# PHASE EVOLUTION BEHAVIOUR OF DOLOMITE-ALUMINA SYSTEM

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OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology in Ceramic Engineering

By

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# CERTIFICATE

This is to certify that the thesis entitled, **"Phase Evolution Behaviour of Dolomite-Alumina System"** submitted by **LIPSA DAS (110CR0605)**in partial fulfilment of the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by them 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.

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# ABSTRACT

Magnesium Aluminate Spinel Refractories are usually prepared by sintering from Calcium Aluminate Cement and Synthetic Mag-Al spinel. But the high cost of electrofused or sintered spinels is a hindrance and hence a suitable alternative is required. Dolomite and calcined alumina can be used for the synthesis of refractory aggregates containing calcium aluminate and spinel that have extensive applications. Spinel phase provides high slag resistance and high thermo mechanical resistance and Calcium Aluminate Cement is commonly used hydraulic binder.So by reaction sintering of dolomite and calcined alumina pellets of 1:2,1:3 and 1:7 compositions by mole ratio sintered at $1200^0$C,$1300^0$C,$1400^0$C and $1500^0$C, such refractory compositions were synthesized. The phase evolution was studied and quantified by XRD analysis and the physical and mechanical properties were measured.

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# INTRODUCTION

## 1.1 Refractories

Refractories are materials with high melting points, and having properties that make them suitable so that they are heat-resisting barriers between high and low temperatures. They are used in construction of application specific high temperature areas/surfaces, particularly in furnaces or broilers, as they minimize heat losses through structure.

The value of refractories is judged not merely by the cost of the material itself, but by the nature of job and/or its performance in a particular situation. Specifically, the performance of a refractory depends on its qualities and quantities in three phases- solid, glass/liquid, and pores- which govern the ultimate property of a refractory material.

A useful material is developed by mixing various sizes of similar refractory material having different strength and property, which changes during firing/heat treatment in the course of service. The qualities of refractories thus depend on their chemical, physical, mineralogical and thermal properties.

In the study of phase evolution of dolomite alumina system, the materials involved are:

## 1.1 Dolomite

Dolomite is a double carbonate of calcium and magnesium having the formula $CaCO_3.MgCO_3$.Theoritically,dolomite contains 30.41% CaO,21.87% MgO and 47.72% $CO_2$.Some dolomites are seen with calcite and therefore have greater percentages of calcium oxide. Dolomite used for making of refractories should be a mixture of equimolar proportions of $CaCO_3$ and $MgCO_3$ with about 45.65% $MgCO_3$ and 54.35% $CaCO_3$.Dolomite is an

imperativemetamorphic and sedimentary mineral, found as the principal mineral in dolostones and metadolostones, and as an essential mineral in limestones and marbles where calcite is the main mineral present. Also observed as a hydrothermal vein mineral, forming crystals in cavities; and found in serpentinites and similar rocks.

Dolomite utilized should be compact andhard with a uniform texture having very low percentages of iron,silica,alumina, etc. as these adversely affect the refractoriness.As mined dolomite is dead burnt at 16000C or more in a rotary kiln in presence of some serpentine.Serpentine (MgO.2SiO2.2H2O) is added for dolomite stabilisation.Dead burnt dolomite has about 58% CaO and 42% MgO. Dolomite undergoes hydrates when exposed to atmosphere even after dead burning because of its hygroscopic nature and hence refractories from dolomite are difficult to make.To avoid hydration of dolomite refractories,they are coated with tar or wax immediatelyafter they are fired or cooled

Physical properties of dolomite are:

| | |
|---|---|
| Lustre | Vitreous, Pearly |
| Diaphaneity | Transparent,Translucent |
| Colour | Brownish-white,orpink,colourless,grey,white |
| Hardness(Mohs) | 3 ½ -4 |
| Tenacity | Brittle |
| Cleavage | Perfect on {1011} |
| Fracture | Sub-Conchoidal |
| Density | 2.84-2.876 |
| Parting | Noted in lamellar twins on {0221} Twin gliding on {0221} |
| Crystallography of Dolomite | |
| Crystal System | Trigonal |
| Class(H-M) | 3-Rhombohedral |
| Space Group | R3 |
| Cell parameters | a= 4.8012(1)A,c=16.002A |
| Ratio | a:c=1:3.333 |

*Table 1: Physical properties of Dolomite*

## 1.2 Applications:

Tar-dolomite mixtures have found wide use as monolithic linings of L.D. and basic Bessemer converters.Dead burnt dolomite mixed with required amounts of tar is also extensively used as the ramming mixture in basic open-hearth and electric furnaces. Dolomite of 3 to 10 mesh size is a crucial fettling material for patch repairs of these furnaces after the metal has been taped from them in hot condition Basic open hearth furnace tap holes are sealed by dead burnt dolomite alone or a mixture of dead burnt dolomite and coke breeze.

## 1.3Calcined Alumina

Calcined (or alpha) alumina is prepared by calcining a source alumina powder at 1200-1300C to alter it to pure $Al_2O_3$. This is the densest and most stable crystalline form of alumina. It is not soluble in water but is soluble in hydrofluoric acid and potassium bisulfate. When nearly 100% of the material transforms to the large hexagonal, elongated tablet shaped crystals linked with the alpha phase, the product is referred to as "Tabular Alumina". Unground calcined aluminas are usually 100-300 mesh, but much finer grades (often called "Ground Alumina") are produced by milling. Calcined aluminas are obtainable in numerous grades on the basis of the heat treatment applied, crystal size, soda content, and extent of thermal conversion to alpha phase. Soda content is a key factor in determining the final use (low soda materials are used for electronic applications, medium soda for electrical insulation and porcelains, high soda for glass, glaze, fiberglass and electrical porcelain). Calcined alumina is normally used in the manufacture of high-grade ceramic shapes, refractories and fused alumina abrasives. It can be compressed tomakea fired density of 3.8 or higher.

Alumina has a very high melting temperature (about 2000C) and alumina ceramics can retain up to 90% of their strength above 1100C. They are thus used in many refractory materials (i.e. Calcium Aluminate Cements have PCEs above cone 35) and utilised to make parts that must sustain high temperature.

Some exceptionally fine 'super ground' grades are present which can be made into casting slurries of extremely high specific gravity and which cast well with very low shrinkage (even though alumina powder is not a plastic material). Deflocculation can be achieved using a low pH (3.5-4.5) positive anion mechanism using hydrochloric or nitric acid, a high pH (11-12) cation mechanism with alkali hydroxide salt additions, or by adding standard alkali polyelectrolyte dispersants. By adding organic binders, alumina bodies can be cast and pressed into a large variety of shapes requiring heat and abrasion resistance. Alumina parts are then sintered to allow discrete crystals to react with each other to form bigger ones. Calcined alumina can replace silica filler in porcelain bodies (325 mesh). Itminimises shrinkage, increases thixotropy, provides strength in the kiln reducing warping, benefits glaze fit, and increases fired strength.

## 1.4 Calcium Aluminate Phases

Calcium aluminates comprise of a range of minerals attained by heating calcium oxide and aluminum oxide together at high temperatures.

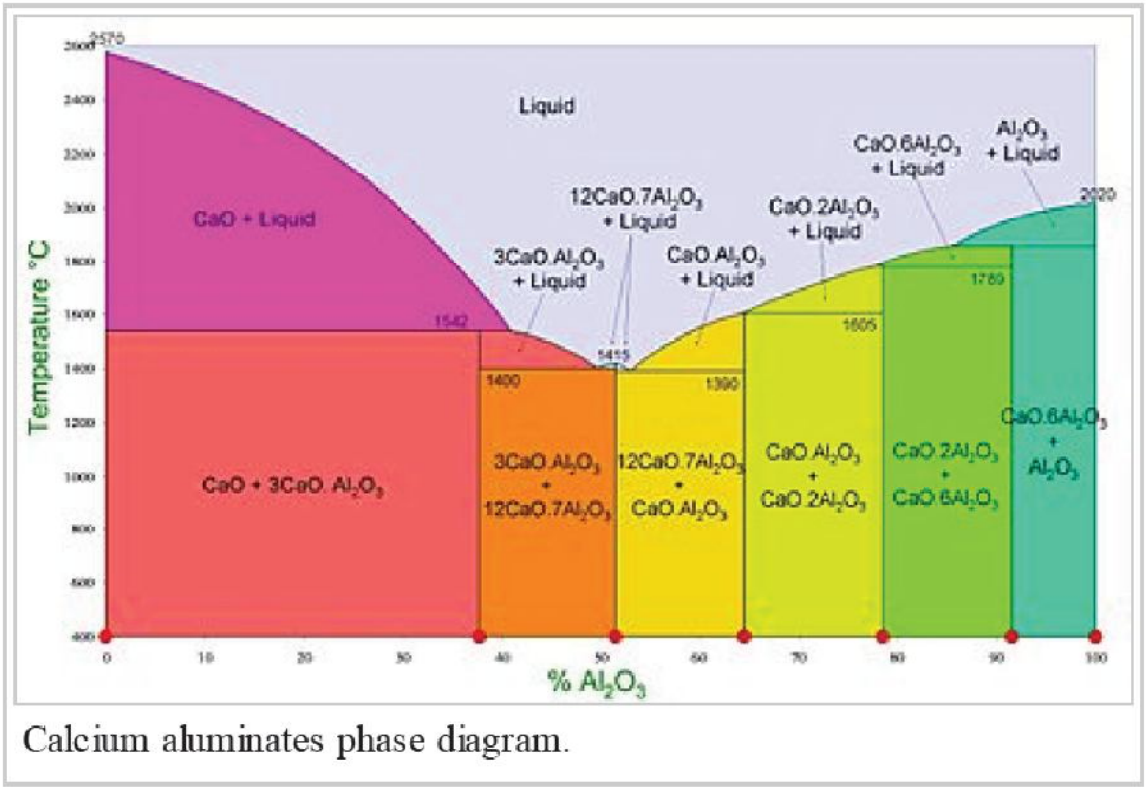


*Fig1. Diagram Showing Different Phases of CaO-Al2O3 binary system*

Different phases in Calcium aluminates are:

**Calcium Monoaluminate**

CA(calcium monoaluminate) is the primary hydraulic mineral present in calcium aluminate cement.The hydration of this phase gives high initial strength of calcium aluminate cements.It is a monoclinic phase,pseudo hexagonal its space group is P21/n, Z=12 and Dx= 2.945 g/cm$^3$. It is comparable to β- trydimitestructure with an infinite three dimensional framework of $AlO_4$tetrahedra sharing corners.But the large ionic radius of the $Ca^{2+}$modifies the trydimite network and a section of calcium atoms has irregular co-ordination polyhedral with oxgen.Under the optical microscope, CA appears as irregular colourless grains,with inference coloursless than

than of $CA_2$. Some of the $Al^{3+}$ ions in the $AlO_4$tetrahedra may be partially replaced by iron.CA has a monoclinic unit cell.

**Calcium Di-Aluminate(CA2)- Grossite**

Calcium di-aluminate(CA2) or Grossite has a monoclinic structure with the space group C2/c Z=4 and D x=2920 kg/m3.Its structure is centered upon a framework of AlO4 tetrahedra. Some of the oxygen atoms are shared between two tetrahedral and the rest distributed between the other three. The $CA_2$ phase inclines to be more refractory in nature than CA, however it is less reactive. $CA_2$ hydrating on its own will impart a lower strength than CA after 24 hours of curing.However the hydration of $CA_2$ is reported to be enhanced at high temperature and also in presence of CA.

**DodecacalciumHepta-Aluminate(C12A7)- Mayenite**

Mayenite has the space group 143d.Its respective crystal structure is composed of $Ca^{2+}$ions with irregular six fold co-ordination with oxygen, which has an incomplete framework of corner-sharing $AlO_4$tetrahedra that has the empirical composition Al7O1611-. In each unit formula one of the $O^{2-}$ ions is distributed between twelve sites, which are thoughtto increase two of the AlO4 groups to AlO5.The calcium ions in mayenitehave a very balanced shell of oxygen atoms, which are roughly distributed on the surface of a hemisphere. These co-ordinating hemispheres occur in pairs along the axes of crystal symmetry, in which the planar faces are defined by vacancies amongst the twelve-fold positions.Mayenite is the most reactive of all calcium aluminate species occurring in HACs, and will hydrate very quickly in contrast to CA. Due to this fact the amount of mayenitepresent incalcium aluminate is very carefully controlled by manufacturers.

**Other Calcium Aluminate Phases**

Calcium hexa-aluminate (CA6) forms as a result of the sintering of CA2. It is non-hydraulicand more refractory than the other phases, having a melting point of 1870°C. CA6 is formedin refractory castable products when they are heated to high temperatures. The C3A phase isvery reactive and is only present in Portland cements.

## 1.5Spinel

Compounds of the general formula AB2O4 where: A=bivalent cation and B=trivalent cation are called spinels.They are of 2 types: normal and inverse spinel.Spinels have a packing arrangement of ABCABC… of cubic closed packing FCC of spheres of oxygen anions with tetrahedral and octahedral voidsinto which divalent and trivalent cations accommodate themselves respectively.

## LITERATURE REVIEW

A.H. De Azaa et al.[4] have worked to produce spinel containing refractory cements formed by the reaction sintering of dolomite and alumina.This has been done to find substitute to the sintered or electrofusedspinels which have high cost and hence limited applications.The reaction sintering was found to occur in two steps: (1) reaction (2) sintering.In the first stage the decomposition of dolomite takes place in the temperature range of 700–900$^0$C and this was followed by the reaction of lime and magnesia in temperature range of 900 to 1250$^0$C with alumina to form spinel and calcium aluminate phases.Non-isothermal study of reaction sintering was carried out and three significant expansive effects were observed at ~950,~1100,~1200$^0$C which were due to the formation of Calcium monoaluminate(CA), spinel and Calcium dialuminate($CA_2$) respectively.The reaction sintering mechanism was established in this paper.The Thermo gravimetric anddilatometric data were used to construct curve that showed the variation of density with temperature.A general equation based on MgO/CaO molar ratio with varying proportions of CA,Spinel and $CA_2$ was established.

Jin hong Li et al.[5] work was based on preparing aluminate cement containing spinel prepared in situ by sintering mixtures calcined bauxite, magnesia and limestone.The sintered clinkers and hydration products were then characterised by X-Ray Diffraction and Scanning Electron Microscopy.The dominant phase was found to be calcium monoaluminate after spinel.The major phases were found to CA, CA2,and Magnesium Aluminate Spinel as main phases and C2AS and residual alumina were present in traces.New phase tunable aluminous cement containing magnesium aluminate spinel was prepared by sintering.The octahedron

shaped Magnesium Aluminate crystals on the order of 2-5 µm and tabular or flaky shaped CA in range of 20-40 µm form agglomerates and disperse in the aluminous cements.Mag-Al spinel played a negative role on the compressive strength of hydrated castables,Five stages of hydration were found to occur including pre-induction, induction, acceleration, deceleration and stabilization.

Araceli et al.[2] studied the effect of α and γ polymorphs of alumina on the preparation of magnesium aluminate spinel containing refractory cements.The behaviour of different batches submitted to firing up to1450$^{o}$C was evaluated by using a combination of spectroscopic FTIR technique and XRD analysis.Two batches of cement samples consisting of appropriate amount of each alumina polymorph and dolomite were studied.Calcite and quartz were present to lesser extent.Over 1250$^{0}$C, spinel was the major component in both the samples.During thermal treatment of Dolomite-α alumina at 1350$^{0}$C,reaction between andCaO formed little FC.The final composition of D γ alumina contained spinel, CA, CA2, CA6, C12A7, C2AS and Magnesium Aluminoferrite. The formation of the phases at lower temperature was found to be favouredby γ alumina.

Nagy M.A. Khalil et al.[1] worked to obtain and study the aluminous cements containing magnesium aluminate spinel from Egyptian dolomite.In this work,three mixes of calcium aluminate cements containing magnesium aluminate cement were prepared using appropriate mixtures of Egyptian dolomite and active alumina.When 10% of such cements were added to refractory grade magnesia aggregate, in presence of Li2CO3nas strength modifier,refractory castable bodies with improved strength and thermal shock resistance was achieved.

## 2.1Objective:

To study the phase evolution behaviour of Dolomite Alumina System in order to determine how the spinel and calcium aluminate phases are varying as a function of composition and temperature. This knowledge would assist us in optimising the composition and temperature so as to get the maximum amount of spinel and calcium monoaluminatephases (CA), thereby giving better properties.

## 2.2Reactions Involved:

The decomposition of dolomite takes place in the temperature range of $700^0$ C to $900^0$ C in two stages.

$$CaMg(CO_3)_2 \xrightarrow{\sim 775^0 C} MgO + CaCO3 + CO_2$$

$$CaCO3 \xrightarrow{\sim 900^0 C} CaO + CO_2$$

Dolomite Alumina sintering reactions:

(1) $2Al_2O_3 + CaCO_3MgCO_3 \xrightarrow{-CaO} Al_2O_3 + MgAl_2O_4 + CO_2$

(2) $3\ Al_2O_3 + CaCO_3MgCO_3 \xrightarrow{-CaO} 2Al_2O_3 + MgAl_2O_4 + CO_2$

(3) $7Al_2O_3 + CaCO_3MgCO_3 \xrightarrow{-CaO} 6Al_2O_3 + MgAl_2O_4 + CO_2$

## EXPERIMENTAL PROCEDURE

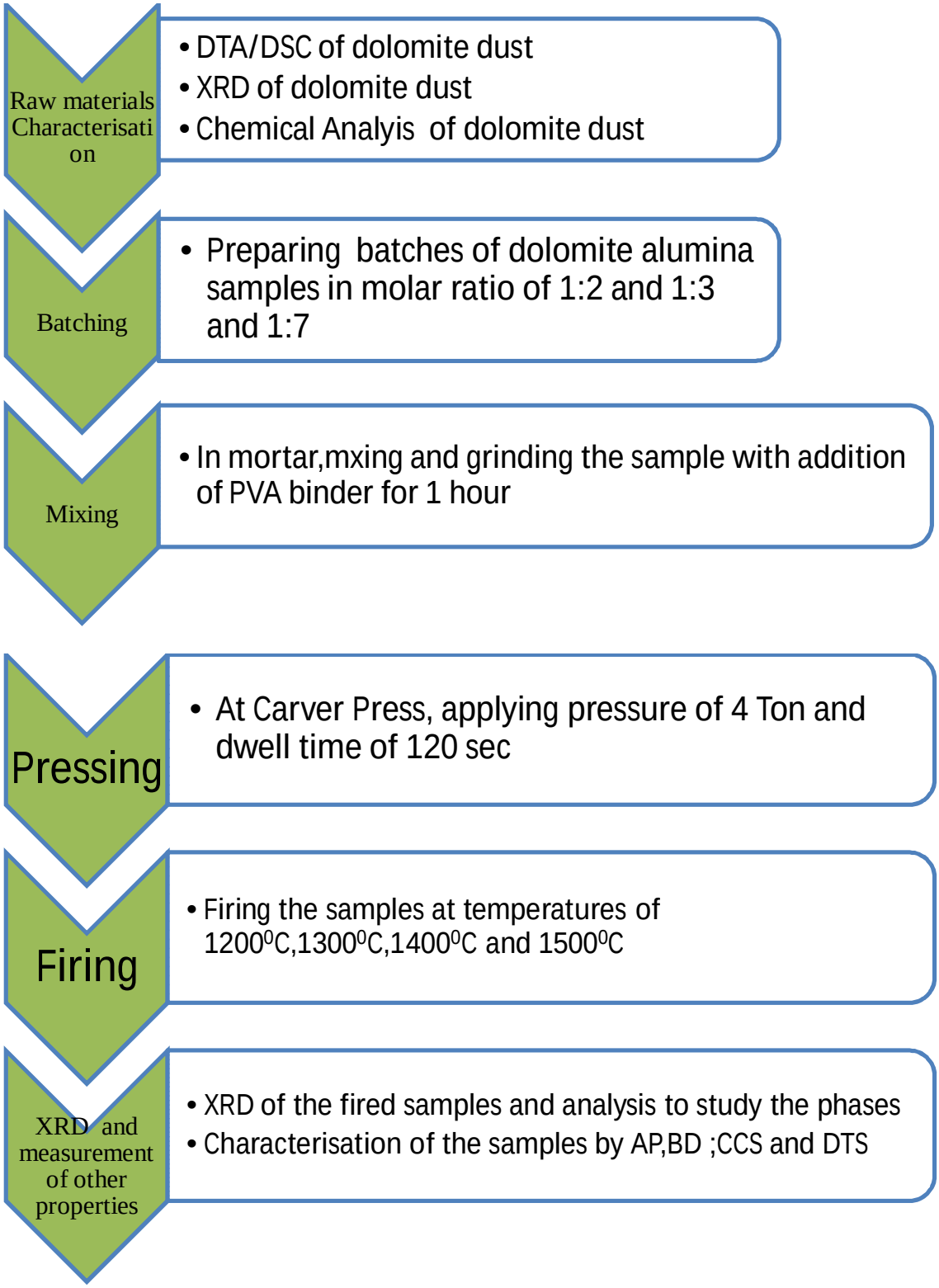


*Fig2. Flow Chart for Calcium Aluminates and Spinel synthesis*

Raw materials characterization was performed by XRD analysis, DTA/DSC and Chemical Analysis of Dolomite dust Sample. Subsequently following this Characterization of raw materials, Batching of Dolomite-Alumina samples in molar ratio of 1:2,1:3 and 1:7 was done. The batches were mixed and ground for 30 minutes in dry state and then for further 30 minutes with the addition of PVA binder. After mixing, the samples were fractioned into samples of 0.7 gm each and each sample was pressed by applying a pressure of 4 Ton and a dwell time of 120 seconds. Then these pressed samples were kept in drier for 24 hours to attain sufficient handling strength. Then these dried samples were fired at respective temperatures of $1200^0$C, $1300^0$C,$1400^0$C and $1500^0$C .The samples after firing were then sent for XRD to observe the phase growth that had taken place in different composition samples fired at different temperatures.The phases were identified in the respective samples by analysis using XPERT high score software and quantification of the phases was also done. These results were analysed to conclude the reaction stages and the phase evolution. From this analysis, the temperature and composition that were ideal for the synthesis of such refractory aggregates could be inferred. Following this, the physical properties like Apparent Porosity and Bulk Density were measured and mechanical properties like CCS and DTS were measured.

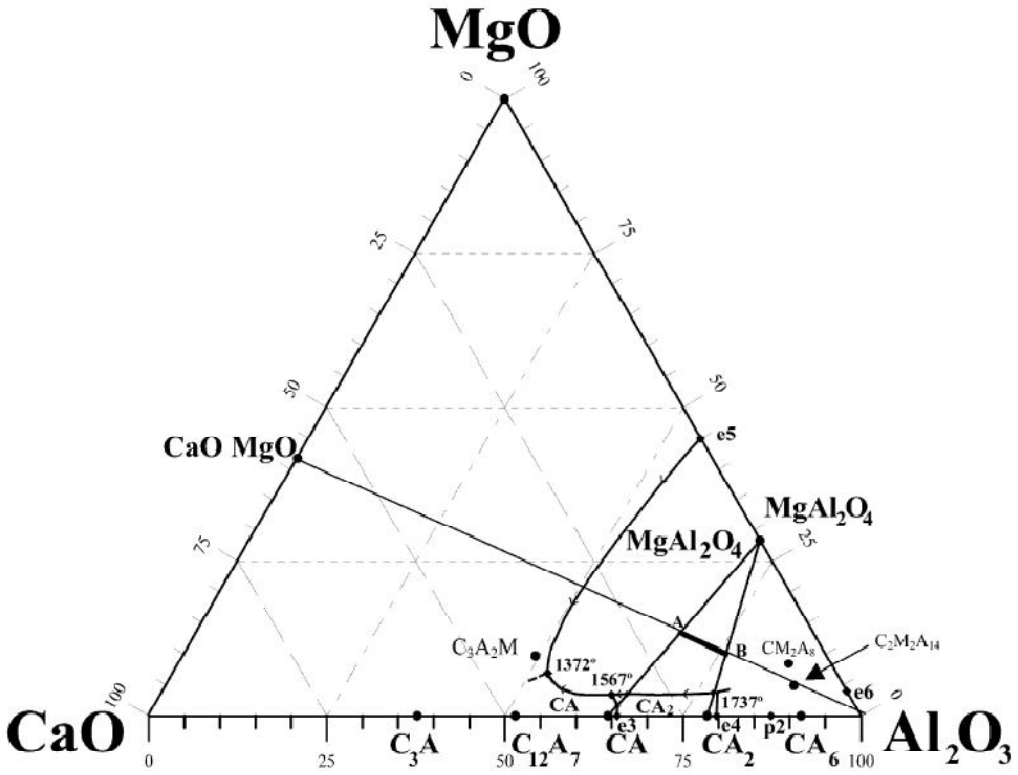


*Fig3. The simplified Al2O3-CaO-MgO ternary phase diagram*

In the above figure the diagram shows the simplified $Al_2O_3$-CaO-MgO ternary system showing the subsystem $CaAl_2O_4$-$MgAl_2O_4$-$CaAl_4O_7$ subsystem In the above figure, C stands for CaO,M stands for MgO and A for $Al_2O_3$.

## X –Ray Diffraction

The properties of a solid can be linked back to the arrangement of atoms in its crystal structure. X-ray diffraction is a non-destructive analytical technique which can give the unique fingerprint of Bragg reflections related to the crystal structure.One can consider a crystal structure as being made up of layers, or planes, which each function as a semi-transparent mirror. X-rays with a wavelength similar to the distances between these planes can be reflected such that the angle of

reflection is same as the angle of incidence. We call this behaviour `diffraction´ and it is described by Bragg's Law:

$$2d\sin\theta = n\lambda$$

When Bragg´s Law is fulfilled, constructive interference of diffracted X-ray beams take place and a Bragg reflection will be taken up by a detector scanning at this angle. The positions of these reflections give information about the inter-layer spacings of atoms in the crystal structure, thanks to Bragg´s Law. Peak intensities give information about how much X-ray scattering contributes to that reflection – e.g. where particular atoms lie in the structure, or how much of a phase is there in a sample.

Analysis of the diffraction pattern permits the identification of phases presentwithin a given sample. With that achieved, it might be possible to quantify each phase that is present, the crystallinity of a sample, the crystal structures and their lattice parameters, crystallite size and strain... all information that can be important in material characterisation and quality control.The scanning rate used was 20C/min and the angle 2θ (degree) was in the range of 20-800 degree.

## DTA/DSC/TGA:

The physical and chemical properties of materials undergoing reaction or transition are studied to find their variation with temperature and time using analytical methods like thermo-gravimetric analysis (TG), differential scanning calorimetry (DSC),differential thermal analysis (DTA)and thermo-mechanical analysis (TMA).

In DTA, the material studied and an inert reference are made togo throughidentical thermal cycles, while keeping records of any temperature difference between sample and reference this differential temperature is then plotted against time, or against temperature (Changes in the

sample, either endothermic or exothermic , can be detected relative to the inert reference. Thus, a DTA curve gives data on the transformations that havetaken place, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not influenced by the heat capacity of the sample.

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to raise the temperature of a sample and reference is measured against variation in temperature. Both the sample and reference are kept at nearly the same temperature through the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature rises linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which change of physical and chemical properties of materials are measured as a function of rising temperature (with heating rate kept constant), or as a function of time (with constant temperature and/or constant mass loss). TGA can give information about physical phenomena, such as second-order phase transitions, comprising vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can give information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

TGA is commonly used to find out selected characteristics of materials that show either mass loss or gain because of decomposition, oxidation, or loss of volatiles (such as moisture).

## Chemical Analysis

The chemical analysis of the dolomite dust sample was done to determine the amount of Calcium oxide, Magnesium oxide and impurities like Silica, Iron oxide etc and the loss on ignition of the sample was also determined.The amount of Silica present was determined by gravimetric analysis and the calcia and magnesia content was determined by titration.The data obtained by chemical analysis helps to estimate the quality of the dolomite considered by giving an estimate of the impurities present.

## Batch Calculation

| RATIO | DOLOMITE(in g) | ALUMINA(in g) |
|---|---|---|
| 1:2 | 4.75 | 5.25 |
| 1:3 | 3.76 | 6.24 |
| 1:7 | 2.05 | 7.95 |

*Table 2. Batch Calculation*

The above weight fractions of alumina and dolomite as calculated from the molar ratio were mixed to create batches of 1:2,1:3 and 1:7 molar ratio which were then mixed and ground to fine particle size so that the reaction would take place properly.

## Apparent Porosity, Bulk Density

The sample after drying and firing was characterised for Apparent Porosity and Bulk Density measurement by boiling water method. The sample after being cooled after firing, its weight was measured termed as Dry weight(D).Since dolomite has tendency to react with water like lime,so this experimental measurement was carried out in kerosene rather than water.The sample Pellets were placed in a beaker placed in dessicator for 2 hours in kerosene and were allowed to boil and then cool to room temperature while still immersed in kerosene. During boiling,it was ensured that the sample pellets were not in contact with the heated bottom and the beaker used to hold the pellets did not give any scaling.After boiling and cooling,the weights of the test specimens were taken which is the Suspended weight(S).After this the samples were removed from kerosene,their surface was wiped with cloth,and again weights were taken.This is the Soaked weight(W) of the samples.

The Apparent Porosity and Bulk Density are given by the following formulas:

Apparent Porosity(AP)=$\frac{W-D}{W-S}$ 100

Bulk Density(BD)=$\frac{D}{W-S}$ * ρ

Where, the notations have same meaning as mentioned above and ρ=density of the liquid(here kerosene for which density=0.78).

## Cold Crushing Strength(CCS):

The cold crushing strength of a refractory is its capacity to provide resistance to compressive load at room temperature.It is the load in pounds per square inch or kilograms per square centimeters at which the refractory breaks.

$$CCS=\frac{Total\ load}{Total\ Area}$$

## Diametricaltensile Strength:

It is the measure of the tensile load that the sample can withstand before fracture.The Compressive Strength(CCS) and the Tensile strength(DTS) of the samples were measured.

## RESULTS AND DISCUSSION

### XRD of dolomite

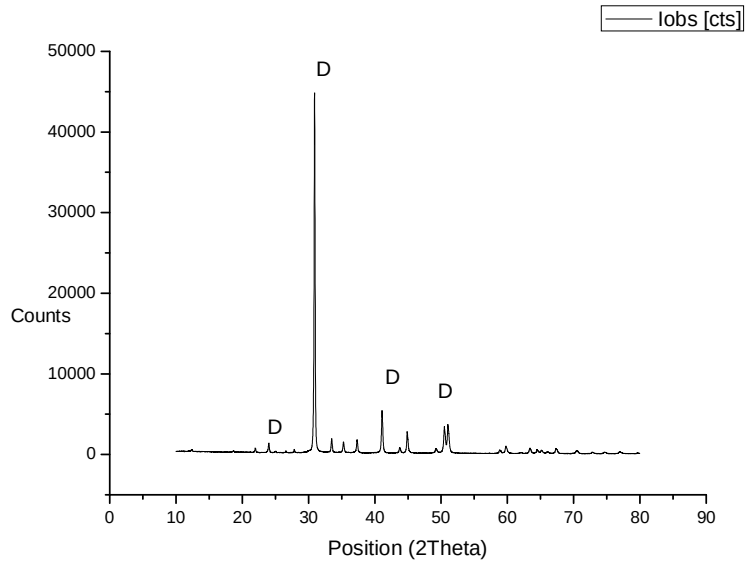


*Fig4. Figure shows the X Raydiffraction pattern of dolomite powder.The most intense peaks showed dolomite as the phase composition when matched with the standard JCPDS file.*

### Chemical Analysis of Dolomite

| Composition | Wt% |
|---|---|
| $SiO_2$ | 2.386 |
| $Fe_2O_3$ | 2.95 |
| $Al_2O_3$ | 1.25 |
| CaO | 33.327 |
| MgO | 18.53 |
| LOI | 46.366 |

*Table3. Chemical Analysis of Dolomite*

**DSC/TGA Analysis Of Dolomite Powder**

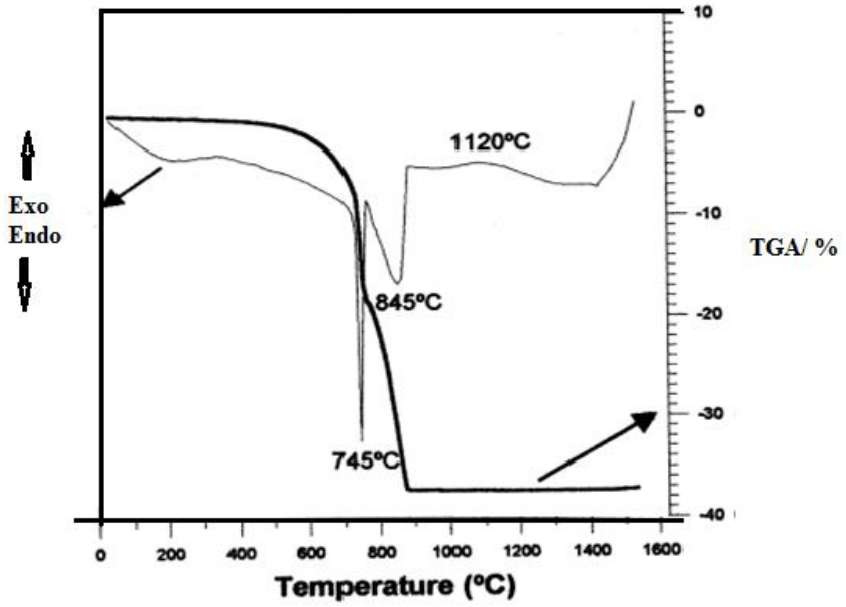


*Fig5. Figure showingThermal decomposition behaviour of dolomite sample.*

The above diagram depicts the thermal decomposition trend of dolomite sample Differentialthermalanalysis (DTA) curve of dolomite shows two peaks at 777·8°C and 834°C. The two endothermic peaks seen in dolomite areessentially due to removal of carbon dioxide of dolomite and calcite, respectively. Measured activation energies range between 97 and 147 kJ mol−1. The large variation in activation energy is attributed to the presence of impurities such as $SiO_2$, $Al_2O_3$, $Fe_2O_3$, etc in the samples.

## XRD Of Dolomite Alumina Aggregates

The XRD of the dolomite-alumina samples as a function of temperature showing the various phases formed.The various phases have been designated by the notations as follows:

| Compound | Notation |
|---|---|
| $CaAl_2O_4$(CA) | @ |
| $MgAl_2O_4$ | # |
| $CaAl_4O_7$(CA2) | $ |
| $CaAl_{12}O_{19}$(CA6) | % |
| $Ca_{12}Al_{14}O_{33}$(C12A7) | ^ |
| MgO | & |
| $Al_2O_3$ | * |
| CaO | + |

*Table4. Compounds and the notions used for XRD.*

**Dolomite–Alumina=1:2**

The figure below shows the X ray diffraction pattern of dolomite alumina sample of the above ratio in form of pellets.The main phases were found to be Calcium monoaluminate and spinel the percentage of which increases with temperature but at temperatures exceeding $1400^0$C,it decreased while the other minor phases were $CA_6$ and $C_{12}A_7$ appeared at high temperatures but were formed in minor amounts.

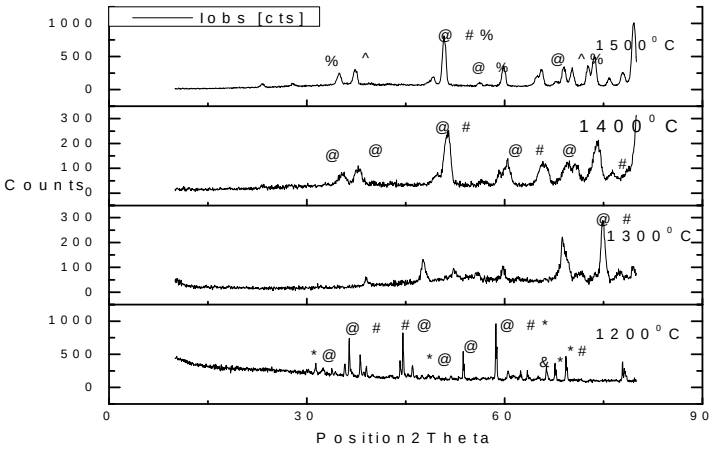


*Fig6. Figure showingX ray diffraction pattern of dolomite alumina sample with 1:2 mole ratio*

**Dolomite-Alumina =1:3**

The following figure shows the X ray diffraction pattern of samples of dolomite alumina ratio 1:3 in form of pellets.The main phases were found to be Calcium monoaluminate and spinel the percentage of which increases with temperature but at temperatures exceeding 14000C it was observed that their quantity decreased while the other minor phases were CA6 and C12A7 which appeared at high temperatures but were formed in minor amounts.The amount of CaO and MgO present declined with increase in temperature because of their participation in reaction sintering process.With increase in alumina content ,the Calcium dialuminate (CA2)content was found to increase due to reaction of Calcium MonoAluminate phase with free alumina present.

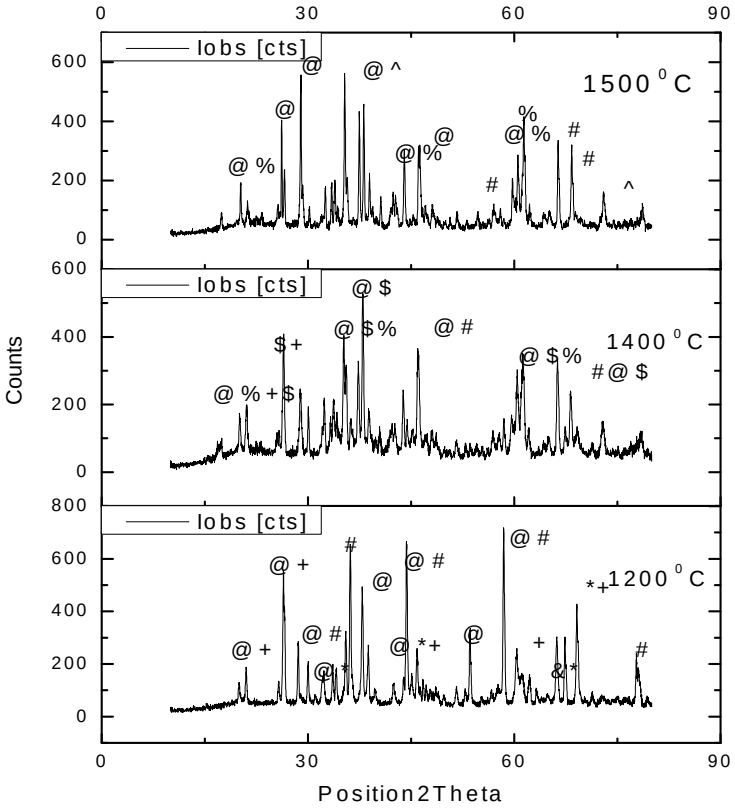


*Fig7. Figure showing X ray diffraction pattern of dolomite alumina sample with 1:3 mole ratio*

**Dolomite-Alumina= 1:7**

The following figure shows the X ray diffraction pattern of samples of dolomite alumina ratio 1:7 in form of pellets.The main phases were found to be Calcium monoaluminate and spinel.Spinel was found to form at temperatures as high as 14000C while Calcium monoaluminate was found even at temperature of 12000C.

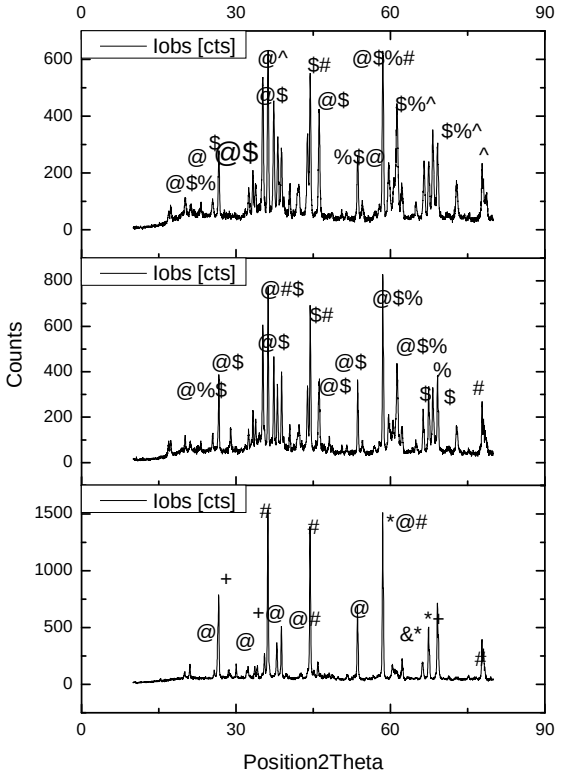


*Fig8 .Figure showingX ray diffraction pattern of dolomite alumina sample with 1:7 mole ratio*

**Dolomite alumina samples fired at $1300^0$ C for compositions 1:3 and 1:7**

The followingfigure shows the X Ray diffraction patterns of dolomite alumina samples of 1:3 and 1:7 dolomite alumina compositions each fired at 13000 C. The main phase was found to be Calcium monoaluminate(CA) and unreacted calcia that was present at a temperature of $1300^0$C but totally disappeared at higher temperatures.

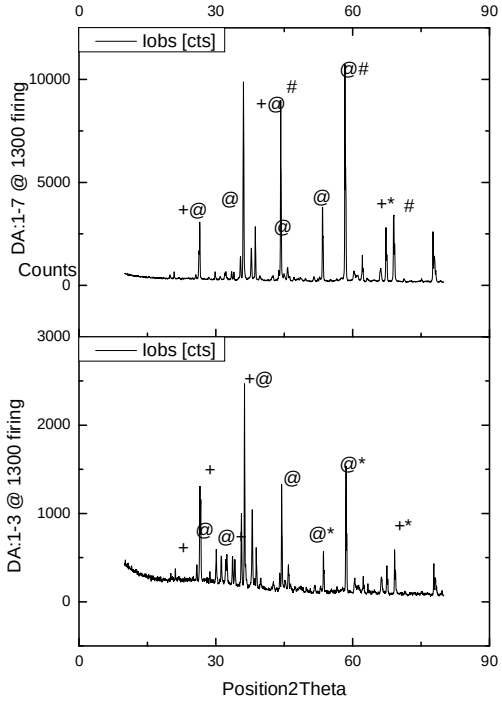


*Fig9. Figure showing X ray diffraction pattern of dolomite alumina sample with 1:3 and 1:7 mole ratio sintered at* $1300^0$ C

## Quantification of XRD Analysis:

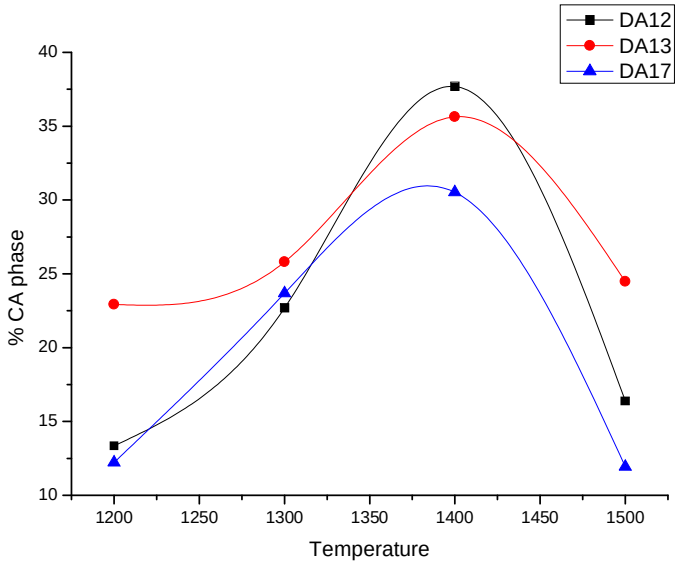


*Fig10. Figure showing the variation of CA phase with temperature for all compositions*

The above figure shows the variation of Calcium monoaluminate phase with temperature.As it can be clearly seen, the percentage of this phase increases till $1400^0$ C and then beyond this there was decrease.And at $1400^0$C,the amount of Calcium monoaluminate phase was maximum for dolomite:alumina sample in 1:2 ratio.

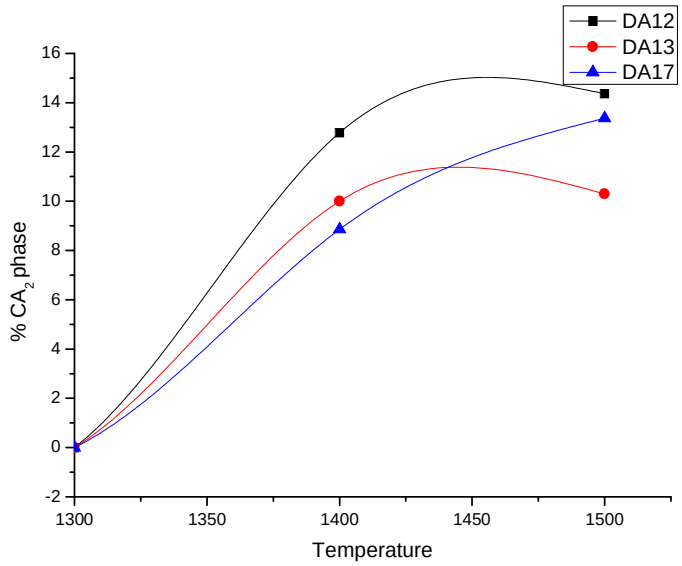


*Fig11. Figure showing the variation of $CA_2$ phase with temperature for all compositions*

The above figure shows the variation of calcium dialuminate phase with temperature.The $CA_2$ phase was found to appear at temperatures above $1300^0$C and increased with increase in temperature till above $1400^0$C but was found to decrease at $1500^0$C.

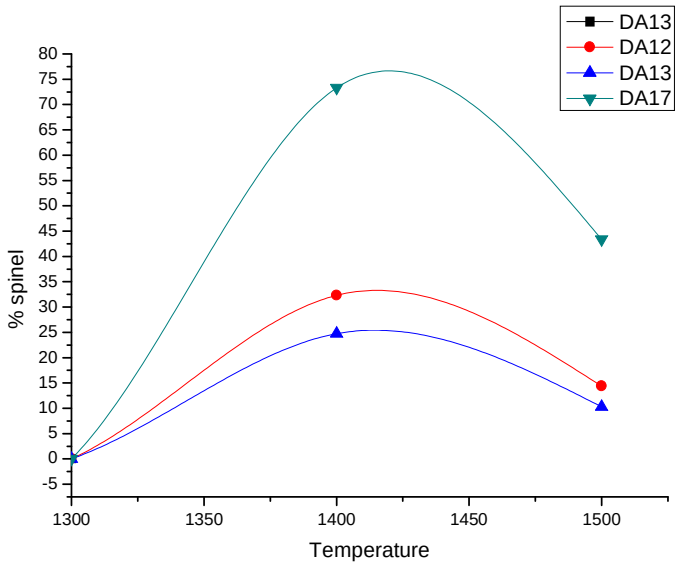


*Fig 12. Figure showing the variation of spinel phase with temperature for all compositions*

The above figure shows the variation of spinel phase with temperature. The spinel phase appeared at temperatures above $1300^0$C but beyond $1400^0$C,its percentage was found to decrease.

## Comparative Graph of CCS and DTS

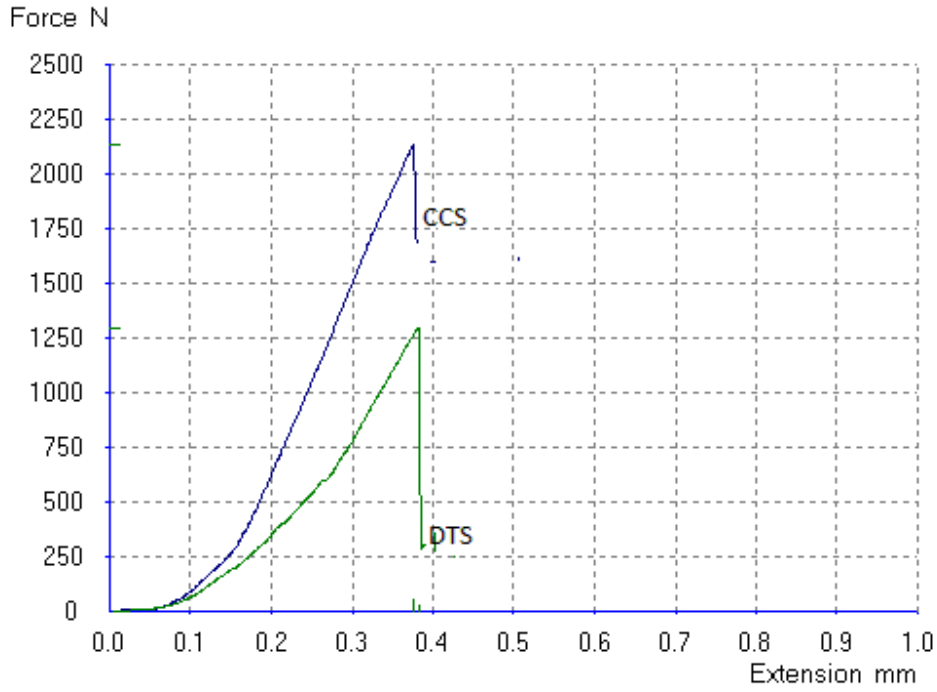


*Fig13. Fig showing the comparision of CCS and DTS value of dolomite alumina pellets*

## APPARENT POROSITY, BULK DENSITY

Typical value of bulk density for dolomite alumina aggregates is around 2.07 g/cm$^3$

- Dry weight(D)= 0.928g
- Soaked weight(w)=1.0496g
- Suspended weight(S)=0.7001g
- Apparent Porosity(AP)= 34.79%
- Bulk Density(BD)=2.071g/cm$^3$

## CONCLUSION

The amount of Calcium mono-aluminate(CA) increases with increasing temperature till $1400^0$C and beyond that the amount of CA phase decreases due to its conversion to Calcium di-aluminate($CA_2$) by reaction with free alumina.Other phases like CA6,C12A7 were formed at temperatures 1400C or higher.

As the reaction sintering process progressed, alumina reacted with dolomite, so the amount of free alumina, calcia and magnesia decreased with increase in temperature and above $1400^0$C, they were no more found.

On increasing Alumina content, CA formed was found to decrease while there was a decrease in $CA_2$ content.

Maximum percentage of calcium mono aluminate phase and spinel phase was found at $1400^0$C and hence better properties can be obtained by synthesizing dolomite alumina aggregates sintered at $1400^0$C.

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