HIGH TEMPERATURE DEFORMATION BEHAVIOUR OF [KIBI] KAOLIN CLAY REFRACTORY BODIES

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ABSTRACT

The proper selection and application of refractory products requires a good knowledge of their high temperature deformation behaviour as a function of time and stress. Resistance to creep failure, an important performance criterion, has been evaluated for [Kibi, Ghana] Kaolin clay bodies using the Netzsch Furnace. During the test thermal expansion was steady until a temperature of ≅845℃ at which point a maximum dilation of 0.29% was recorded. The heat treatment continued, after the maximum dilation, until the furnace attained a soak temperature of ≅1280℃. Heating over an extended time period at elevated temperatures was carried out to allow the various stages of creep, i.e., the initial elastic extension through primary and secondary creep to the tertiary creep level, to be monitored. The per cent deformation (creep) and creep rate recorded between the 20th and 50th hours of heating, which is an important indicator of the load bearing capacity of refractory bodies was found to be 0.241% and 0.009%/hr respectively.

Keywords: *Kaolin clay, refractory, deformation, load-bearing capacity.*

I. INTRODUCTION

The importance of aluminosilicate refractory brick as a lining material is well known. The thermal expansion and hot load deformation data are indispensable for lining design and construction of refractory structures. Refractories of high thermal expansion are very susceptible to in-service thermal spalling in severe cycling environments [1].

The primary load on a refractory lining is its own weight. This causes stresses of only a few MPa. At such low stress levels the deformation and creep rates are expected to be very low. However, the total subsidence over a refractory lining's entire service life may be significant. Thus, the deformation and creep rates at elevated temperatures can be especially important in tall structures such as blast furnaces, and regenerators, which operate continuously for a number of years [2]. Generally, when stress is initially applied an instantaneous elastic strain appears. This is followed by a decrease in strain rate leading to a deformation referred to as primary or transient creep. Transient creep is followed by a secondary or steady state creep. At longer times an accelerating creep rate or tertiary creep results and this may lead to a rapid failure [3]. Thus, data on deformation under load at elevated temperatures are necessary for assessing the load bearing capabilities of refractories to avoid catastrophic failures of refractory structures in service.

Refractory products from Kibi kaolin clay are not yet in use, however, preliminary work [4] carried out to find out the suitability of this clay for refractory production gave positive results. The good refractory nature of the Kibi clay might be related to the topography and rainfall pattern of the area. The Kibi deposit is situated about 8 - 13 km North East of Kibi on the Atewa range, a highly dissected plateau with an altitude of about 690 - 803m. Heavy rainfall, strong leaching and favourable topography have helped to remove some calcium, sodium and potassium; aluminium content was proportionately increased [5,6]. Also, Banning [5] states that abundant vegetation coupled with decaying organic matter have provided bacteria and acids which served to remove iron and other colouring materials, thus improving colour and refractory properties. In the previous work [4] resistance of the refractory bodies to creep failure was not investigated, thus no data exist in the literature on the thermal expansion behaviour and hot load deformation of the [Kibi, Ghana] kaolin clay refractory bodies at elevated temperatures. This work is therefore an attempt to provide this data which can serve as a performance criteria for design purposes. Since thermal expansion and deformation properties are influenced by the nature of raw materials, the chemistry of the raw material before and after calcination was also evaluated.

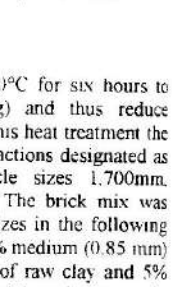
II. EXPERIMENTAL PROCEDURES

1. The Chemistry of Raw and Calcined Clay

This was carried out by using the standard spectrochemical analysis of silicates employing the lithium metaborate ($LiBO_2$) fusion method. A representative sample of the raw and calcined material of particle size less than 0.075 mm was fused at 900°C for 15 minutes after which it was dissolved in a mixture of HCl and HNO_3. The resulting solution was analysed using a DC Plasma Spectrometer.

2. Preparation of Test Pieces

The raw clay was fired at 1500°C for six hours to produce a dead-burned material (grog) and thus reduce shrinkage during the final firing. After this heat treatment the resulting grog was screened into three fractions designated as coarse, medium and fine with particle sizes 1.700mm, 0.850mm and 0.075 mm respectively. The brick mix was prepared by mixing the three different sizes in the following proportions: 15% coarse (1.700 mm), 60% medium (0.85 mm) and 25% fine (0.075 mm). About 10% of raw clay and 5% water were added to the granular material to improve the



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workability and green strength. The entire batch was blended into a macrohomogeneous mixture to enhance good packing based on the gap grading system. The gap-type system is based on the principle that proper sizes and portions exist, so that the larger voids created by the coarsest particles are filled with smaller particles and the newly created smaller voids are in turn, filled with even smaller particles. Cylindrically shaped test pieces were produced by shaping in a cylindrical steel mould under a uniaxial pressure of about 104 MPa. The test pieces were dried and fired at 1500°C. After cooling the centre of the test piece was bored to allow the passage of the creep rod (of the Netzsch Unit) in which a thermocouple was located.

3. Thermal Expansion and Creep Under Load

This test was carried out to assess the thermal expansion and load bearing capacity of the refractory bodies. In this investigation the standard American Society of Testing Materials (ASTM) method designated as C832-84 was used. The heating rate was 0.97°C/min. and the maximum soak temperature and heating duration were ≅1280°C and 50 hours respectively. The maximum load applied was 391N. The atmosphere was air and the diagram of the Netzsch Furnace used is shown in Fig. 1.

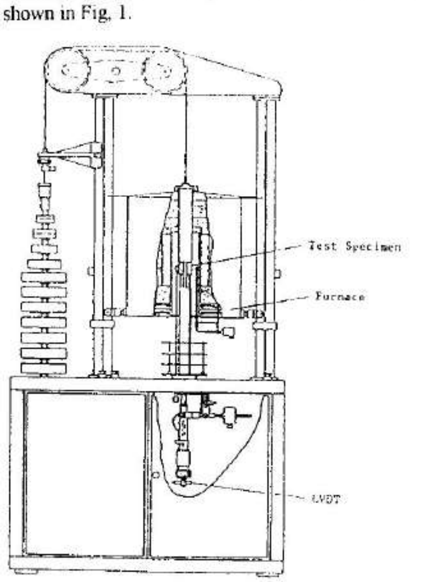

Fig. 1: Schematic Diagram Of The Netzsch Unit

During the run, readings from all the three thermocouples of the creep furnace as well as the digital signals were monitored. Furnace Temperature was taken from the control thermocouple located inside the furnace near the heating elements. A second thermocouple located outside and right next to the sample gave the External Temperature readings. Located inside the creep rod or LVDT (Linear Variable Differential Thermocouple) which passed through the sample during the run was a third thermocouple which was centrally positioned in the sample and gave the Sample Temperature (or Internal Temperature). Control Out Raw was a digitised signal from an interface box to the computer to drive the electrical package used in increasing and decreasing voltage for output. LVDT Out Raw was a digitised signal from the interface box to the computer to calculate the movement of the LVDT (creep) rod during the run. Time HH: MM: SS: was the run time giving actual time from the beginning of run.

III. RESULTS AND DISCUSSION

The chemical analysis of the raw and calcined material are as in Tables 1 and 2. Since creep resistance of aluminosilicate refractories is essentially dependent on the development of well-crystallised mullite matrix the importance of any condition affecting the rate of mullite formation cannot be overemphasised. Fe_2O_3 and TiO_2 present in the raw material as impurities (Table 1 and 2) have the ability to enhance the mullitisation process which gives rise to mullite which enhances creep resistance of aluminosilicate refractories [7,8]. The ability of Fe_2O_3 and TiO_2 to enhance mullitisation is probably due to the fact that both Fe_2O_3 and TiO_2 can form solid solution with mullite [9] through a substitution which is permitted by valence and ionic criteria [9,10]. The presence of alkalis is generally detrimental to aluminosilicate refractories since they have a strong fluxing action on Al_2O_3 - SiO_2 mixtures.

Table 1: Chemical Analysis of Raw Kaolin Clay From Kibi

Constituent	Composition (%)
Al_2O_3	36.60
SiO_2	43.40
TiO_2	1.80
Fe_2O_3	1.50
CaO + MnO	0.10
MgO	0.45
Total Alkalis	2.17
L.O.I	14.00

Table 2: Chemical Analysis of Kaolin Clay From Kibi After Calcination

Constituent	Composition (%)
Al_2O_3	41.70
SiO_2	52.10
TiO_2	2.02
Fe_2O_3	1.52
Alkalis	2.14

Results, shown in a tabular form (Table 3) to give details of linear change at 30s intervals during the deformation test conducted over an extended period of 50 hours, showed a steady initial expansion which continued until a temperature of 865.18°C. A corresponding maximum dilation of 0.29% was recorded at this temperature. The test piece could withstand further heating up to ≅ 1280°C. Generally, thermal expansion is taken to be a function of the individual phases which are present in the refractory product, their distribution,

Table 3: Thermal Expansion/Creep Data Obtained Under a Load of 391N on a Sample with a Diameter of 33.98mm.

Time HH:MM:SS	Furnace Temp.	External Temp.	Internal (Sample) Temp.	Control Out Raw	LVDT Out Raw	% Linear Expansion/Creep
0:1:0	51.94	39.91	33.5	89.00	-1.00	0.03
0:30:0	79.45	68.44	51.94	85.00	2.00	0.02
1:0:0	109.09	90.41	70.90	113.00	3.00	0.03
1:30:0	137.18	115.61	91.77	155.00	4.00	0.04
2:0:0	165.35	142.17	114.30	165.00	6.00	0.05
2:30:0	196.04	170.12	139.70	176.00	7.00	0.06
3:0:0	224.62	197.21	165.35	177.00	8.00	0.07
3:30:0	253.58	225.74	192.53	222.00	10.00	0.08
4:0:0	283.07	254.68	221.25	210.00	12.00	0.09
4:30:0	312.00	282.00	249.16	216.00	14.00	0.10
5:0:0	341.53	312.00	278.76	239.00	15.00	0.11
5:30:0	370.57	341.53	308.79	250.00	17.00	0.12
6:0:0	399.32	371.61	339.44	256.00	19.00	0.14
6:30:0	428.79	400.34	369.54	296.00	21.00	0.15
7:0:0	457.97	430.82	400.34	284.00	23.00	0.16
7:30:0	486.82	460.97	430.82	289.00	25.00	0.17
8:0:0	515.44	490.77	461.97	307.00	27.00	0.18
8:30:0	545.77	522.33	493.73	333.00	29.00	0.19
9:0:0	573.97	552.61	524.28	328.00	31.00	0.20
9:30:0	602.85	582.66	555.54	339.00	33.00	0.21
10:0:0	632.34	613.33	587.47	348.00	34.00	0.23
10:30:0	661.62	643.70	618.10	361.00	37.00	0.23
11:0:0	690.56	673.78	649.37	375.00	39.00	0.24
11:30:0	719.22	703.55	680.32	389.00	40.00	0.26
12:0:0	748.54	732.98	710.92	400.00	43.00	0.26
12:30:0	778.59	764.04	742.15	411.00	45.00	0.28
13:0:0	807.38	793.91	772.22	429.00	48.00	0.28
13:30:0	835.99	824.39	802.90	440.00	51.00	0.28
14:0:0	865.18	854.60	833.31	454.00	54.00	0.29
14:30:0	894.17	884.53	864.30	468.00	58.00	0.28
15:0:0	923.73	915.06	894.17	482.00	61.00	0.28
15:30:0	952.21	945.32	924.59	492.00	66.00	0.27
16:0:0	982.13	975.32	954.79	512.00	71.00	0.26
16:30:0	1010.97	1005.90	984.68	528.00	77.00	0.24

d)

Time HH:MM:SS	Furnacc Temp.	External Temp.	Internal (Sample) Temp.	Control Out Raw	LVDT Out Raw	% Linear Expansion/Creep
17:0:0	1039.65	1035.44	1015.20	541.00	81.00	0.24
17:30:0	1068.84	1065.51	1044.66	557.00	84.00	0.24
18:0:0	1097.79	1096.14	1075.49	569.00	86.00	0.25
18:30:0	1126.62	1125.80	1105.21	595.00	89.00	0.25
19:0:0	1156.18	1156.18	1135.65	603.00	94.00	0.24
19:30:0	1185.52	1185.52	1165.17	621.00	99.00	0.23
20:0:0	1214.77	1214.77	1194.48	638.00	106.00	0.20
20:30:0	1243.14	1243.95	1223.69	658.00	113.00	0.18
21:0:0	1272.21	1273.82	1253.63	675.00	123.00	0.13
21:30:0	1280.28	1283.51	1268.17	627.00	131.00	0.08
22:0:0	1280.28	1282.70	1268.17	614.00	137.00	0.04
22:30:0	1280.28	1283.51	1268.17	596.00	142.00	0.00
23:0:0	1278.67	1282.70	1267.36	596.00	146.00	-0.02
23:30:0	1279.47	1283.51	1268.17	598.00	149.00	-0.04
24:0:0	1279.47	1283.51	1268.17	587.00	153.00	-0.07
24:30:0	1278.67	1282.70	1268.17	578.00	155.00	-0.08
25:0:0	1278.67	1283.51	1268.17	585.00	157.00	-0.10
25:30:0	1279.47	1283.51	1268.17	583.00	159.00	-0.11
26:00:00	1278.67	1283.51	1268.17	582.00	161.00	-0.13
26:30:00	1278.67	1283.51	1268.98	588.00	163.00	-0.14
27:00:00	1278.67	1283.51	1268.17	577.00	165.00	-0.16
27:30:00	1278.67	1283.51	1268.17	584.00	166.00	-0.16
28:00:00	1279.47	1283.51	1268.98	580.00	168.00	-0.18
28:30:00	1279.47	1284.32	1268.98	571.00	169.00	-0.18
29:00:00	1279.47	1284.32	1268.98	574.00	170.00	-0.19
29:30:00	1279.47	1283.51	1268.98	570.00	172.00	-0.21
30:00:00	1279.47	1283.51	1268.98	573.00	173.00	-0.21
30:30:00	1278.67	1283.51	1268.98	567.00	175.00	-0.23
31:00:00	1279.47	1283.51	1268.17	570.00	175.00	-0.23
31:30:00	1279.47	1283.51	1268.17	572.00	176.00	-0.24
32:00:00	1279.47	1283.51	1268.17	567.00	178.00	-0.25
32:30:00	1279.47	1283.51	1268.17	569.00	179.00	-0.26
33:00:00	1279.47	1283.51	1268.17	568.00	180.00	-0.27
33:30:00	1279.47	1283.51	1268.17	564.00	179.00	-0.26
34:00:00	1279.47	1283.51	1267.36	574.00	180.00	-0.27
34:30:00	1278.67	1282.70	1267.36	572.00	180.00	-0.27
35:00:00	1279.47	1283.51	1268.17	569.00	181.00	-0.27

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Time HH:MM:SS	Furnace Temp.	External Temp.	Internal (Sample) Temp.	Control Out Raw	LVDT Out Raw	% Linear Expansion/Creep
35:30:00	1278.67	1283.51	1268.17	580.00	182.00	-0.28
36:00:00	1278.67	1283.51	1268.17	574.00	182.00	-0.28
36:30:00	1278.67	1282.70	1267.36	568.00	183.00	-0.29
37:00:00	1279.47	1283.51	1268.17	570.00	184.00	-0.29
37:30:00	1279.47	1283.51	1268.17	574.00	185.00	-0.30
38:00:00	1279.47	1283.51	1268.17	572.00	185.00	-0.30
38:30:00	1278.67	1283.51	1268.17	555.00	186.00	-0.31
39:00:00	1278.67	1282.70	1267.36	580.00	187.00	-0.32
39:30:00	1279.47	1283.51	1268.17	567.00	187.00	-0.32
40:00:00	1278.67	1282.70	1267.36	578.00	188.00	-0.32
40:30:00	1279.47	1283.51	1267.36	568.00	189.00	-0.33
41:00:00	1278.67	1283.51	1268.17	566.00	189.00	-0.33
41:30:00	1278.67	1282.70	1268.17	567.00	190.00	-0.34
42:00:00	1278.67	1283.51	1267.36	562.00	191.00	-0.35
42:30:00	1278.67	1282.70	1267.36	579.00	191.00	-0.35
43:00:00	1278.67	1282.70	1267.36	570.00	191.00	-0.35
43:30:00	1278.67	1283.51	1267.36	566.00	192.00	-0.35
44:00:00	1278.67	1282.70	1267.36	569.00	193.00	-0.36
44:30:00	1279.47	1283.51	1268.17	567.00	194.00	-0.37
45:00:00	1279.47	1282.70	1267.36	564.00	194.00	-0.37
45:30:00	1279.47	1282.70	1267.36	566.00	194.00	-0.37
46:00:00	1279.47	1283.51	1267.36	570.00	197.00	-0.39
46:30:00	1279.47	1282.70	1267.36	571.00	198.00	-0.40
47:00:00	1278.67	1282.70	1267.36	564.00	199.00	-0.40-
47:30:00	1279.47	1283.51	1268.17	568.00	200.00	-0.41
48:00:00	1279.47	1282.7	1267.36	567.00	201.00	-0.42
48:30:00	1278.67	1282.70	1267.36	578.00	202.00	-0.43
49:00:00	1278.67	1283.51	1267.36	569.00	203.00	-0.43
49:30:00	1279.47	1282.70	1267.36	568.00	204.00	-0.44
50:00:00	1279.47	1283.51	1268.17	563.00	204.00	-0.44

and the extent of micro-cracking which is present as well as firing temperature which affects the extent of the mullitisation. This result (Table 3) is, for a raw kaolin clay, indicative of good refractoriness. Figure 2 is the X-Ray analysis of fired samples which shows predominantly mullite and cristoballite peals. According to Mazdiyasni and Brown [11] low creep rate arises from the interlocking needle-like acicular polygonal grains of the mullite phase. The good result of the deformation test can thus be attributed to the appropriate level of mineralisers which favoured mullitisation.

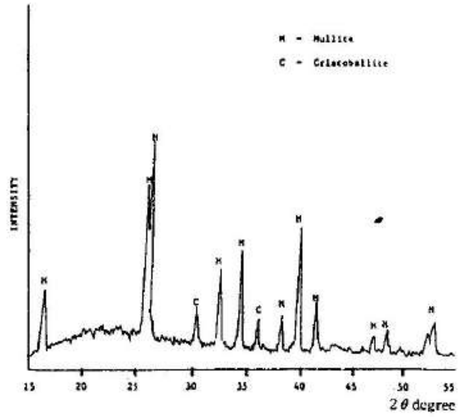

Fig. 2 XRD Of Refractory Body Fired At 1550°C Mullite Peaks

The proportion of the various sizes of particles is also important. This is discernible from Equation 1, which gives the general expression for the creep rate in the secondary or steady state region [12].

$$\varepsilon = A\,\sigma^{n}\,d^{m}\,exp\left(\frac{-\Delta H}{RT}\right) \qquad (1)$$

where ε is the steady creep rate in %/hr
A is a constant
σ is the applied stress in KPa
n is the stress exponent
d corresponds to grain size in mm
m is a constant known as grain size exponent
ΔH is the activation energy of the creep process in kcal/mole
T is the absolute temperature in °K
R is universal gas constant cal/(mol. K)

From Equation 1 an increase in grain size implies a decrease in creep rate thus, making the size distribution of the refractory mix an important parameter. The particle size distribution also controls to some extent the macrostructure (grain size, porosity, phase distribution) and microstructure. Even though large-sized particles tend to improve creep the percentage of large particles must be such that good particle-packing is enhanced to give the entire refractory body a high modulus of rupture. Thus, in this experiment proper selection and batching of the various particle sizes might have contributed to the good result.

The criterion adopted by most of the American Steel Industry is to report the subsidence percentage between 20th and 50th hours at specific temperatures [13]. This is done on the assumption that after 20 hours the steady state region in the technical creep curve has been reached. In this investigation the creep data recorded according to the above assumption is shown in Table 4. The 20th to 50th hours creep data (in Table 4) are of utmost importance in characterising the load bearing capacity of refractories because the percent deformation between the 20th and 50th hours of run is used to rank refractory products and gives an indication of the relative load bearing capacity [14]. At extended times of heating under constant stress, regardless of the type of bonding, the bond strength decreases. This decrease in bond strength leads to a decrease in the resistance to dislocation motions and gives rise to increased relaxation of cohesive forces, which in turn results in increased deformation. Creep of 0.241% and a creep rate of 0,009%/hr at ≅ 1280°C under such extended periods of heating are excellent, thus making this clay a source of raw material for refractory production. Creep and creep rate values of 0.562% and 0.019%hr respectively, which are not as good as those for Kibi clay, have been obtained for fireclays being employed as raw materials for aluminosilicate refractory production [15].

Table 4: Creep Data

Time Interval(Hours)	Creep(%)	Creep Rate (%)/hr.
0 to 14	0.408	0.030
0 to 20	0.474	0.024
20 to 50	0.241	0.009
0 to 50	0.714	0.015
14 to 24	0.095	0.010

However, the refractories products from the Kibi clay may be limited to non-ferrous environments since the alkali content may cause fluxing at the high temperatures required in the ferrous environments.

IV. SUMMARY AND CONCLUSION

The Kaolin clay investigated was found to have good resistance to high temperature deformation. This result can be attributed to chemistry of the raw material and the processing and production of the test pieces. Mullitisation was good and gave rise to a preponderance of mullite phase which in turn led to the low creep rate. Total alkalis are, however, high and this may result in fluxing at high temperatures thus making products from this unprocessed clay suitable for non-ferrous environments. Processing the raw clay material to reduce the level of impurities, particularly alkalis, would enhance the use of the refractory products made from it at higher temperatures.

From the results of the deformation test: 0.241% creep at 1280°C and a creep rate of 0.009%/hr it can be concluded that the properties of this material are good enough to make it a source of raw material for the production of aluminosilicate refractories in Ghana.

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