DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

EEFECT OF REPLACEMENT OF QUARTZ BY FLY ASH IN TRI-AXIAL PORCELAIN BODIES

THESIS SUBMITTED

BY

SAURAV KUMAR BETALA

(110CR0599)

(Under the guidance of Dr. Mrs. S.Bhattacharyya)

In the partial fulfillment of the requirements of degree

Of

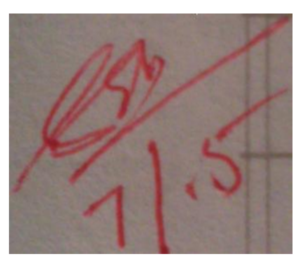
Bachelor of Technology

NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "**Effect of replacement of quartz by flay ash in tri-axial porcelain body.**", submitted by **Mr. Saurav Kumar Betala (Roll no. 110CR0599)** in partial fulfillment of the requirement of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

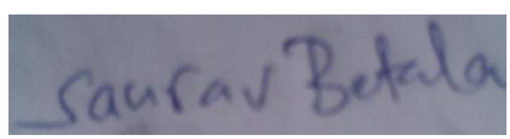


Prof. Sunipa Bhattacharyya
Department Of Ceramic Engineering
National Institute of technology
Rourkela-769008

ACKNOWLEDGEMENT

With deep respect, I avail this opportunity to express my gratitude to **Prof. Sunipa Bhattacharyya** Department of Ceramic Engineering, National Institute of Technology, Rourkela for her inspiration and guidance and valuable suggestion throughout this research work. Her vast knowledge in the field of Science and Technology helped to enlighten me. It would have been impossible on my part to come out with this project report without her. I would like to thanks to the HOD, Ceramic Department and all other faculties for their support and valuable suggestions throughout this research project. I would also take this opportunity to express my gratitude to the non-teaching staff for their help and kind support at various stages of work.

I am also thankful to the Research Scholar in the Department of Ceramic Engineering for helping out in laboratory and analysis. And lastly I am thankful to my parents and friends for their constant support.



SAURAV KUMAR BETALA

110CR0599

ABSTRACT

Quartz is replaced by fly ash in tri-axial porcelain body. Three different batches were prepared with first batch being composed of normal porcelain composition and the other two containing fly ash with partial substitution of quartz and total substitution of quartz. Effect of this substitution was studied by measuring linear shrinkage, volume shrinkage, bulk density, apparent porosity, cold compressive strength and microscopy study by optical microscope. It was found that the fly ash incorporated sample shows better density and strength than normal porcelain sample. Also the optical microstructure of fly ash sample shows less porosity and more crystalline phase. This is mainly due to reduction in amount of quartz and increase in mullite content with fly ash addition.

CONTENTS

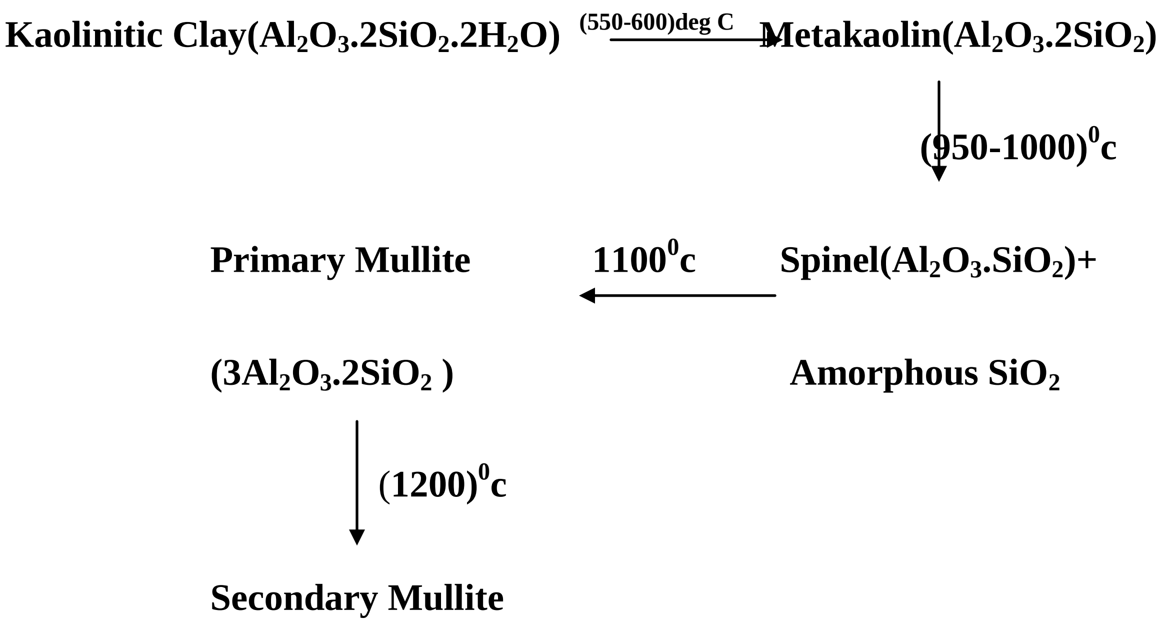
TABLES AND FIGURES

CHAPTER-1 : INTRODUCTION AND OBJECTIVE

Tri-axial porcelain bodies are a very significant part of ceramic research studies. The main composition of tri-axial porcelain body comprises of Clay, Quartz and Feldspar. Basically Kaolinitic clay is used which helps in mullite formation upon firing and impart plasticity to the green mass, Thus, helping in shape-forming. Feldspar is a low-melting material which melts upon firing and acts as Flux. Thus, it forms a liquid phase which helps in mullite growth and ensures densification of the body through filling of interconnected pores. Quartz is used as a filler material reducing deformation and shrinkage of fired bodies.

On heating kaolinitic clay at (550-600)^{0}c, dehydroxylates to form metakaolin. This metakaolin at temperature (950-1000)^{0}c is transformed to Spinel phase and amorphous silica. Above 1100^{0}c spinel phase transforms into Primary mullite and silica and above 1200^{0}c Secondary mullite is formed by reaction of clay relicts and feldspar relicts. Primary mullite are Scaly type Cubodial crystals formed from kaolinitic clay. These are surrounded by highly viscous matrix of molten quartz. This inhibits mass transport and thus the growth of primary crystals. Their aspect ratio is low of about 1-3:1. The mullite crystals derived from clay and feldspar relicts are secondary mullite. They are larger in size than primary mullite because these are surrounded by less viscous melt as feldspar melt at a low temperature. Thus, they have a high aspect ratio of about 3-10:1. Size of primary mullite particles is $<0.5\mu m$ and that of secondary mullite is $>1\mu m$[1].

REACTIONS :-



Quartz forms a silica rich amorphous layer around quartz grains. These grains dissolves in this solution and the dissolution rate depends on the size of quartz particle. Fine quartz particle dissolves more rapidly than coarse particles[2].

Fly ash is the by-product of Thermal power plant obtained from combustion of pulverized coal in the coal furnaces. In India annually 90 million tons of Fly ash is produces out of which only 10% is utilized and rest is disposed causing serious environmental problems. Fly ash being a cheap source of Alumina-Silicate compound and providing highly valuable properties like Low porosity, High strength, High Scratch hardness, Thermal Shock Resistance, etc has attracted attention of many researchers on valuable usage of this waste product. Areas of its usage are Building construction, Road construction, Fly ash bricks, Land filling, Agriculture, etc.

Fly ash is a mixture of several oxides comprising bulk of Al_2O_3, SiO_2, Fe_2O_3 and also contain oxides like TiO_2, CaO, Na_2O, ZrO_2.

Feldspar used is Potash feldspar of chemical formulae $K_2O.Al_2O_3.6SiO_2$.

Since Fly ash is a cheap Alumina-Silicate source and also helps in improving various properties, so, here attempt has been made to replace quartz by Fly ash by different weight percentage and properties are studied.

CHAPTER-2 : LITERATURE REVIEW

Study of microstructure of porcelain bodies containing fly ash replacing Quartz was done by **Kausik Dana and Swapan Kumar das[1].** 15wt% fly ash was added into a normal kaolin-quartz-feldspar tri-axial body by replacing equivalent amount of quartz. Normal sample preparation technique were used starting from Wet Grinding in Pot Mill for 12-14 hours, then drying the slip at $(110\text{-}120)^0$c.Then powdering and granulation was done at (5-6)% moisture. Shaping and Pressing was done by Hydraulic compaction at a pressure of (300-350) kg/cm^2 and the samples are again dried at $(110\text{-}120)^0$c for 24 hours. Then firing is done at temperatures $(1150\text{-}1300)^0$c. Characterization of samples is done by SEM, XRD, MOR. The microstructure study revealed that uneven and not enough dense glassy matrixes were seen in case of normal porcelain sample at 1200^0c. Presence of primary and secondary mullite formed from clay relicts and feldspar penetrated clay relict respectively was observed at 1250^0c. Quartz grains surrounded by rims of amorphous silica were also seen. In fly ash porcelain the glass was more fluid at 1200^0c and presence of primary mullite was observed. This was due to high fluidity of silica-less glass. Formation of more Muliite in case of fly ash samples is because presence of mullite in calcined fly ash. Thus, it was concluded that the fly ash incorporated porcelain composition reaches its standard porcelain microstructure, consisting of Quartz, Mullite and Glass at a lower temperature of 1200^0c compared to normal composition at 1250^0c. The substitution increases the flexural strength due to strong reinforcement of needle shaped crystals of mullite in glassy matrix, thus, leading to techno-economic advantages.

Effect of fly ash addition on mechanical and other properties of stone ware porcelain tiles were studied by **S.Kumar, K.K Singh, P.Ramchandra Rao[2].** Fly ash additions in the range of (0-40) wt% have been added to the tile body composition wet milled, spray dried, shaped and fires at 1250^0c. Samples containing 5, 10, 15, 20, 25, 30, 35, 40 wt% fly ash were named T1, T2, T3, T4, T5, T6, T7, T8 and t9 respectively, with T1 being the conventional tile composition. It is observed that with increase in fly ash content Al_2O_3, SiO_2, and Fe_2O_3 content increases. A gradual loss in Flexural strength is observed with increase in fly ash content. This may be due to non-plastic fly ash replacing for plastic clay. Linear shrinkage of Vitrified tiles decreases with fly ash content. This may be because as fly ash replaces clay, a less amount of fluxing oxides is required. Thus, viscosity rises and the rate of consolidation is reduced. There is an increasing behavior in Bulk density till T6 composition. From T7-T9 it reduces because of reduced rate of sintering. The Compressive strength, Micro hardness, bending strength, young's modulus and abrasion resistance increases with fly ash content because of increase in mullite content. Microstructure of T6 composition showing best of properties was studied and it was characterized by dense microstructure and small number of pores. Interlocked mullite and quartz crystals were embedded in glassy matrix.

Mechanical properties of clay based ceramics containing coal fly ash was studied by **R.C.C Monteria, M.M.R.A Lima and S.Alves [3].** Powder fractions of each Clay and Fly ash with a particle size >75µm were selected because smaller size particle ensures chemical homogenization and mixing and it favors the sintering process. The Loss on Ignition is higher for clay than fly ash due to presence of residual unburned coal and some organic residues. Density of 50% fly ash incorporated sample is lower than that of 25% because of the presence of unburned coal which hinders densification and gas formational during final firing process leads to increase in porosity. Water absorption reduces with increasing temperature because the fluxing material melts at higher temperature into the pores and thus reducing porous channels for water absorption. From XRD of normal clay and clay with 25% and 50% fly ash shows that the amount of crystalline phases decreases with increase in fly ash content. This is because amount of glassy phase increases with increase in fly ash content. Flexural strength of 25 and 50 wt% fly ash sample is lower than normal clay. It has higher value at 1130^0c than at 1080^0c because of increased density.

Mullite development on firing in porcelain stoneware bodies was studied by **Jorge Martin-Marquez [4].** A normal porcelain composition comprising 50% Clay, 40% Feldspar and 10% Quartz was fired between temperatures $(500\text{-}1400)^0$c and the mullite formation was studied by SEM. Samples fired between temperatures of $(500\text{-}1000)^0$c show under fired microstructure comprising of clay agglomerates, feldspar particles, quartz grains and a fine matrix of clay, quartz and feldspar. Even at 1100^0c SEM does not detect mullite formation only clay relicts, clay-feldspar relicts and quartz grains embedded in a ceramic matrix are observed. Mullite formation was observed in the samples fired at 1200^0c and beyond. Type I primary mullite of small crystals are developed between $(1200\text{-}1400)^0$c . The proportion of these crystals reduces with increasing temperature and its size increases reaching maximum at 1400^0c. These have aspect ratio of about 3:1. Type II Secondary mullite having needle-shaped crystals increases from $(1200\text{-}1400)^0$c. Higher firing temperature also leads to increase in its size from 5:1 aspect ratio to 20:1 at 1400^0c finally. Type III mullite crystals from viscous ceramic matrix are seen between $(1250\text{-}1400)^0$c . Like the Type II mullite, their proportion as well as length increases with increase in temperature. From microstructure studies it can be said that when primary mullite grows in a low viscosity region, it may transform to secondary mullite. Clusters or packs of Type III mullite fibers are observed in the 1250-1280ºC intervals.

Effect on mechanical properties of tri-axial porcelain on replacement of quartz by fly ash was studied by **Kausik Dana, Sukhen Das, Swapan Kumar Das[5].** Quartz was replaced by fly ash in the range of (5-10) Wt%. Bulk density, Apparent porosity, Water absorption, Flexural strength and XRD of fired samples between (1150-1300)^{0}C was analyzed. Four batches were prepared with original composition being 45WT% Kaolinitic clay, 30% Fly ash and 25% Quartz. In the subsequent samples quartz was .replaced by fly ash with fly ash being 5, 10, 15 wt%. The oxide composition of calcined samples was studied and it was noted that with increase in fly ash content the amount of Alumina increases followed by decrease in quartz content. The percentage of other mineralizing oxides like TiO_2, CaO, Fe_2O_3 and MgO also increases with increase in fly ash content. The linear shrinkage of all the samples increases with increase in temperature. The fly ash incorporated sample shows higher linear shrinkage because of the presence of fluxing oxides which reduces the viscosity of the glassy phase and thus leading to higher shrinkage. Bulk density shows increasing trend in all the samples and it is higher for sample with 15wt% fly ash. This is because with increase in fly ash content amount of alumina increases and the viscosity of silica melt reduce leading to better liquid phase sintering. The apparent porosity of all the samples reaches minimum value by 1300^{0}C. It is minimum for sample with 15wt% fly ash. This may be due to presence of low viscous glassy melt containing less silica which fills up the pores easily. The flexural strength is higher for fly ash incorporated sample containing 10 and 15 wt% respectively. This is because of formation of more mullite in fly ash samples which increases the overall strength. The trend shows a less increasing behavior from 1250^0C to 1300^0C in fly ash samples. This is because of formation of more low silica melt due to presence of fluxing oxides. The mullite content is higher in fly ash samples because of high mullite already present in fly ash and also because of mullitization which results in formation of mullite from glass by replacing Al^{3+} in its structure. The microstructure study of the samples show α-Quartz and mullite crystals embedded in glassy matrix.

CHAPTER-3 : EXPERIMENTAL METHODS

BATCH PREPARATION:-

Raw material used:-

- Clay
- Quartz
- Feldspar
- Fly ash

The chemical compositions of raw materials were analyzed by wet chemical method and the results were shown in table-4, 5, 6. Raw materials were taken in powder form according to the batch composition given in table-1 and mixed by pot milling method.

TABLE-1

BATCH	CLAY (WT %)	FELDSPAR(WT%)	QUARTZ(WT)%	FLY ASH(WT)%
Batch 1	45	30	25	0
Batch 2	45	30	5	20
Batch 3	45	30	0	25

After pot milling the wet mixed batches were dried in oven for 24hrs. Pressing of the powder was done by hydraulic pressing. Pellets of weight 1gm each were formed by pressing at a pressure of 2 tons and dwelling time of 90 seconds. About 1-2% water was added as binder. Total 36 pellets were pressed.

After pressing the samples were fired at four different temperatures of (1150, 1200, 1250, 1300)^{0}C with uniform heating rate. Soaking time for each firing temperature was 2 hrs.

FLOW CHART FOR SAMPLE PREPARATION

CLAY + QUARTZ + FELDSPAR + FLY ASH

↓ (MIXED BY POT MILLING)

DRYING OF WET RAW MATERIAL FOR 24 HRS

↓

PRESSING OF POWDER (2 TONN PRESSURE)

↓

FIRING AT FOUR DIFFERENT TEMPERATURES

(1150,1200,1250,1300)0C

CHAPTER-4 : TESTING AND CHARACTERIZATION

1) **CHEMICAL ANALYSIS OF RAW MATERIAL** :- The raw materials china clay, fly ash, feldspar and quartz were chemically analysed by Chemical analysis method. The composition of each component was found in weight %.

2) X**RD analysis of raw material** :- The XRD characterization was done by Philips' X-ray diffractometer with Nickel filtered Cu Kα radiation (1.54A°).

3) **GREEN AND FIRED MEASUREMENTS** :- Green thickness and diameter of the pressed pellets was measured and its weight was also taken. Same process was carried out after firing too. This was done to find out mass loss ,Linear and Volume shrinkage.

4) **BULK DENSITY AND APPARENT POROSITY** :- These measurements were done by Archemedies principle method. First the dry weight of the fired sample was taken (D). Then the samples were boiled in water for removal of trapped air inside the pores. Boiling was done for 1 hr. Then the suspended weight of sample was measured by dipping it completely into a beaker full of water (S). Then the surface of sample was wiped with a wet cloth and Soaked weight was taken (W).

BULK DENSITY (**BD**) = (D/W-S) * (Density of water at room temperature)

APPARENT POROSITY (AP) = W-D/W-S *100

5) **COLD CRUSHING STRENGTH** :-

$$CCS = L/A$$

where, CCS= Cold Crushing Strength (kg/cm2), L=Load at which fracture occurs (kg) and A= Area of the sample (cm2). The CCS was determined for 3 specimens and the mean of the 3 values were reported.

6) **MICROSTRUTURE ANALYSIS**:- Microstructure analysis of samples fired at 1250 and 1300 degree celsius was done by The images were taken using optical microscope which was attached with a CCTV camera using Image analysis software. The samples were first polished with sand paper and den kept under the microscope.

<u>CHAPTER-5</u>: <u>RESULT AND DISCUSSION</u>

1) **Chemical composition of raw materials** :-

TABLE 2- **FLY ASH**

COMPONENT	WEIGHT %
SiO_2	60.63%
Al_2O_3	25.685
Fe_2O_3	4.25%
CaO	3.22%
Mgo	1.40%
K_2O	0.6%
Na_2O	0.5%
TiO_2	2.32%
LOI	1.31%

TABLE 3- **CHINA CLAY**

COMPONENT	WEIGHT%
SiO_2	49.28%
Al_2O_3	32.95%
Fe_2O_3	0.58%
CaO	1.88%
Mgo	0.59%
K_2O	0.42%
Na_2O	0.86%
TiO_2	0.89%
LOI	12.41%

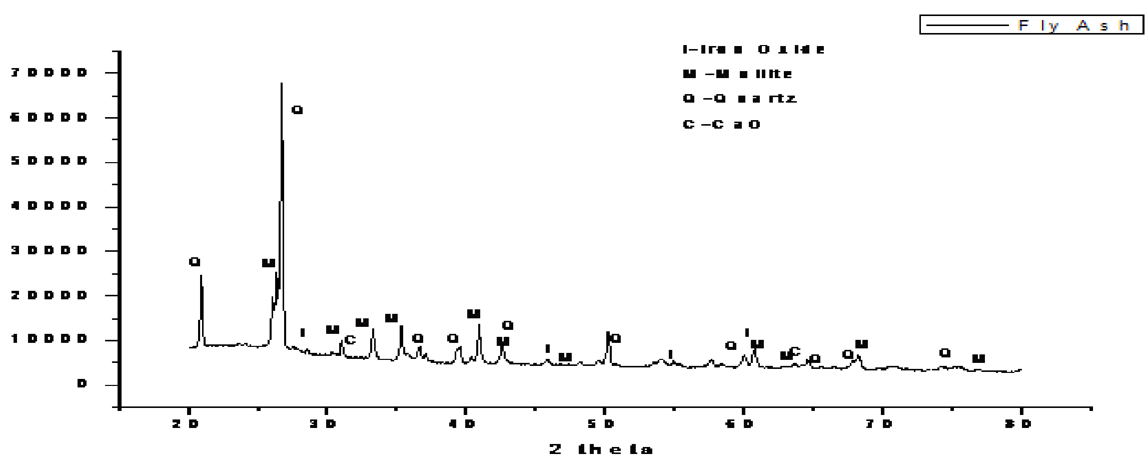
TABLE 4- **FELDSPAR**

COMPONENT	WEIGHT%
SiO_2	61.23%
Al_2O_3	15.31%
Fe_2O_3	0.12%
CaO	0.3%
Mgo	TRACE
K_2O	10%
Na_2O	3%

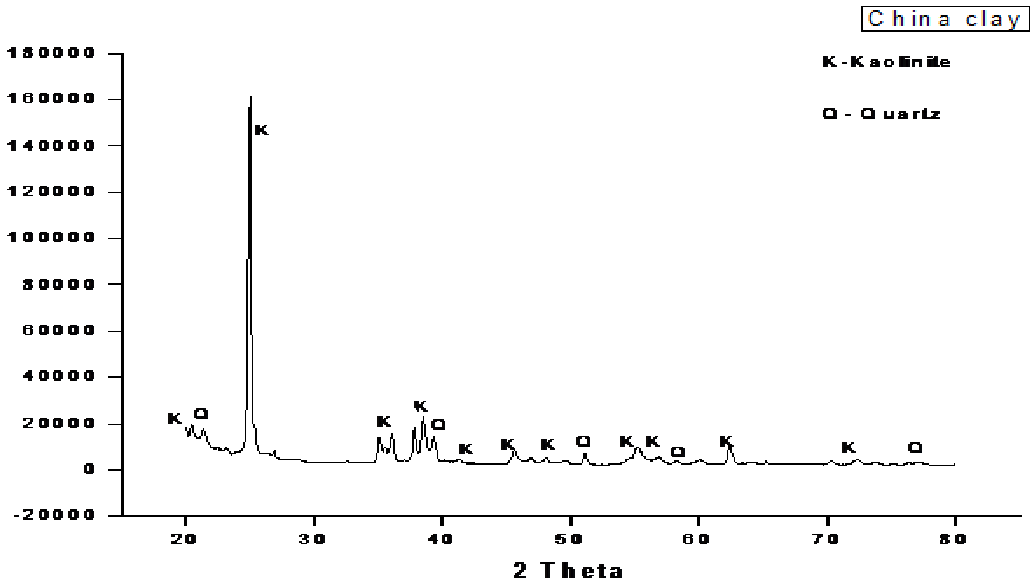
TiO_2	0.43%
LOI	9.1%

<u>2) XRD OF RAW MATERIALS</u>

(FIGURE 1)



F



(FIGURE 2)

- From the XRD analysis it can be seen that main phases in fly ash are mullite and quartz. It also contains some amount of iron oxide as well.
- China clay mainly consists of kaolinite and Quartz as its main phases.

3) LINEAR SHRINKAGE

TABLE 5-SAMPLE FIRED AT 1150^{0}C

BATCH	LINEAR SHRINKAGE%
BATCH 1	7.68%
BATCH 2	8.53%
BATCH 3	10.31%

TABLE 6-SAMPLE FIRED AT $1200^{0}C$

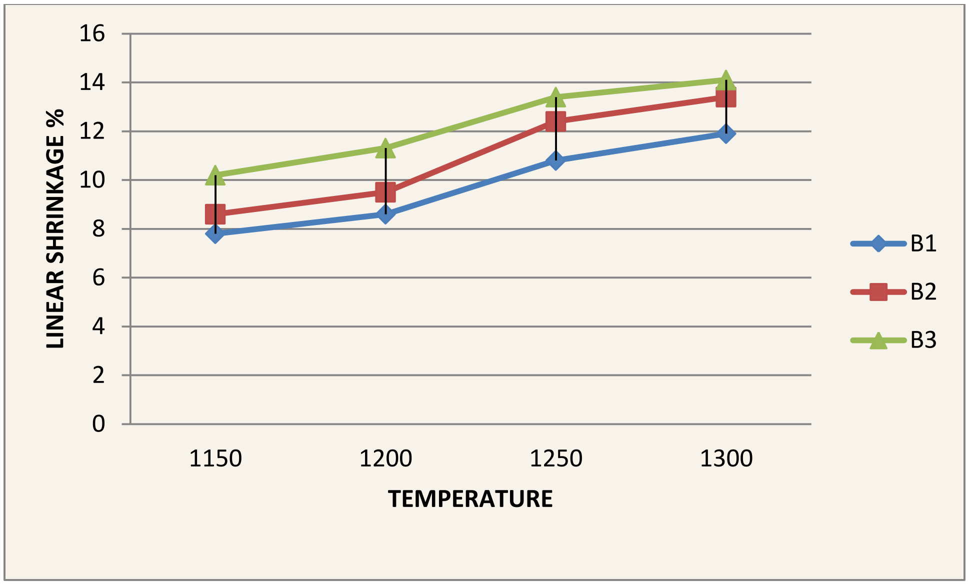
BATCH	LINEAR SHRINKAGE%
BATCH 1	8.68%
BATCH 2	9.53%
BATCH 3	11.31%

TABLE 7- SAMPLE FIRED AT $1250^{0}C$

BATCH	LINEAR SHRINKAGE%
BATCH 1	10.61%
BATCH 2	12.45%
BATCH 3	13.4%

TABLE 8-SAMPLE FIRED AT $1300^{0}C$

BATCH	LINEAR SHRINKAGE%
BATCH 1	11.9%
BATCH 2	13.45%
BATCH 3	14.%



DISCUSSION:-

In the above plot it is observed that the linear shrinkage for all the batches increases till 1250^{0}C and then it gets flattered. The linear shrinkage is more for fly ash samples because of the oxides TiO_2, Fe_2O_3, CaO, etc which acts as fluxing oxides and reduces the viscosity of silica rich amorphous melt and thus enhance shrinkage in these materials. Also as the amount of quartz is reduced due to replacement by fly ash, the amount and viscosity of silica rich liquid decreases and leads to easy growth of mullite crystals embedded in it. Thus, on cooling higher shrinkage takes place.

BULK DENSITY AND APPARENT POROSITY

SAMPLE FIRED AT 1150^{0}C

TABLE 9

Batch	Bulk Density (BD)	Apparent Porosity %
Batch 1	2.21	7.2
Batch 2	2.32	7
Batch 3	2.4	6.8

TABLE 10 -SAMPLE FIRED AT 1200^{0}C

Batch	Bulk Density (BD)	Apparent Porosity %
Batch 1	2.35	6.7
Batch 2	2.46	5.6
Batch 3	2.5	5.2

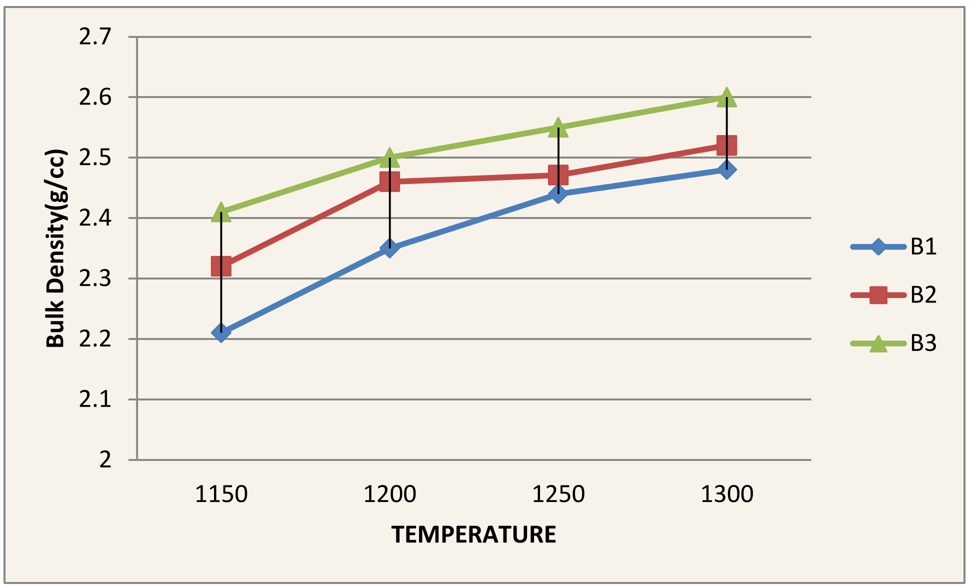
TABLE 11-SAMPLE FIRED AT 1250^{0}C

Batch	Bulk Density (BD)	Apparent Porosity %
Batch 1	2.44	4.7
Batch 2	2.471	3.8
Batch 3	2.55	3.2

TABLE 12-SAMPLE FIRED AT 1300^0C

Batch	Bulk Density (BD)	Apparent Porosity %
Batch 1	2.48	3.4
Batch 2	2.52	3
Batch 3	2.6	2.6

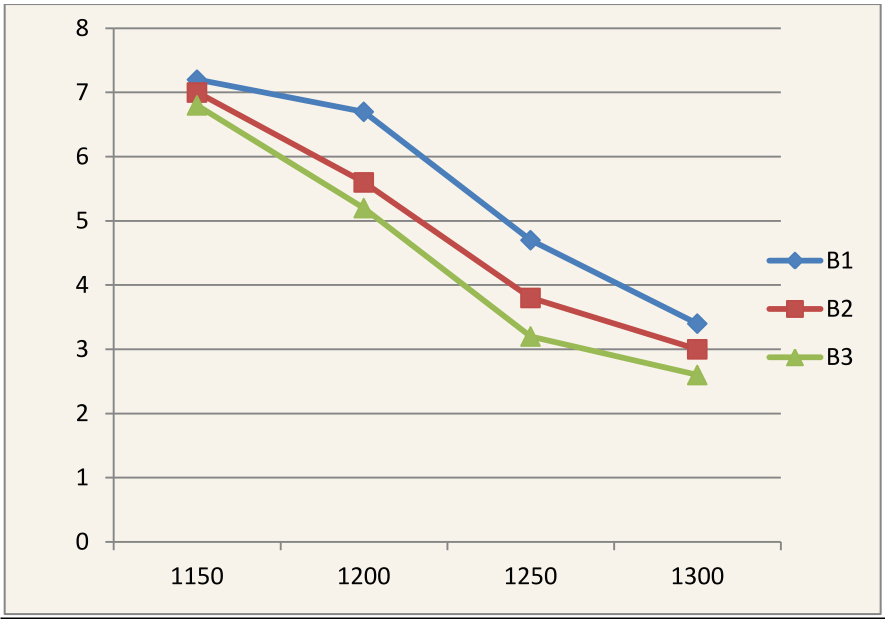
BULK DENSITY Vs TEMPERATURE



Discussion :-

All the composition shows increase in bulk density with temperature which is due to increase consolidation with rise in temperature. Bulk density increases with increase in fly ash content and is maximum for Batch 3 at 1300^0C. With increase in fly ash content, the amount of quartz is reduced and thus the viscosity of amorphous silica melt also reduces leading to easy liquid phase sintering and thus increased density. Also there is an increase in Al_2O_3 with increase in fly ash content .Alumina being a highly dense oxide, in turn increases density of the body.

APPARENT POROSITY Vs TEMPERATURE



Discussion:-

Apparent porosity is highest for all three batches at 1150^{0}c. This is because the Quartz grains are partially melted at this temperature and thus fewer amounts of pores are filled by the liquid phase of amorphous glass. Batch 3 has the highest porosity at 1150^{0}c because of no quartz phase present and so no melting of quartz occurs to produce liquid phase. Batch 1 has lowest porosity at 1150^{0}c because it has highest amount of quartz.

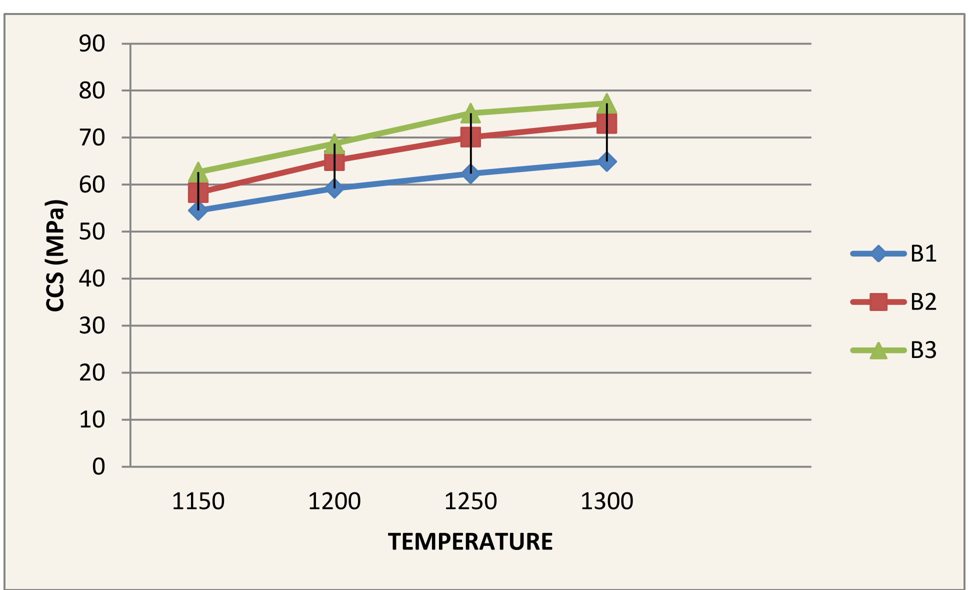
With increase in temperature, at 1250^{0}c apparent porosity of all batches decreases as there is an increase in liquid phase due to melting of quartz.

With further increase in temperature, in normal porcelain body crack develops due to large thermal expansion mismatch between crystalline quartz grains and amorphous silica melts leading to increase in porosity. Thus, Batch 1 has highest apparent porosity at 1300^0c.

4) **Cold crushing strength:-**

TABLE 16

SAMPLE (B-BATCH)	CCS(MPA)
1150 B1	54.5
1150B2	58.3
1150B3	62.7
1200B1	59.2
1200B2	65.1
1200B3	68.7
1250B1	62.3
1250B2	70.11
1250B3	75.21
1300B1	64.9
1300B2	73
1300B3	77



DISCUSSION :-

The cold crushing strength of all the samples increases with increase in temperature. This is because of increased sintering at higher temperature. More and more pore fills up to improve consolidation and hence increasing strength. The strength of fly ash containing sample is higher than that of normal porcelain sample and it increases with increase in fly ash content. This is due to increase in mullite content in fly ash incorporated sample. As can be seen from XRD of fly ash powder, it has large amount of mullite content which in turn, is responsible for high mullite for fly ash containing sample at higher temperature. CCS is highest for Batch 3 sample at 1300^0C. The strength of fly ash samples is higher than that of normal porcelain sample also because of less amount of quartz which melts and form amorphous silica rich solution which reduces the overall strength.

5)MICROSTRUCTURE ANALYSIS:-

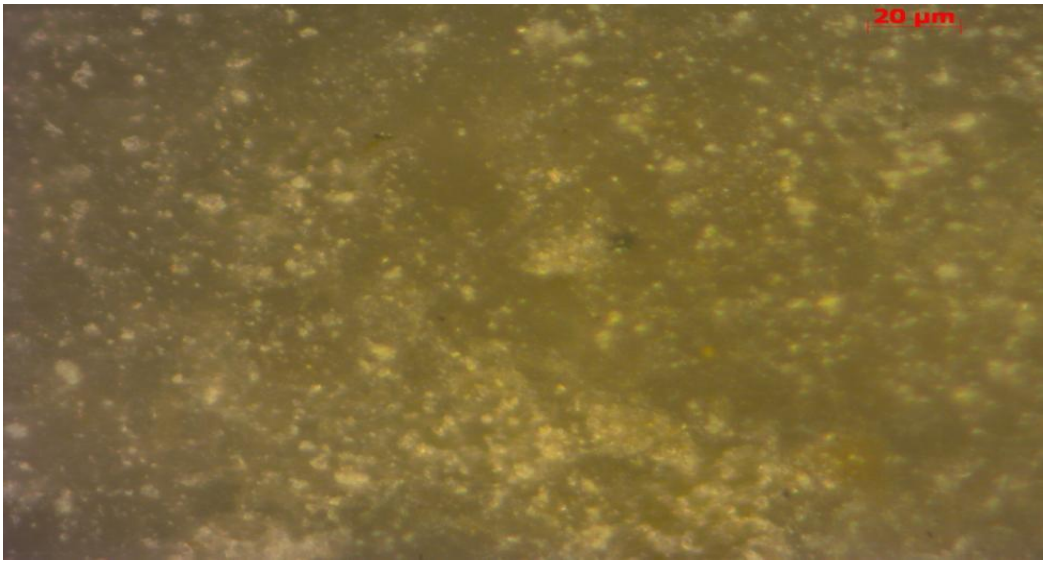


Figure 1

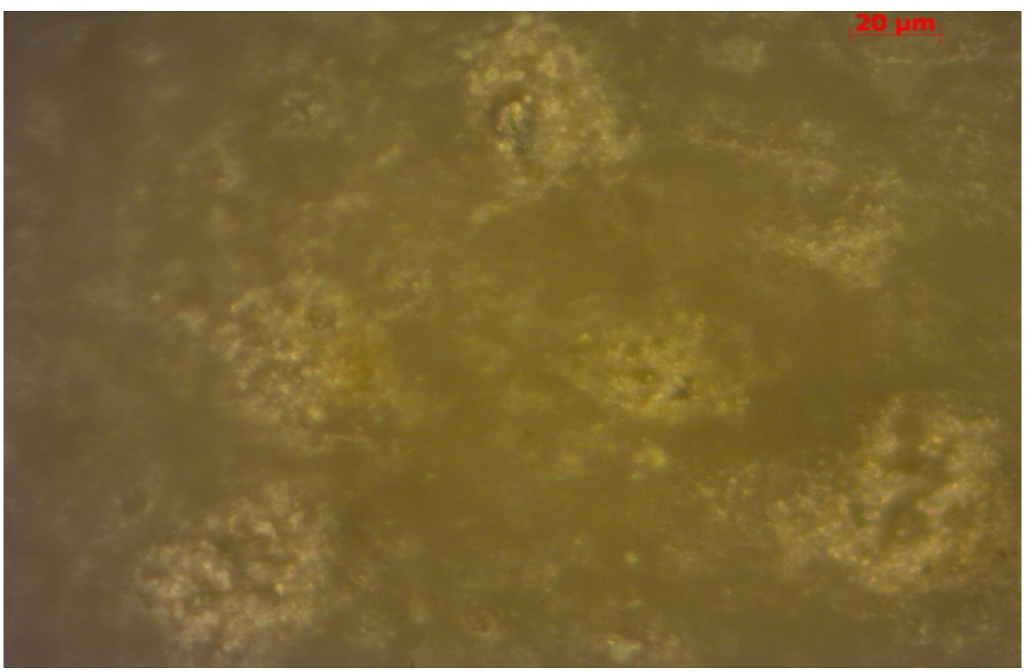


Figure 2

Figure 1 - Batch 3 at 1300^0C

Figure 2 - Batch 1 at 1300^0C

DISCUSSION:-

At 1300^oC batch 1 has some pores and more amount of glassy phase are present whereas in batch 3 at 1300^0 Celsius there are larger grains and more crystalline phase with very less porosity.

CHAPTER-6 : CONCLUSION

From the above discussion it can be said that total replacement of quartz by fly ash in a porcelain composition helps to increase the bulk density and to reduce the apparent porosity of the fly ash containing samples than normal porcelain samples. Fly ash samples also show higher strength than porcelain samples. Optical microstructures show low porosity and high crystalline structure for fly ash samples. All these results indicate fly ash can be used for total replacement of quart which helps in waste utilization.

CHAPTER-7 : REFERENCE

1:-Kausik Dana and Swapan Kumar Das. "**Evolution of microstructure in fly ash-containing porcelain body on heating at different temperatures".** Bull.Mater.Sci., Vol.27, No.2, April 2004, pp.183-188, Indian Academy of Sciences.

2 :- S.Kumar , K.K.Singh, P.Ramachandrarao . "**Effects of fly ash additions on the mechanical and other properties of porcelainised stoneware tile**s". Journals of Materials Science 36(2001)5917-5922.

3:- R.C.C.Monteiro, E.M.M.R.A Lima, E S. Alves ."**Mechanical characteristics of clay structural ceramics containing coal fly ash".** Springer Science Business Media B.V.2007

4:- Jorge Martín-Márquez, Jesús Ma. Rincón, Maximina Romero **" Mullite development on firing in porcelain stoneware bodies."** Eduardo Torroja Institute for Construction Sciences-CSIC, 28033 Madrid, Spain.

5:- Kausik Dana, Suken Das, Swapan Kumar Das. " Effect of substitution of fly ash for quartz in tri-axial Kaolin-Quartz-Feldspar system". J.Eur.Ceram. Soc.,24(2004)3169-3175