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Studies on pore deformation mechanism in particles

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Abstract

Pore deformation mechanism in shrinking Nigeria clays, was studied over a range of heating temperature from 1000-1300^{0}C. The results of the study indicate that pores pre-existing before sintering deformed by the collapsing of the wall surrounding the pores. It was discovered that the wall surrounding the pre -existing pores collapsed as a result of the weakening of the clay-binder contact surface and loosening of the macro structure of the formed clays, occasioned by the response of the clay and binder to temperature increase. It was also found that binder burn-out which releases gases, elimination of gaseous product of decomposition and oxidation of some clay constituents as well as evaporation of free water between clay and binder particles, all played very vital roles in decreasing the pre-existing inter-particle separation, hence deforming the pores.
Keywords: Pore deformation, mechanism, shrinkage, Nigerian clays.

1. INTRODUCTION

Pores have a profound Influence on the strength of engineering materials such as ceramics, It is also generally accepted that pores play an important role in controlling 'the property of these materials (Unal 1986). Pore provides diffusion paths for reactant gases and surface area (pore wall surface) for reaction. Without pores, reactions can only occur through the exterior surface and follow an unreacted core model (Levenspiel 1972). Barsoum (1997) studied the relationship between strength and porosity in ceramics in which he discovered that pores are usually deleterious to the strength of ceramics not only because they reduce cross sectional area over which the load is applied, but more importantly act as stress concentrators. Deformation of those pores during shrinking involves closing them so as increase the cross-sectional area over which load is applied and also reduce stress concentration posed by those pores.

The object of this study is to investigate the pore deformation mechanism in shrinking Nigerian clays. For the purpose of this study, pore deformation is viewed as reduction in the size of pores pre-existing in the sample (before heating) to a much smaller size after heating.

2. EXPERIMENTAL

All clays (Olokoro, Ukpor, Otamiri and Nsu) used were collected in lumps from deposits. These clays were allowed to dry in air for 96 hours. Each of those clay samples were crushed and sized to a fine particle size of 125µm using assembly of sieves and sieve shaker. Each sample was manually homogenized separately in a mixing drum using 2% starch as binder. Samples were mixed with water (6% of the total weight of dry materials)

Different configurations of clay were used in carrying out this study. They include

2.1. RECTANGULAR CLAY FORMATION

The plastic clays from the three clay samples were kneaded using hand to expel any trapped air from the clays. The samples were moulded in a rectangular wooden mould of dimension 70mm by 30mm for each of the clay sample. These samples were dried under the laboratory temperature condition (25^{0}C) for 18hrs after which they were carefully packed in saw-dust to prevent them from cracking and absorbing moisture from the surrounding. These samples were then fired using electric kiln. The samples were charged at lower temperature (125^{0}C) after which the temperature was increased to 1200^{0}C. These samples were fired for 18hrs and then cooled in furnace for

the same time limit. The end of sintering was taken as the moment when the temperature of exhaust gases reached maximum.

As it was discovered, that reaction between clay water and starch particles had already occurred during the heating period, the sintering time which will be referred in the following means the time from the moment the sample was charge into the kiln to the moment the exhaust gas temperature was maximum, heating period inclusive. During this period, shrinkage is expected to have spontaneous occurred. Fired shrinkage was calculated using the equation;

$$Fs = 100\left(\frac{L_1 - L_2}{L_1}\right)$$

…. (1)

Where

L = Original length of sample before air-drying (mm)

L_1= Dried length of sample after air-drying (mm)

L_2 =Fired Length (mm)

F_s = Linear fired shrinkage due to firing (%)

Quantity of water lost by evaporation during firing was calculated using the expression;

$$E = \mu_1 - \mu_2 \quad \ldots (2)$$

Where

E = Mass of water lost by evaporation (g)

(μ_1) = Initial mass of water (before firing) (g)

(μ_2) = Final mass of water (after firing) (g)

2.2 PELLETIZING AND BRIQUETING

Pellets and briquettes were also made from the three clay material already highlighted. These clay samples were first heated in the laboratory oven to 120^0C for one hour to expel any moisture and any other matter present. The particle size of the clay samples was 125µm and the specific surface area was around 1700 cm^2/g. the three clay fines were rolled to give 12 to 13mm diameter pellet using 7.5% moisture.

Cylindrical shaped briquettes (12mm diameter x 14mm height) were also made from each of the three clay material fines by compaction and marks made on each sample. For this purpose, steel die and punch were used. To also know the effect of shape of the agglomerates, briquettes having higher porosities were made under different compaction pressure. The samples were allowed to dry under the laboratory temperature condition for 18hrs. These briquettes and pellets were fire at 1200^0C for 24hrs.

The shrinkage behaviour of the formed clays was studied using 45mm inner diameter and 100mm long stainless steel tube having water cooled quartz windows at both ends as the reaction chamber (Sharma,Gupta and Prakash,1990).

3.0 RESULTS AND DISCUSSION

Effects of fired shrinkage on pore deformation

Results of the investigation carried out (as in Figs.1-4) showed that during sintering of green clay, pores originating from the inter particle voids tend to close up (deform) as shrinkage sets in and increases, resulting to decrease in the inter particles separation. This is in accordance with past report (Keey,1978).

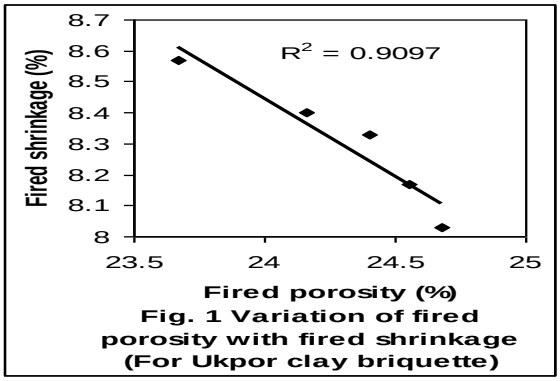

Fig. 1 Variation of fired porosity with fired shrinkage (For Ukpor clay briquette)

It was found that in the sintered clay samples, there were always some pores which were much smaller than the inter particle voids in the raw samples.

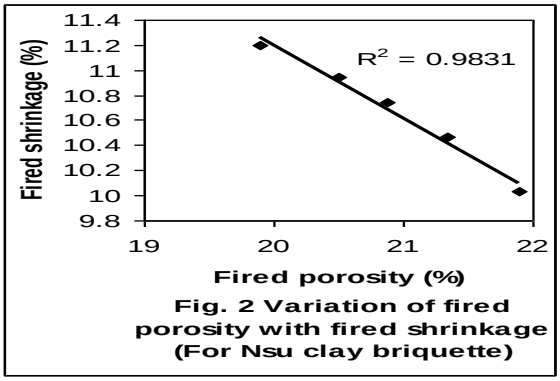

Fig. 2 Variation of fired porosity with fired shrinkage (For Nsu clay briquette)

The question here is, what was the origin of these smaller pores, as pores from the inter-particle voids could not be expected to be that much smaller than the voids when the sample did not shrink.

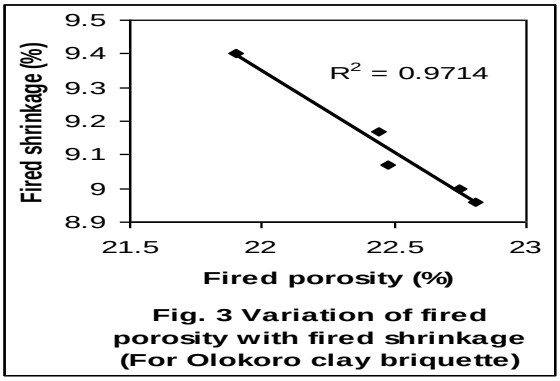

Fig. 3 Variation of fired porosity with fired shrinkage (For Olokoro clay briquette)

This question proved to be the key question which led to the successful finding of the pore deformation mechanism in this research work.

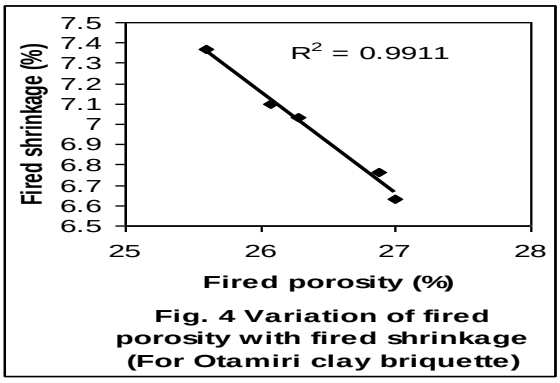

Fig. 4 Variation of fired porosity with fired shrinkage (For Otamiri clay briquette)

Effect of water evaporation on pore deformation

Following an extensive investigation of various factors considered to be related to shrinkage, Keey (1978) found that the sizes of the smaller pores resulting from shrinkage were closely related to the amount of free water removed as well as the evaporation rate and evaporation surface which invariably decreases inter-particle separation. This is in agreement with findings made in this work (comparing Figs. 1-4 and Figs. 5-8 respectively).

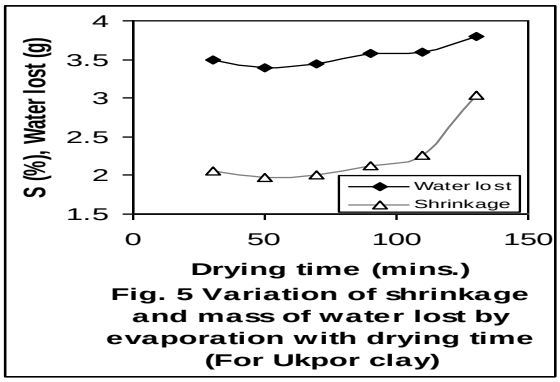

Fig. 5 Variation of shrinkage and mass of water lost by evaporation with drying time (For Ukpor clay)

This is so because water evaporation during drying of the clay brings about shrinkage which in turn leads to decrease in the sizes of the pores. Therefore this decrease in the sizes of the pores implies deformation of pores.

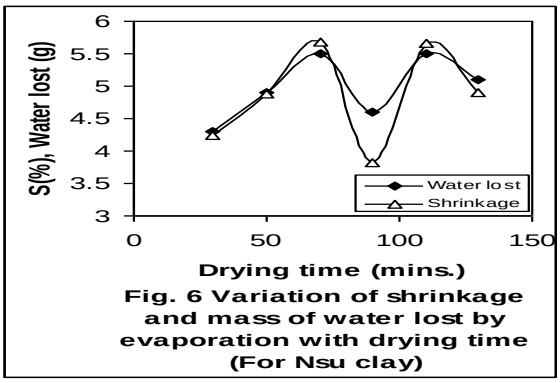

Fig. 6 Variation of shrinkage and mass of water lost by evaporation with drying time (For Nsu clay)

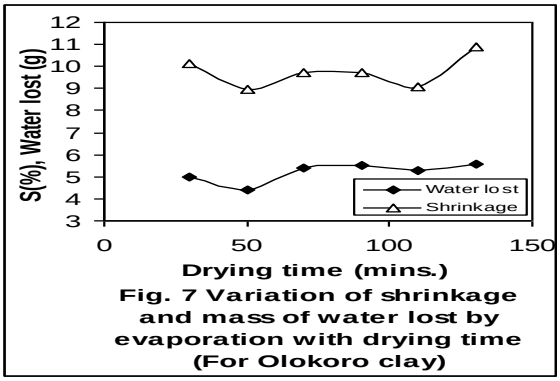

Fig. 7 Variation of shrinkage and mass of water lost by evaporation with drying time (For Olokoro clay)

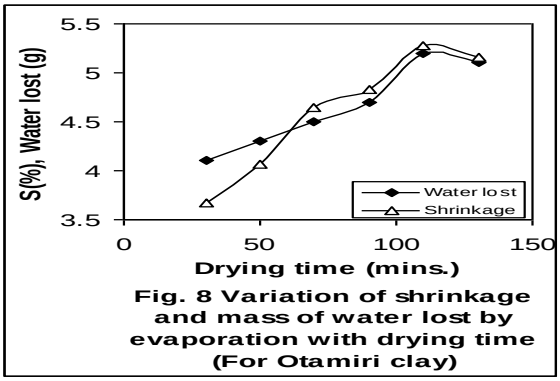

Fig. 8 Variation of shrinkage and mass of water lost by evaporation with drying time (For Otamiri clay)

(S(%) in Figs. 5-8 implies shrinkage (%))

Reed (1988), in a similar study revealed that the onset of shrinking results from preliminary reactions which include binder burnout, elimination of gaseous product of decomposition and oxidation some clay constituents. Based on the foregoing, to prove a pore deformation phenomenon, briquette tablets samples were made from 90% clay (for each of the three clay types), 7% water and 3% starch as binder, compacted with a small die having both its diameter and height

as 5mm, and then heated at varying temperatures (1000-1200^{0}C). It was clearly observed that pores were indeed deformed at sites between particles which comprise free water, clay and starch particles put together during sintering. Initially a gap containing free water was observed to have formed between starch and clay particle around it and as the size of starch particles reduces due to its burnout, elimination of gases resulting from decomposition and oxidation of some clay constituents increase and evaporation of the free water resident between particle become smaller due to the collapse of the wall surrounding the pore. It was observed that when starch particles reduced by burning out and gases eliminated, the whole macro structure of the sample being sintered become “loose” and hence collapse into the voids left behind by the evaporated free water. This results in the reduction of the volume of the pores originally existing in the unheated sample. When the free water had completely evaporated, simultaneously with the consumption of starch particle and maximum gas elimination at the same site, a very small pore was thus created out of the same site, from the pre-existing one as a result of deformation of the later.

Another question that was important to answer was whether the pores deformed between clay and starch particle have anything to do with the burning of the starch (binder) used.

To clarify this, a test was carried out using 3% bentonite as binder (samples were made from same composition as above i.e. 90% clay for each of the three clay types and 7% water) and the results were very much the same as when starch was used, i.e. pores were again smaller than pre-existing pores between the clay and bentonite particles from where free water was removed. Also it was discovered that the greater the amount of free water removed, the greater the shrinkage (as in Figs.5-8) in the clay, elimination of gases due to decomposition and oxidation of some clay constituents and burn out of binder, the smaller the pores after heating. It was also observed through the water cooled quartz windows that shrinkage occurs just as pre-existing pores were deformed. This strongly indicated that the original pores existing between clay and bentonite particles before sintering were partly deformed as a result of burnout of binder. In other words burnout of binder which enhances gaseous emission and collapsing of the wall surrounding the pore played a contributory role in ensuring deformation of the pre-existing pores.

Also another question worth answering was whether clay particles play any role in the deformation of the pre-existing pores in the unheated samples. To answer this question, another test was carried out by making briquette tablets from 90% and 3% starch, compacted with a small die initially used and heated at different temperatures (1100-1300^{0}C). Also the results obtained were very much the same as when Olokoro, Ukpor, Nsu and Otamiri clays were used i.e. pores were again smaller than pre-existing pores between the clay and starch particles. It was also discovered that this decrease in the inter-particle separation stems on a combination of factors which include elimination of gaseous product of composition and oxidation of clay constituents (since the clays used have similar constituents) burnout of the starch, as well as evaporation of the free water available between clay and starch panicles. The roles played by clay and starch particles were to "loosen" the wall surrounding the pores at the elevated temperature. This invariably collapse the wall and particles fall towards the centre of the pore and hence reducing its dimension. It is also pertinent to state that when tests were carried out to prove pore deformation mechanism using in separate cases, Ukpor, Olokoro, Nsu and Otamiri clays, the factors discovered to have played vital roles prevailed at different rates, but the result was generally the same. This is possibly because, though the different clay samples used have the same constituents, the percentages of these constituents vary from one clay type to another (Table 1).

In order to understand the process of pore deformation, samples consisting of 90% (for each of Otamiri, Olokoro, Nsu and Ukpor clay) and 2% .starch with a porosity of 25.4% were heated at 1250°C for different times from 0 to 40 minutes and then examined on a microscope after being polished. On the evidence of the examination, the pore deformation process is summarized as follows:

(1) On heating, the binder used (starch/bentonite) burned-out, releasing gases, accompanied by a collapse of the binder-clay particle contact point .The collapsing of the binder-clay particle contact point results in filling up the pores partly.

(2) Gases were also eliminated at the contact surface between clay and binder particles as well as from the surface of the clay particles. The released gases were the products of decomposition and oxidation of some clay constituents. This result is accordance with the result obtained by Brindley (1959). This is also evident in the notable colour changes observed for the three clay types used after heating. Olokoro, Ukpor, Nsu and Otamiri clay possesses brown, dirty milk and grayish colour respectively before heating. After heating, the colours changed to dark brown, white and light brown respectively (Table 2).

3. The amount of free water between the clay and binder particles was observed to be decreasing with time. It was also observed that while this was taking place, the space so created between the clay and binder particles was gradually being occupied by collapsed clay and binder particles due to the "loose" nature; of the particle surfaces or walls surrounding the surface at the elevated temperature applied. This

activity of the free water partly reduced the dimensions of the pre-existing pores in the sample after heating. It is also pertinent to note that as free water was being evaporated, the steam evolved adds to the gas eliminated.
Based on the foregoing, the pore deformation mechanism can be clearly understood and stated by considering the three factors, which play very vital roles together during the deformation process.
(1) Removal of free water between clay and binder particles by evaporation.
(2) Binder burn-out (releasing gases)
(3 Elimination of gaseous products of decomposition and oxidation of some clay constituents.

4. CONCLUSION

The fundamental pore deformation mechanisms in clay moulded shapes, pellets and briquettes are:

(a) Pores already existing between clay and binder particles are deformed/reduced in dimension between same particles. Binder burns-out, releasing gases, weakening of the contact surface and points it makes with clay particles and also loosening the macrostructure of the formed clays results in the collapsing of the walls surrounding the pores and hence closing the pores partly.

(b) Clay constituents are possibly decomposed and oxidized during heating resulting in elimination of gases which also results in collapsing of the walls surrounding the pores and hence decreasing the interparticle separation.

(c) Free water is removed between clay and binder particles by evaporation. This result in voids between clay and binder particles which are in turn closed partly by the collapsing of the walls surrounding the pores. When binder particles are consumed completely by burning out and clay constituents (susceptible to decomposition and oxidation at the prevailing temperature) are completely decomposed and oxidized and also free water filling pre-existing pore (before heating) completely removed between clay and binder particles, the interparticle separation between clay particles is decreased and the pore originally existing between the clay and binder particles are said to be deformed owing to the decrease in the original dimension of the pore.

2. The shape of agglomerate has no effect on pore deformation.

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TABLE 1: CHEMICAL COMPOSITION OF CLAYS USED

SOURCE	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	SiO_2	N_2O	K_2O	Loss of ignition
Model	38.52	0.50	0.16	0.08	0.08	45.44	0.66	0.14	13.60
Otamiri	15.56	0.05	1.09	-	0.29	69.45	0.01	0.21	13.10
Olokoro	20.10	7.05	-	0.75	1.26	45.31	0.05	0.09	11.00
Ukpor	31.34	0.63	2.43	0.14	0.06	51.43	0.04	0.10	12.04

TABLE 2: RESULTS OF VISUAL EXAMINATION ON OLOKORO, UKPOR AND OTAMIRI CLAYS

Colours

Source	Before heating	After heating
Olokoro	Brown	Dark brown
Ukpor	Dirty-milk	White
Otamiri	Grayish	Light brown

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