton total pressure). The bricks were air dried for a week and fired in a laboratory-made down-draught furnace at 1575° with a soaking period of 4 hr. These fire bricks were crushed, disintegrated and graded as follows:



**Grain size composition.** The grog of Choi clay after crushing and grinding was graded as follows:

1. Passed 4 and retained on 25 mesh i.e. (-4+25) coarse
2. Passed 26 and retained on 72 mesh i.e. (-25+72) medium
3. Passed 72 mesh i.e. (-72) fine

B.S.S. Sieves were used for the grading.

The raw clays used as binder throughout these investigations were ground to pass through a 100 mesh sieve.

**Preparation of test pieces.** Two batches of the brick compositions with different clay: grog ratios were prepared (Table 2). In compositions 1,2,3 the clay/grog ratio was 65:35 while in compositions 4-6, the ratio of grog to clay was 75:25. In compositions 1 and 4, only high alumina clay was used while in compositions 3 and 6 only fire-clay was used as binding material. In compositions 2 and 6, both high alumina and fireclay were utilized. All the six compositions under study were prepared by taking weighed amounts of clay and grog. Each composition was thoroughly mixed, moistened with about 5% of water and aged for 24 hr. before pressing. Standard size bricks (9"x4½"x3") were pressed at a total pressure of 200 ton using locally fabricated heavy hydraulic press available in the laboratories.

**Firing.** The bricks were air dried for two days and then oven dried for about 16 hr. at 110° before firing. The bricks were fired in a laboratory made down-draught furnace at 1525° keeping the soaking temperature constant for a period of 4 hr. Segar cones were used measuring the firing temperatures.

#### EVALUATION

**Porosity and bulk density.** The porosity and bulk density of the bricks were determined on 50-60 ml sized samples cut from the bricks. The determination was done according to the British Standard Methods of testing refractory materials [11].

**Crushing strength.** Crushing strength tests were made on a standard compression machine "Whykekamm furnace" using standard ASTM Method [12]. Test specimen of 2 cu, in, were cut from the bricks. In some cases half bricks of size (4½" x 4"x3") were employed.

**Linear shrinkage.** The shrinkage of the bricks was determined using usual standard method [13].

**Refractories.** Pyrometric cone equivalents of all the compositions were determined by comparison with segar cones. Samples were prepared according to the procedure described in Standard Test No. 5 [14].

**Thermal expansion.** Thermal expansion was determined [15] by using horizontal type dilatometer. The size of the

sample was 2"x1½" and was cut from the brick.

**Thermal shock resistance.** Thermal shock resistance was determined by using usual standard method [16].

**Re-heat-linear change.** The samples were refired at 1500° with a soaking period of 2 hr. The linear changes was determined in the form of contraction or expansion [17].

**Mullite estimation.** Mullite formation alongwith the formation of compounds such as Sillimanite, Kyanite and Corundum were followed by X-ray diffraction.

#### Results and Discussion

Mullite formation in compositions 1-6 when fired at 1525° for 4 hr. is presented in Table 3. "The maximum possible amount of mullite formation in compositions No. 1-6 is 41.07, 65.88, 90.7, 41.07, 55.09 and 76.07%". Maximum amount of mullite is formed in composition No. 3, which contained 65% grog of high alumina clay and 35% raw fire

TABLE 1.

	High alumina clay from Choi	Fireclay from Mianwali
I/L	13.03%	13.06%
SiO <sub>2</sub>	10.48%	42.30%
Al <sub>2</sub> O <sub>3</sub>	71.50%	41.10%
Fe <sub>2</sub> O <sub>3</sub>	0.59%	0.50%
TiO <sub>2</sub>	4.50%	1.18%
CaO	Traces	0.35%
MgO	Traces	-
Na <sub>2</sub> O	0.081	0.17
K <sub>2</sub> O	0.045%	0.23%

TABLE 2.

Composition No.	Grog (%)	High alumina clay (%)	Fire clay (%)
1.	65	35	-
2.	65	17.5	17.5
3.	65	-	35
4.	75	25	-
5.	75	15	10
6.	75	-	25

TABLE 3.

Sample No.	Phases identified (%)			
	Mullite	Corundum	Sillimanite	Kyanite
1.	40	46	12	2
2.	60	20	15	5
3.	75	20	5	Traces
4.	42	42	14	2
5.	55	30	13	3
6.	60	30	7	3



clay. The amount of mullite decreased as we replaced some of the raw fireclay with raw high alumina clay in composition No. 2 and 1. The same trend of mullite formation is shown in compositions No. 6, 5 and 4. Maximum mullite formation is shown by composition No. 6 and the mullite formation decreases in composition No. 5 and 4.

Mullite formation has its effect on various properties of the bricks. Table 4 shows the specific gravity of the fired bricks. It is clear that the specific gravity decreases from No. 1-3 and then again from No. 4 to 6. This shows that increased formation of mullite decreases the specific gravity because the specific gravity of mullite is 3 which is much less than 4.0 which is the specific gravity of corundum. In all these compositions the amount of corundum formation decreases as the amount of mullite increases.

Permanent linear change on reheating the refractories is shown in Table 5. Composition No. 1 shows the maximum contraction. Contraction decreases in No. 2 while composition No. 3 shows an expansion. A similar behaviour is shown by composition No. 4, 5 and 6. There is no possibility of any

further reaction and contraction is due to excessive sintering while composition No. 3 and 6 show expansion because in these compositions the mullite formation is not complete and there is a possibility of further mullite formation.

Bulk density of the bricks decreases with the increased formation of mullite. This trend is shown by the bulk density values of composition No. 1 - 3 and then again by 4 - 6 although mullite formation is not the only factor affecting the bulk density.

Thermal shock resistance of all the refractories is quite good and above 30 cycles. Refractories of the bricks was determined upto a temperature of 1650° attainable in our laboratories. The refractoriness of all bricks was higher than cone 26. TiO<sub>2</sub> content of composition 1-3 and 4-6 on the basis of batch composition is 4.42, 3.74, 3.07, 4.48, 4.04, 3.46. Decreasing TiO<sub>2</sub> content has a positive effect upon mullite formation. This trend is clear in both the sets of compositions i.e. 1,2,3 and 4,5,6. A similar trend is shown by increasing Fe<sub>2</sub>O<sub>3</sub> content in both the sets of compositions. Fe<sub>2</sub>O<sub>3</sub> content of compositions 1-3 and 4-6 is 0.678, 0.662, 0.644 and 0.678, 0.668, 0.655. This data confirms the findings of Chaudhuri [18]. This study shows that the properties of refractory bricks can be improved by proper formulation and firing of refractory bricks. Quality control of commercially produced bricks may be done by following the mullite formation in these products.

TABLE 4. SPECIFIC GRAVITY OF BRICKS.

Sample No.	1525°	1450°
1	3.341	3.555
2	3.050	3.176
3	2.988	3.139
4	3.150	3.416
5	3.103	3.227
6	3.085	3.306

TABLE 5. PROPERTIES OF HIGH ALUMINA BRICKS FIRED AT 1525°.

	1	2	3	4	5	6
Porosity (%)	21.94	28.2	26.9	20.93	25.17	27.82
Bulk density (gm/ml)	2.696	2.358	2.31	2.74	2.41	2.334
Cold crushing strength lb.	5907	5776	2886	8283	5070	3532
Thermal shock resistance	30+	30+	30+	30+	30+	30+
Thermal expansion (%)	.7473	8043	.7826	.618	.5805	.8113
Refractoriness (Cone)	26+	26+	26+	26+	26+	26+
Re-heat linear change at 1500° for 2 hr.	<u>2.2</u> Cont	<u>1.15</u> Cont	<u>3.25</u> Exp	<u>1.14</u> Cont	<u>1.16</u> Cont	<u>4.22</u> Exp

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