THE EFFECT OF CHEMICAL AND MINERALOGICAL CONSTITUTION ON THE PHYSICAL CHARACTERISTICS OF CERAMIC TRIAXIAL BODIES

C.N.K. KOKOROKO MSc (Ceramic Science)

Department of Industrial Art

University of Science and Technology, Kumasi

ABSTRACT

The effect of chemical and mineralogical constitution on the physical characteristics of ceramic triaxial bodies composed from feldspar, quartz and kaolin is investigated. Results show that suitable whiteware bodies can be manufactured from the raw materials investigated.

To support a meaningful interpretation of observed phenomena in processing techniques, scientific investigations have been reviewed in this paper.

Keywords: Triaxial bodies, pyrochemical reaction, chemical constitution

INTRODUCTION

The major raw materials used for the manufacture of ceramic whiteware products are potassium feldspar, clay and silica. These materials have the formula, $K(AlSi_3)O_8$, $Al(Si_2O_5)(OH_4)$, and SiO_2 respectively. Found in nature they contain accessory minerals which introduce oxides as Na_2O, CaO, MgO, TiO_2 and Fe_2O_3. The mineralogical and chemical compositions of raw materials do differ from one deposit to the other and are known to affect the pyrochemical behaviour of products designed from these raw materials.

The various oxides bring about a glassy matrix which coexist with crystalline materials when heated but the amount of each depends on the chemical composition of the ceramic, temperature and time of heat treatment. The glassy matrix formation of the minerals is also controlled by the particle size of the raw materials [1].

Reaction between feldspar and silica alone produces incongruent melting point temperature at $1150° \pm 20°C$ [2]. Silica-alumina eutectic also occurs at $1675°C$ [3] which is above the melting temperature of ordinary whiteware. At $1170°C$, however, the conguent melt of feldspar in clay - feldspar-silica system takes allumina and silica into solution [4]. Liquid formation which is attributed to pyro-chemical reaction of the clay - feldspar - system collects in spaces between the less soluble particles and welds them together with the bond of glass during cooling. The amount of glass formed is an important factor in determining the properties of the ceramic in use [5].

The present work wishes to establish scientific basis to assist exploitation of the raw materials under study for whiteware products development. In this connection the researcher undertook the study of the effect of the chemical and mineralogical compositions of the locally available raw materials to help deduce general principles governing their appropriate use in accordance with their pyrochemical behaviour and provide a quantitative and qualitative guide for the production of specific ceramic products.

EXPERIMENTAL PROCEDURE

Several triaxial bodies were experimented upon. Six of these bodies as shown in Table 1 and presented on a triangular grid in Fig.1 were selected and prepared for study. The chemical composition and mineral assemblages of raw materials used are presented in Table 2. Table 3 shows the calculated chemical constituent in each body and the calculated mineral constituent (calculation with norm) of the various bodies are shown in Table 4.

All batches were coarse crushed and passed through 8 mesh sieve after jaw and roll crushing. This done, a 3kg pot mill was used for milling each batch. Each batch weighs 2kg and was milled with 2kg porcelain balls and with 2 litre addition of water. Milling time for each batch was 20 hours.

After milling all batches were passed through 80 mesh sieve, owing to the thick nature of slurry obtained. The sieved batches were dried in a dryer at $80°C$ for 24 hours. Later the dried batches were subjected to crushing and were passed through 12 mesh sieve by using net disintegrator with dry base water content of 7%.

Using hydraulic press with a forming pressure of $250kgf/cm^2$ the batches were formed into test tiles of

Table 1: Batch composition of bodies (wt. %)

Test Sample No.	1	2	3	4	5	6
Toyane Silica Stone	70	40	10	40	10	10
11R Clay	20	50	80	20	50	20
Ayana Feldspar	10	10	10	40	40	70

Table 2: Chemical analysis (wt. %) and mineral assemblages of raw materials

Raw Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Ig-loss	Total	Mineral Assemblages
Toyane Silica Stone	98.0	1.2	0.2	tr	tr	0.2	tr	0.1	0.3	100	Q
11R Clay	52.5	29.7	1.1	0.1	tr	0.5	0.1	1.1	13.6	99.7	K,Q>F,S
Ayana Feldspar	78.0	12.3	0.1	0.1	tr	4.9	2.9	tr	0.4	99.1	Q > F

K	=	Kaolin	S	=	Sericite	Q	=	Quartz	F	=	Feldspar

Table 3: Chemical composition of bodies (calculated wt. % in measured values)

Sample No.	1	2	3	4	5	6
SiO_2	87.0	73.4	59.6	81.0	67.3	74.9
Al_2O_3	8.0	16.6	25.1	11.3	19.9	14.7
Fe_2O_3	0.4	0.6	0.9	0.3	0.6	0.3
CaO	0.1	0.1	0.1	0.2	0.3	0.4
MgO	tr	tr	tr	tr	tr	tr
K_2O	0.9	1.3	1.7	2.3	2.7	3.8
Na_2O	0.3	0.3	0.4	1.2	1.2	2.1
TiO_2	0.3	0.6	0.9	0.3	0.6	0.2
Ig loss	3.0	7.0	11.0	3.0	7.0	3.0
Total	100	99.9	99.7	99.6	99.6	99.4

Table 4: Percentage mineral composition of bodies(Mineral composition calculated with NORM)

Sample No.	1	2	3	4	5	6
Orthoclase	5.5	7.8	10.1	13.8	16.2	22.2
Albite	2.6	2.9	3.1	10.0	10.3	17.4
Kaolinite	16.4	36.9	57.3	17.4	37.8	18.3
Quartz	74.1	49.2	24.3	57.1	32.2	40.1
Others	1.4	3.1	4.9	1.4	3.1	1.4
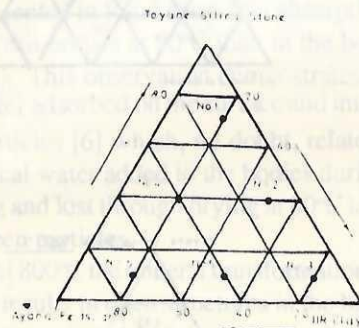
100 x 30 x 7mm. These tiles were later fired using an electric furnace at 800, 1000, 1100, 1180 and 1230°C respectively.

All samples were subjected to the determination of change in dimensions, bulk density and water absorption tests in the dry state. Later, firing shrinkage, water absorption and bulk density of fired samples were studied.

RESULTS AND DISCUSSION

Figures 2 through 4 present characteristic features on shrinkage, expansion, water absorption and bulk density of the bodies experimented upon.

EXPANSION AND SHRINKAGE PHENOMENA IN BODIES

In Figure 2, all bodies except body No.3 expand at and below 800°C. In the region of up to 1000°C it is observed that the No.1 body which has the highest quartz content also suffers expansion. This expansion characteristic is attributed to the inversion of quartz during which process the SiO^{4-} structure in the bodies rotates with respect to each other.

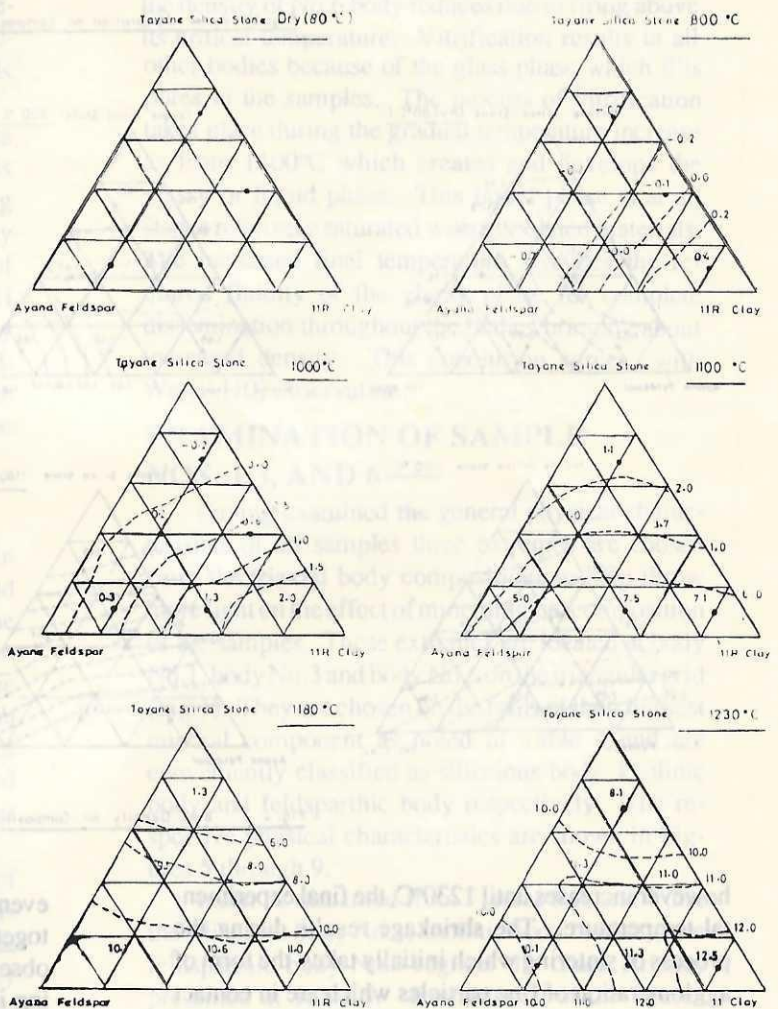Shrinkage for all bodies, except No.1 body, starts setting in about and at 1000°C. This shrinkage

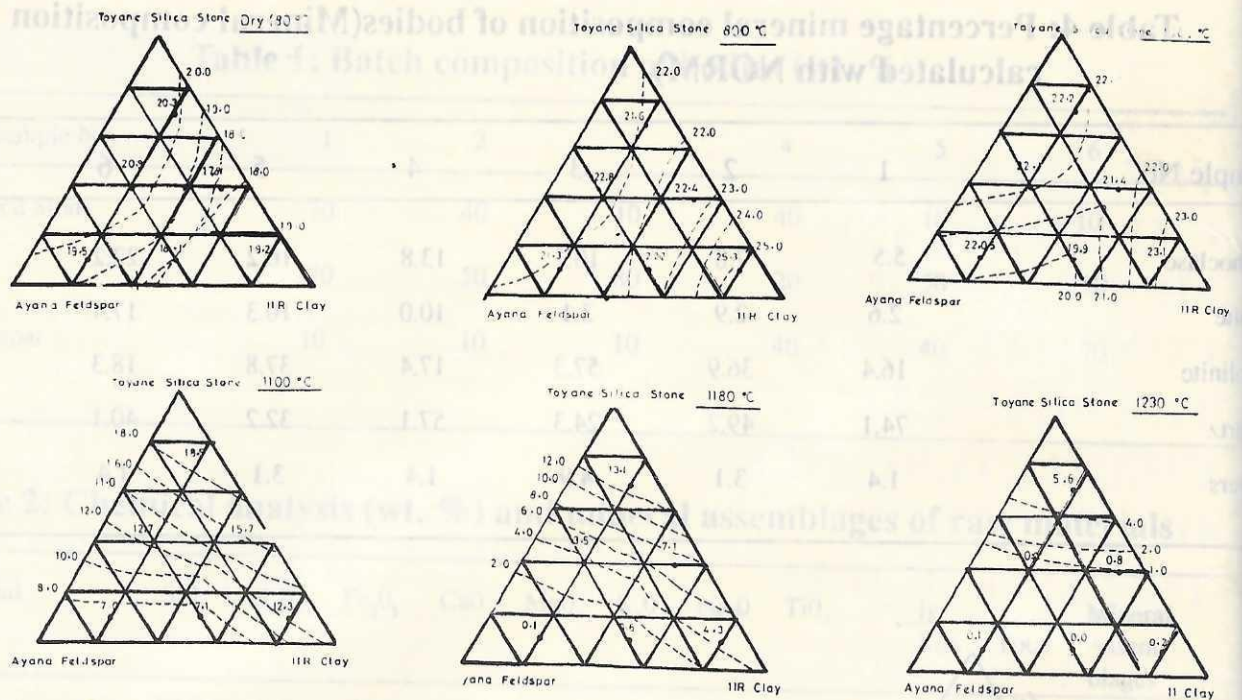Fig. 2. Firing Shrinkage on Composition Diagrams

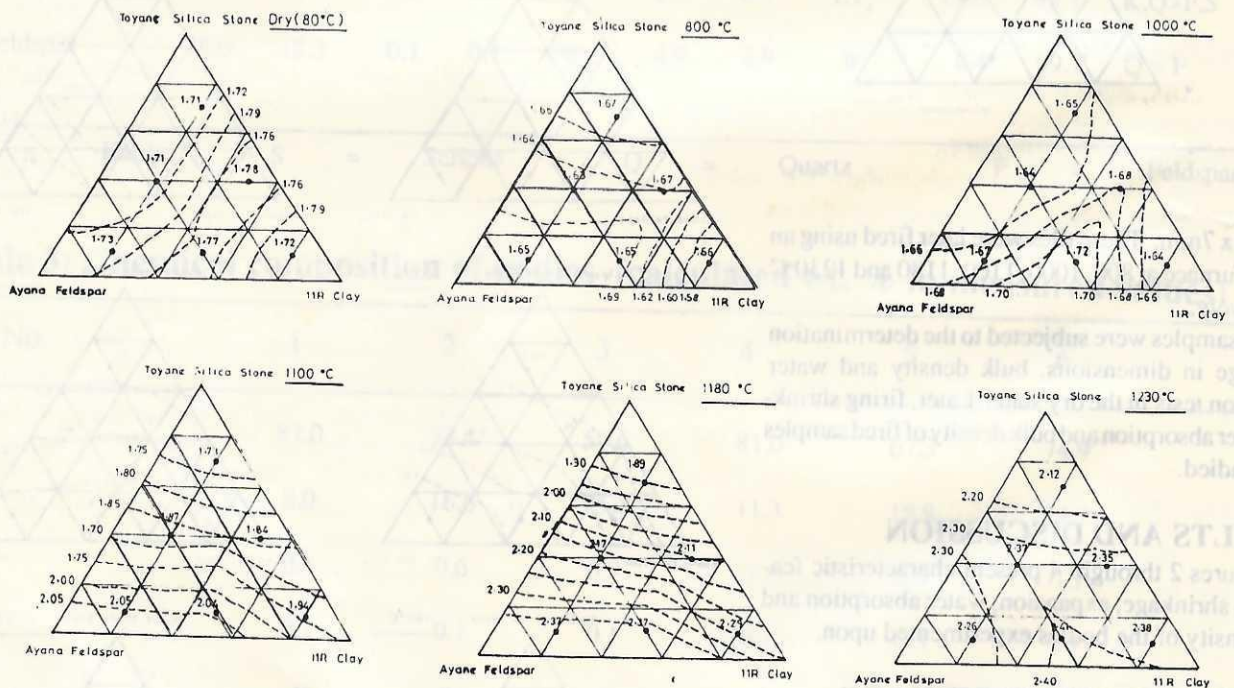32

Fig. 3. Water Absorption on Composition Diagrams

Fig. 4   Bulk Density on Composition Diagrams

however increases until 1230°C, the final experimental temperature. The shrinkage results during the process of sintering which initially takes the form of agglomeration of fine particles which are in contact with each other; a phenomenon which reduces surface area. Another aspect of sintering that brings about shrinkage is the resultant viscous flow of liquid, on application of high temperatures, which eventually fills voids in the body and welds particles together on cooling. In these high temperatures it is observed that pyrochemical activity increases resulting in progressive solution of some constituents of the bodies into glass. Feldspar is considered melting first and taking other constituents into solution. Increased temperatures also bring about a considerable degree of fluidity of glass which consequently

fills pores, and welds refractory or unmelted materials, a process which results in increased shrinkage of the bodies. This increased shrinkage mechanism results from surface tension forces of the liquid or glass phase which also produces a minimum surface area. The forces act by compressing the whole mass by external glassy films. The whole process finally results in filling pores or reduction of size of the individual pores by internal pressure built up by surface tension forces.

Generally, however, No.6 body is the only one body which has shown a sign of deformation due to over firing.

WATER ABSORPTION PHENOMENA IN THE BODIES

It is noted that water absorption characteristics as presented in Fig.3 show low absorption figures in the green bodies at 80°C than in the bodies fired at 800°C. This observation demonstrates the removal of water adsorbed on the surface and interlayer water of particles [6] which, no doubt, relates to the mechanical water added to the bodies during wet processing and lost through drying at 80°C leaving voids between particles.

At 800°C the mineral transformation which takes place results in open structures in the bodies. In this temperature impurities in the bodies burn out leaving voids. Also noted is the break down of the clay mineral structure which alters the entire structure of the body above 450°C through the removal of OH groups. The loss of OH⁻ leaves holes in the clay mineral structure. This claim agrees with the findings of Brown and Gregg [7]; in a unit cell of kaolinite mineral there are $8OH^-$ which undergoes a change as:

$$8OH^- \longrightarrow 4H_2O + 4O^{--}$$
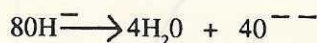
There also occurs a rearrangement of the structure in such an irregular manner, as noted by Evans and White[8], which results in open structure in the bodies. This inversion of SiO_4^- structure is also a contributing factor to the open mineral structure in the bodies in this temperature. All these phenomena result in water absorption of the bodies. The effect of silica inversion on absorption is much more observed in No.1 body which has the greatest quartz content at 1000°C.

With a rise in temperature the gradual closure of pores within the mineral structures by the fine particle agglomeration at 1000°C and liquid formation at 1100°C, both of which reaction reduces porosity continues to decrease by the reaction of more glass results.

At 1180°C and 1230°C porosity continues to decrease by the reaction of more glass formation or liquid flow which fills the pores until absorption values of betwee 0 and 0.1 per cent are obtained in

body Nos. 3,4,5 and 6.

BULK DENSITY RELATIONS IN BODIES

The characteristic bulk density of the various bodies as shown in Fig.4, is observed as having corelation with shrinkage and porosity which are discussed above. It is noted that the density of the green bodies at 80°C is higher than the fired samples of 800°C and 1000°C. This phenomenon as mentioned above is caused by the non-reactivity of minerals in the samples at the drying state.

In the 800°C and 1000°C temperatures the open mineral structures which result from SiO^{4-} structural inversion and the loss of OH⁻ groups cause reduction in density values of samples. Also at 1000°C it is expected that alumina spinel [9] which breaks down into chainlike mullite could result in open structure which here again reduces density.

It can be discerned that density increases as 1100°C is exceeded. In the 1230°C temperature, however, the density of No.6 body reduces due to firing above its critical temperature. Vitrification results in all other bodies because of the glass phase which fills pores in the samples. The process of vitrification takes place during the gradual temperature increase as from 1100°C which creates and develops the glassy or liquid phase. This liquid phase is at all stages relatively saturated with associated materials. The increased final temperature provides the required fluidity of the glassy phase for complete dissemination throughout the bodies bringing about increased density. This conclusion agrees with Watts' [10] observation.

EXAMINATION OF SAMPLE NOS. 1,3, AND 6

Having examined the general physical characteristics of all samples three extremes are chosen from the triaxial body compositions to help throw more light on the effect of mineralogical composition of the samples. These extremes are located at body No.1, body No.3 and body No.6 on the triangular grid (Fig.1). They are chosen on the basis of their highest mineral component as noted in Table 4 and are conveniently classified as siliceious body, kaolinic body and feldsparthic body respectively. The respective physical characteristics are shown in Figures 5 through 9.

It can be discerned from Figures 5,6, and 7 that the siliceious body No.1, kaolinic body No.3 and the feldsparthic body No.6 register the characteristics presented in Table 5. Examination of the figures shows that the feldsparthic body is not suitable for 1230°C. Its critical temperature is set at 1180°C where porosity of the body decreases to the minimum and above which temperature there is elongation or expansion of the body with consequent reduction in

Inax Corporation, Japan, and the encouragement given by the Technical Training Officers of Inax Corporation on this subject of study.

REFERENCES

1. Weymouth, J.W. and W.O. Williamson, Some observations on the micro-structure of Fired Earthenware J. Amer. Cer. Soc. 52:311 (1953)

2. Shairer, J.F. and N.L. Bowen, Phase diagram for ceramists. Figure 412 p. 158. The Amer. Cer.Soc. (1964)

3. Bowen, N.L. and J.W. Greig, The system Al_2O_3-SiO_2; J. Amer. Cer.Soc. 7(4) 238-54 (1924)

4. McVay, T.N., Physical-Chemical Reactions in Firing Whitewares. J. Amer. Cer. Soc. 19(7) 195-201 (1936)

5. Parmelee, C.W. and C.R. Amberge, Solubility of quartz and clay in feldspar. J. Amer. Cer. Soc. 12 (11) 699-710 (1929)

6. Mackenzie, R.C. edit., The Differential Thermal Investigation of clays, p.102 Mineralogical Society. (Clay Minerals Group) London 1957

7. Brown, M.J. and S.J. Greg, A Study of the effect of Heat on Kaolinite by Absorption Methods; Clay Minerals Bull. 1:228 (1952)

8. Evans, J.L. and J. White, Further Studies of the Thermal Decomposition (Dehydration of clays. Trans. British Cer. Soc. 57: 289) (1958).

9. Brindley, G.W. and M. Nakahira, Kinetics of Dehydroxilation of Kaolinite and Halloysite. J. Amer. Cer. Soc. 19(6) 175-176 (1939)

10. Watts, A.S., Data on the influence of firing time on the Properties of Some whiteware bodies. J.Amer. Cer. Soc. 19 (6) 175-176 (1939)

11. Johnson, A.G. and D.B. Underwell, Quantitative determination of the glassy phase in Ceramic body. J. Amer.Cer.Soc. 27: 40, (1944)

12. F.H. Novton, Fine Ceramics, Technology and Applications. McGraw-Hill Book Company, New York. 1970 p.261