PREPARATION OF CALCIUM ALUMINATE-SPINEL SYNTHETIC AGGREGATES USING ELECTROSTATIC PRECIPITATED DOLOMITE DUST AND CALCINED ALUMINA

A Thesis Submitted

In Partial Fulfilment of the Requirement for the Degree of

BACHELOR OF TECHNOLOGY

BY

SANJEEV KICHE RAI

Roll No-108CR027

DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTION OF TECHNOLOGY
ROURKELA

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Under The Guidance Of

Prof. Swadesh Kumar Pratihar

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CERTIFICATE

This is to certified that the work contained in the project entitled "***Preparation Of Calcium Aluminate-Spinel Synthetic Aggregates Using Electrostatic Precipitated Dolomite DustAnd Calcined Alumina.***" submitted by ***Mr. Sanjeev Kiche Rai*** (*108CR027)* is an authentic work carried out by him under my supervision and guidance for the partial fulfilment of the requirements for the award of ***Bachelor of Technology Degree*** **in** ***Ceramic Engineering*** at ***National Institute of Technology, Rourkela.***

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.

Date-

Prof. Swadesh Kumar Pratihar
Dept. of Ceramic Engineering
NIT Rourkela

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SANJEEV KICHE RAI

108CR027

ABSTRACT

Calcium alumniate-spinel phases have been developed for synthetic aggregate from ESP dolomite dust and calcined alumina. A huge amount of dolomite dust is collected at electrostatic precipitator (ESP) during dead burning of raw dolomite in Rotary Kiln. This dust is waste material and does not have any practical use in refractory plants. The Present thesis focuses the utilization of these waste dolomite dust for the development of value added calcium aluminate spinel aggregates. Dolomite is a double carbonate of calcium and magnesium. An attempt has been made to different calcium aluminates and spinel aggregates by solid state reaction between the ESP precipitated dolomite dust and calcined alumina. The phase formation behaviour has been reported from the study of the XRD diffraction pattern as function of calcination temperature. The different physical properties of the aggregated have also been reported.

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CHAPTER-1

INTRODUCTION:

1. DOLOMITE

Dolomite is a sedimentary carbonate rock containing calcium carbonate and magnesium carbonate $CaMg(CO_3)_2$ found in crystals nature. The calcium carbonate content is ~54.35% and magnesium carbonate is about 45.65%. It is also associated with minor impurities like silica, alumina, iron oxide etc. The mineral dolomites crystallized in the trigonal-rhombohedral systems. Dolomites deposits have wide colour ranges from white, gray to pink. Generally dolomite has physical properties similar to those of the calcite mineral, however, it does not quickly dissolve in dilute hydrochloric acid unless it is scratched or in powdered form. The Mohs hardness of dolomite is in the range 3.5 to 4 with the specific gravity is 2.85. Crystal twinning is common in dolomite. A solid solution series exists between dolomite and iron rich ankerite. Less amounts of iron in the structure give the yellow to brown tint. Manganese contained in the structure also up to about three percent MnO. The high manganese content gives the crystals a rosy pink colour. A series with the manganese rich kutnohorite may also exist. Zinc and lead also substitutes in the structure for magnesium. The different physical properties of dolomite are provided in Table I.

colour	White, gray to pink
Specific gravity	2.84 to 2.86
fracture	conchoidal
Crystal system	trigonal
cleavage	Perfect, rhombohedral

Table1.1 Physical Properties of dolomite

1.1 Formation of dolomite

Although huge dolomite deposits can be found in the geological record till in reality the refractory grade dolomite deposit is very rare in India. Preparation of synthetic dolomite in laboratory is difficult at room temperature however, it form at temperature of greater than 100°C but dolomite found in the rock record appears to form under low-temperature

conditions. The high temperature is required for the formation of magnesium and calcium carbonates. The less formation of dolomite today is due to some lack of temperature and kinetic energy. In the 1950s, dolomites were found to be form in highly saline lakes in the Coorong region of South Australia. Crystal dolomite occurs in deep-sea sediments where organic matter content is very high. This dolomite is termed "organogenic" dolomite.

Most dolomites appear to formed different types of environment and having with structural and chemical characteristics. Some researchers have proved that the dolomites formation is not governed by a single mechanism. Most modern dolomites are quite different from the dolomite found in the rocks, researchers have proved that the dolomite formed in the past are quite different from dolomite formed today.

1.2 Uses of dolomite

Dolomite is sometimes used as an ornamental stone and dolomite is a source of magnesium oxide, in the Pidgeon process for the production of magnesium and source of calcium oxide using concrete aggregate. Dolomite is an important petroleum reservoir rock and serves as the host rock for strata bound. Calcite limestone is uncommon and too costly. Dolomite is sometimes used in place as a flux for the smelting of steel and iron. Large amount of processed dolomite are used in the float glass production.

In horticulture dolomite is added to soils and soilless potting mixed to lower their acidity and magnesium source. Dolomite is also used as the substrate in marine aquariums to help in pH of the water buffer changes.

1.3 ELECTROSTATIC PRECIPITATED DUST (DOLOMITE DUST)

ESP dolomite dust collected from the dolomites dead burning plants are used as a raw material for the preparation of the synthetic aggregates. These materials are collected from the dolomite dead burning plant, where it is the waste generated from the Electrostatic Precipitator. Hence, it is sometimes known as the ESP dust, actually that is dolomite dust.

1.4 CHEMICAL COMPOSITIONS AND REACTIONS OF DOLOMITE DUST:

Dolomite dust contained Lime ($CaCO_3$), Magnesia ($MgCO_3$), Silica (SiO_2) and Alumina (Al_2O_3). $CaCO_3$ reacts with alumina to form several Calcium Aluminate phases and $MgCO_3$ reacts with Al_2O_3 to form Spinel phases. Sometimes SiO_2 present in the dolomite dust also forms a phase called Gehelenite chemically ($2CaO.Al_2O_3.SiO_2$). This reaction was reported to

occur in the temperature range 1350^{o}C to 1450^{0}C. Generally calcined dolomite is hygroscopic in nature, it reacts with moistures present in the atmosphere to form Calcium hydroxide ($Ca(OH)_2$) and Magnesium Hydroxide ($Mg(OH)_2$), this might be undesirably part of the dolomite.

1.5 CALCINED ALUMINA

Calcined alumina is aluminium oxide formed by calcinations of aluminium hydroxide at a temperature above 1050°C to remove nearly all chemically combined water. In generally this form of alumina has extreme hardness, chemical purity, high density and a high melting point (2,050°C)

Aluminium oxide is amphoteric in nature with the chemically formula of Al_2O_3, it is commonly known as corundum in its crystalline form. Also it has many other names, reflecting its widespread occurrence in nature and industry. Aluminium oxide is mostly used in the production of aluminium metals, although it is also used as an abrasive due to its high hardness and used in refractory material due to its high melting point.

Aluminium oxide is generally an electrical insulator but it has relatively high thermal conductivity. The most commonly occurring crystalline form of aluminium oxide is called corundum or α-aluminium oxide, its high hardness makes it suitable for use as an abrasive and as components of cutting tools. Aluminium oxide is responsible for resistance of metallic aluminium to weathering. An aluminium metallic is very reactive with atmospheric oxygen, and a thin passivation layer of alumina (4 nm thickness) in about 100 picoseconds on any exposed aluminium surface. This layer protects the metal from further oxidation. The thickness and properties of this oxide layer can be enhanced using a process called anodizing. A number of alloys, such as aluminium bronzes, exploit this property by including a proportion of aluminium in the alloy to enhance corrosion resistance. The alumina generated by anodising is typically amorphous, but discharge assisted oxidation processes such as plasma electrolytic oxidation result in a significant proportion of crystalline alumina in the coating, enhancing its hardness.

1.6 THE CALCIUM ALUMINATE PHASES: CaO of dolomite dust reacts with alumina to form various calcium aluminate phases. The $CaO\text{-}Al_2O_3$ system is involved in practical applications in the cement and concrete industry, in steel-making and refining of steel, in abrasive and refractory productions. These phases are popularly known as Calcium Aluminate phases. The most prominent Calcium Aluminate phases are CA, CA_2, CA_6, C_3A,

C_6A and $C_{12}A_7$. But this project only CA, CA_2 and CA_6 phase are separately studies which is contained with spinel phase. The prominence and occurrence of these phases is dependent on temperature and percentage composition of the solids.

1.7 COMPOSITIONS

The mineral as normally encountered is a solid solution series with end-members $Ca_{12}Al_{14}O_{33}$ and $Ca_6Al_7O_{16}$ (OH). The latter composition loses water only at high temperature, and has lost most of it by the melting point (around 1400°C). If material heated to this temperature is rapidly cooled to room temperature, the anhydrous composition is obtained. The rate of re-absorption of water to form the hydrous composition is negligible below 930°C. The mineral is cubic. The crystal of $Ca_{12}Al_{14}O_{33}$ has cell dimension 1.1983 nm and density 2680 $kg.m^{-3}$ while that of $Ca_6Al_7O_{16}$(OH) has 1.1976 nm and 2716 $kg.m^{-3}$.The confusion regarding composition contributed to the mistaken assignment of the composition $Ca_5Al_3O_{33}$, studies of the system have shown that the solid solution series extends also to the accommodation of other species in place of the hydroxyl group, including halides, sulphide and oxide ions.

1.8 PROPERTIES

The mineral reacts rapidly with water with considerable heat evolution to form $3CaO.Al_2O_3.6H_2O$ and $Al(OH)_3$ gel. The formation of the hydrate from this mineral and from monocalcium aluminate represents the first stage of strength development in aluminous cements. Because of its higher reactivity leading to excessively rapid hydration, aluminous cements contain relatively low amounts of dodecacalcium hepta-aluminate($12CaO.7Al_2O_3$), or none at all. In Portland cement kilns, it is an early reaction product of aluminium and calcium oxides in the temperature range 900-1200°C. With the onset of melt-phases at higher temperatures, it reacts with further calcium oxide to form tricalcium aluminates. It thus can appear in under-burned kiln products. It also occurs in some Natural cement.

1.9 SPINEL: Spinel is chemically magnesium aluminate ($MgAl_2O_4$). In reality it is a member of a larger spinel group of minerals. The general formula is AB_2O_4, where A and B are cations in the in the +2 and +3 state. The oxygen ions are in the FCC staking, the cations, on the other hand, occupy one-half of the octahedral voids and one-eighth of the tetrahedral voids.

CHAPTER-2

LITERATURE REVIEW

L.A. Diaz et al. [1] performed a comparative study on the microstructural evolution of alumina rich refractory concretes containing spinel, periclase and dolomite as function of temperature. Three refractory Castables compositions within the alumina rich zone of the Al_2O_3-MgO-CaO ternary phase equilibrium diagram have been studied. The starting ingredients were mixtures of (a) Calcined alumina, synthetic spinel and calcium aluminate cements, (b) Calcined alumina, calcium aluminate cements and magnesia, (c) Calcined alumina, calcium aluminate cements and dolomite. It has been reported that the $C_{12}A_7$ phase formed at 600^0C onwards moreover, highest degree of crystallisation of $C_{12}A_7$ phase was observed at a low temperature in the case of magnesia and dolomite formulations rather than that in synthetic spinel formulation. The CA phase has been reported to be formed 800^0C, although the highest degree of crystallisation has been sensed at 1000^0C. It has also been reported that above 1000^oC, CA reacts with the alumina and initiates the formation of the CA_2 phase.

Nagy M. A. Khalil et al. [2] prepared aluminous cements containing spinel-magnesium phase using Egyptian dolomite. Calcium aluminate cements has been made with the approximately mixtures of Egyptian dolomite of MgO~20.16% and CaO~31.32% and with active alumina~99.50%. The mixture cement has been fired at the temperature of 1600^OC. The properties of mixture cement had been studied with the help of appropriate techniques. The mixtures were finely grounded to homogenize the powder and to check the properties of the compositions. Physical and thermo-mechanical properties of the refractory also had been tested. The existence of CA and CA_2 phases depends on the compositions. When certain amount of cement has been added to refractory magnesia, the properties of the refractory improved with the presence of strength modifier like Li_2CO_3.

Excellent quality castable compositions had been synthesis from the mixture of magnesia and aluminous cement with the presence of strength modifier such as Li_2CO_3. These types of castable compositions are easily cast into desired shapes without pre-firing. Good strength with low shrinkage in the dried and fired conditions. These are having good thermal shock resistance and high strength value.

M Gobbels et al. [3] studied the Al-rich part of the system CaO-Al_2O_3-MgO. Electron probe microanalysis was used to study the sample. Hibonite ($CaAl_{12}O_{19}$), with magnetoplumbite structure, and two magnesium bearing phases, CAM-1 ($Ca_2Mg_2Al_{28}O_{46}$), and CAM-11, ($CaMg_2Al_{16}O_{27}$) were reported to form at temperatures above 1600^0C. XRD patterns of the CAM-1 and CAM-11 were related with corresponding to magnetoplumbite phases X and W in the BaO-Fe_2O_3-ZnO system. Due to this reasons close structural relationship between the hibonite and spinel structures mixed layer model based on an intercalation of hibonite layers and spinel layers are proposed for the ideal structures of the ternary phases. The investigations on the Al-rich part of the system CaO-Al_2O_3 suggests that hibonite has a rather wide solid solution range due to planar structural defects.

Objective:

The synthesis of different calcium aluminate namely CA, CA_2, CA_6 and spinel ($MgAl_2O_4$) composite using waste ESP dolomite dust and calcined alumina following solid state rule. The different reactions are follows:-

1. $CaCO_3MgCO_3 + 2Al_2O_3 = CaO.Al_2O_3+MgOAl_2O_3+ 2CO_2$

2. $CaCO_3MgCO_3 + 3Al_2O_3 = CaO.Al_4O_7+MgOAl_2O_3+ 2CO_2$

3. $CaCO_3MgCO_3 + 7Al_2O_3 = CaO.Al_{12}O_{19}+MgOAl_2O_3+ 2CO_2$

CHAPTER-3

Experimental

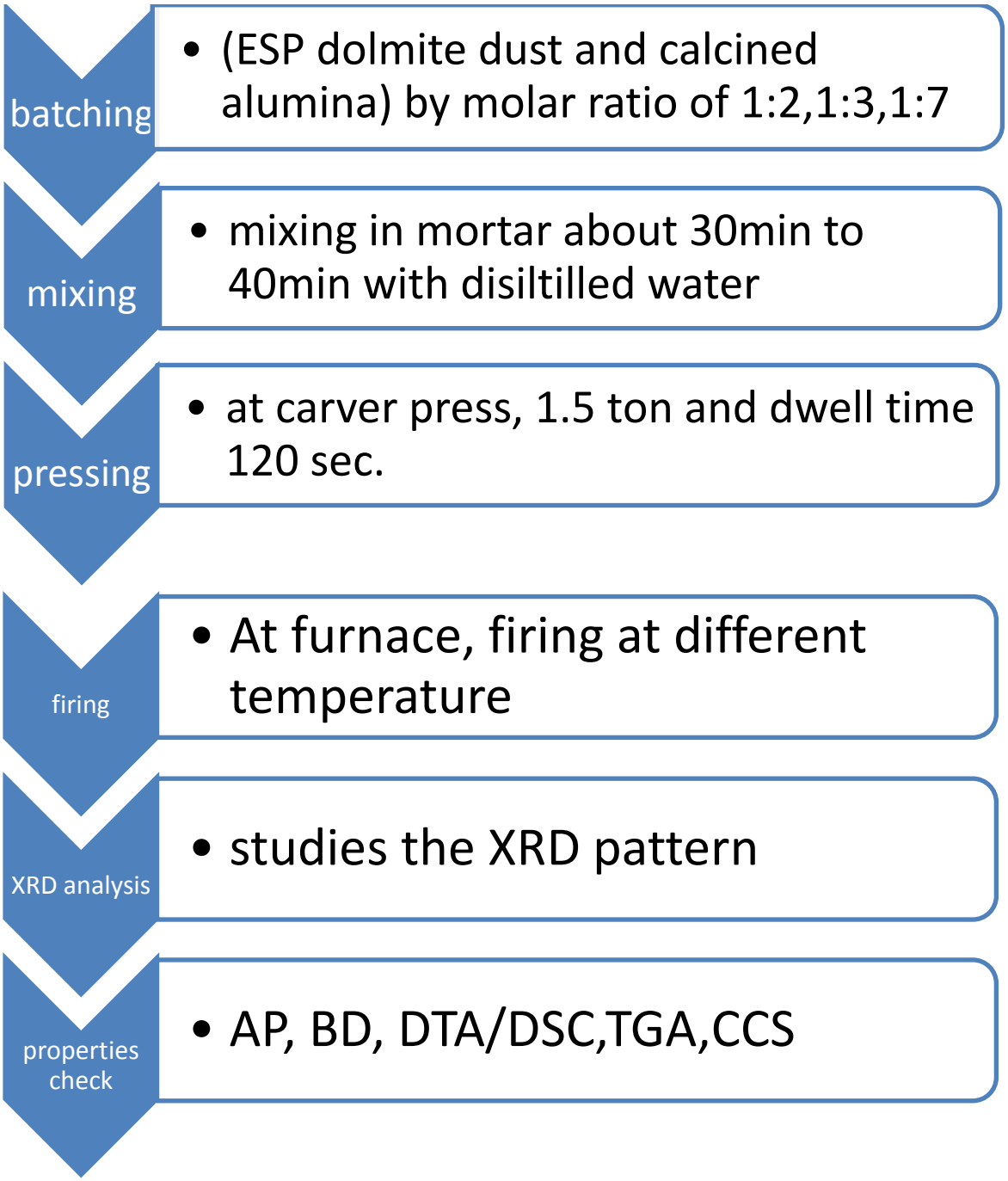

Fig.3.1 Flow chart for calcium aluminate spinel synthesis

Synthetic aggregate was prepared by the calcining Electrostatic Precipitated (ESP) dolomite dust and Calcined alumina. Both the raw materials were mixed in mortar to a homogeneous powder. The raw materials were mixed with water to achieve the desired homogeneity. The

entire mixed were pressed in at carver press to make a pellets maintaining one gram for each pellet in a circular die. The pellets were fired in chamber hearth furnace at different temperatures, 1350^{o}C, 1400^{o}C, 1450^{o}C, 1500^{o}C, 1550^{o}C, 1600^{o}C and 1650^{o}C for 4 hours soaking time and heating rate of 2^{o}C/min and at 850^{o}C 2 hours soaking time were given so that dolomite decomposed to CaO and MgO to react with alumina to form CA phases and spinel phase. The phase analysis, physical properties, some mechanical properties of the samples was also studied. Phase analysis of sample was carried out using X-ray powder diffractometer, diffract angle between 20^{o}-80^{o} for 40min. different phases were identified using X-pert high score software.

3.1 DSC/DTA and TGA:

The thermal decomposition behaviour of ESP dolomite dust and calcined alumina mixture has been studied using DSC/DTA and TGA. The heating rate was 10^{o}C/min.

3.2 X-RAY DIFFRACTION (X-RD)

The different phases present in the sample has been analysis using the XRD powder techniques. The sample has been scan at a rate of 2^{o}C/min. In the angle of 2theta(degree) in the range of 25^{o}C to 75^{o}C. The current in the voltage were at 34mA and 40kV.The phase in the sample has been analysis using from the XRD pattern using X-pert high score software.

3.3 DETERMINATION OF APPARENT POROSITY AND BULK DENSITY

Water boiling method is used to measure AP and BD. First of all, dry specimen is weighed and noted down. The dry specimen is placed in beaker then filled water and boiled it 30min to 35min. On weighing that wet sample, we get its suspended weight. Then tested sample is dried using blotting paper. After which soaked weight is calculated. Then using the formulae of apparent porosity and bulk density is given below.

$$BULK\ DENSITY = \frac{Dry\ Weight}{Soaked\ Weight - Suspended\ Weight} \times density\ of\ liquid$$

$$\text{APPARENT POROSITY} = \frac{Soaked\ Weight - Dry\ weight}{SOaked\ weight - Suspended\ weight} \times 100$$

3.4 Cold Crushing Strength

The ESP dolomite dust and calcined alumina mixture sample has been measure in the HORNSFILED UTM machine the maximum crushing load has been noted down. Cold crushing strength (CCS) of samples signify that its strength. Cold crushing strength is calculated by dividing the maximum load by the cross-sectional area of a specimen in a compression test. Using the formula

$$\text{CCS} = \frac{Total\ load}{Total\ Area} \quad ,\text{CCS} = \frac{2F}{\pi DT}$$

CHAPTER-4

RESULTS AND DISCUSSION

4.1 DTA/DSC and TGA

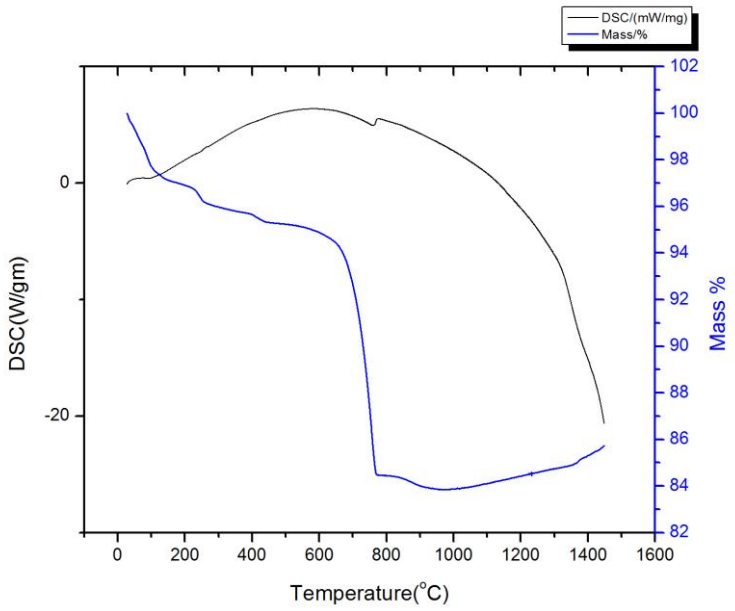

Fig.4.1 DSC/TGA plot of molar ratio dolomite alumina1:3 mixture

The typical thermal decomposition behaviour of the sample prepared with ESP dolomite dust and calcined alumina raw molar ratio 1:3 is shown in the Fig.4.1. The DSC plot has been characterized by two endothermic peaks. The small endothermic peaks 110^{o}C is attributed to the removal of physically adsorb water from the sample mixture. This could be supported from the small weight loss observed in the temperature of 200^{o}C. The second endothermic peak is at 800^{o}C and is the decomposition of dolomite which is associated with the substantial weight loss observed in the TG Curve. Although dolomite undergoes a double decomposition, in the present case the same behaviour could not be observed in DSC curve. The amount of dolomite was small in the sample which resulted single stage decomposition in the sample. The entire sample studied in the present study showed the similar behaviour. The different reaction between $CaO\text{-}Al_2O_3$ and $MgO\text{-}Al_2O_3$ could not be detected in the DSC pattern.

4.2Phase Analysis

(a) CA-SPINEL (CaAl2O4-MgAl2O4)

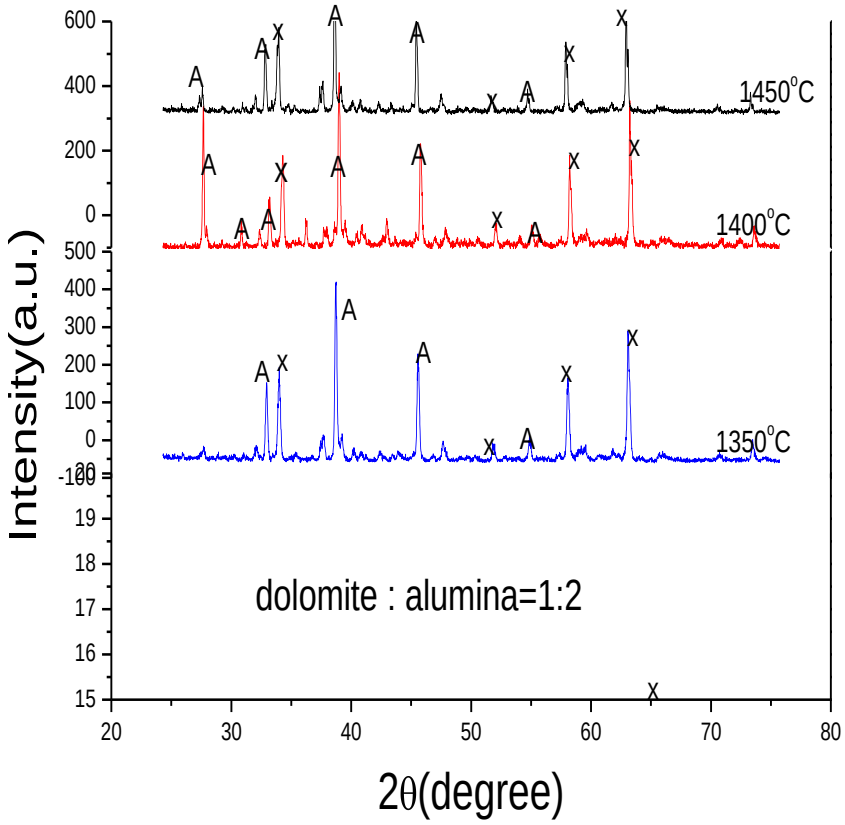

Fig.4.2 XRD Patterns of calcium aluminate spinel aggregate prepared with molar ratio of dolomite to alumina 1:2

The XRD pattern of the powder containing ESP dolomite dust and calcined alumina 1:2 has been shown in the Fig.4.2. as the function of calcination temperature. It could be seen from the pattern that the sample calcined at 1350^{o}C contains all the CA and spinel phase. It indicates the reaction between dolomite dust and calcined alumina took place below 1350^{o}C resulted in the formation of calcium aluminate and spinel in the sample. The increase in calcination temperature causes stabilization of the phase. The entire sample calcined in the studied temperature range shows the presence of spinel and CA phases.

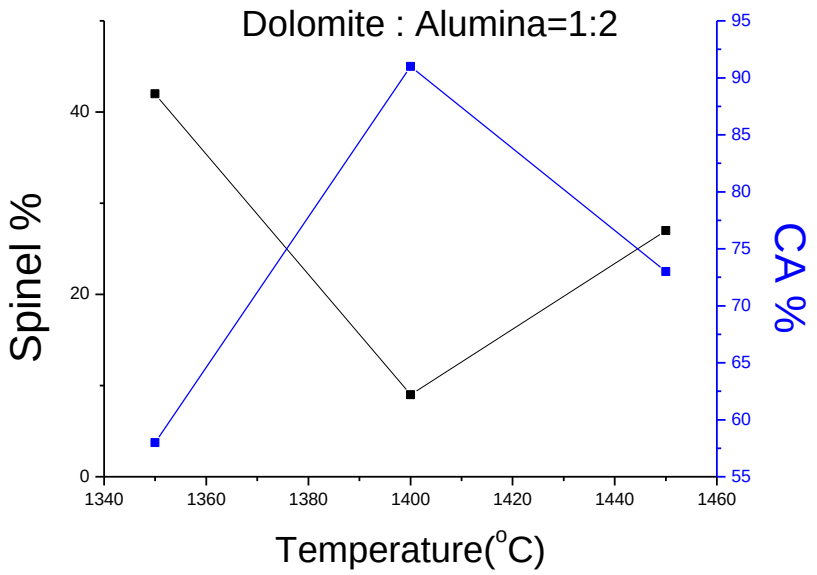

Fig.4.3 Phase analysis of calcium aluminate spinel synthetic aggregate prepared with molar ratio of dolomite to alumina 1:2 as a function of temperature.

The amount of different phase present in the sample has also been calculated from the XRD patterns using intensity ratio of the phases present as a function of firing temperature. The results have been presented in Fig. 4.3. At the temperature of 1350^{o}C very less amount of spinel was found this may be related to the slow reaction of MgO with alumina due to this less amount of spinel phase found and CA phase was more because of CaO reacted quickly with the alumina so more amount of CA phase was found. At temperature of 1400^{0}C, 9 percent of spinel ($MgAl_2O_4$), about 90 percent of CA ($CaAl_2O_4$) phases were found and little unknown peak was also found at the position of diffraction angle of 28^{o}. This unknown peak may be due to the presence of impurities like silica, iron present in the dolomite dust. Sample was fired at 1450^{0}C, spinel (MgAl2O4) percentage was more increase than that of lower temperature and CA ($CaAl_2O_4$) percent also increase as compared to that of 1450^{o}C fired samples and little unknown impure peak was also found at diffraction angle of 61^{o}. At 1500^{0}C, dolomite alumina ratio 1:2 sample was melted due to liquid phase formation. At lower temperature spinel percent is less as compare to higher temperature due to slow reaction of MgO and Al_2O_3.The different phases observed as a function of firing temperature is also presented in Table 4.1

File name	Temperature (^{0}C)	Time (hour)	Dolomite (mol%)	Alumina (mol%)	Spinel (percent)	CA Phase (percent)	Other phases
140CA12	1400	4	1	2	9	91	<1
145CA12	1450	4	1	2	27	73	<1
CA12	1350	4	1	2	42	58	<1

Table 4.1Phase analysis of calcium aluminate aggregate prepared with ESP dolomite dust to calcined alumina ratio 1:2

(b) CA_2-Spinel ($CaAl_4O_7$-$MgAl_2O_4$)

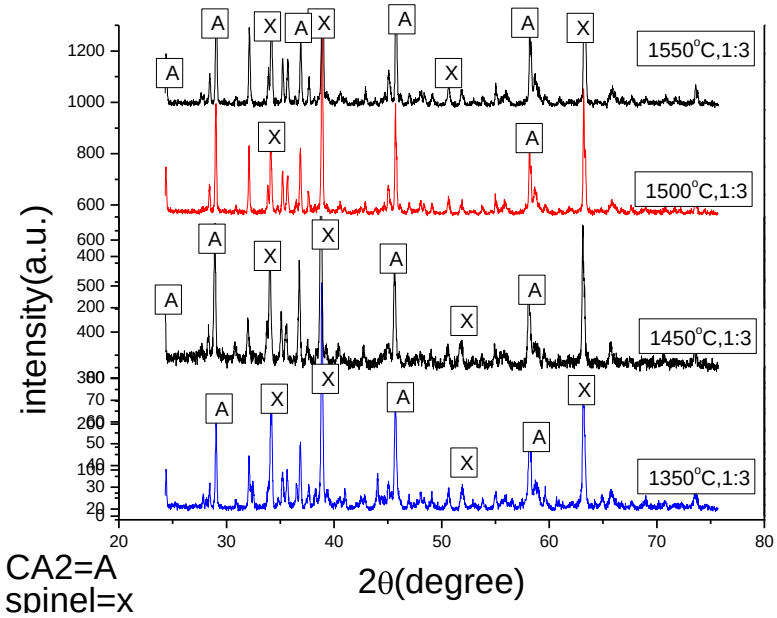

Fig.4.4 XRD Patterns of calcium aluminate spinel aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:3

The XRD patterns of the samples prepared with ESP dolomite dust and calcined alumina mixture ratio 1:3 as a function of calcination temperature has been presented in Fig.4.4. It could be seen that samples fired at 1350^{o}C contains spinel ($MgAl_2O_4$) and CA_2 ($CaAl_4O_7$) phases. When sample has been fired above 1450^{o}C, the sample showed only the presence of spinel and CA_2 phase. In the case 1:3 ratio of ESP dolomite dust and calcined alumina, CA_2($CaAl_4O_7$) phase and spinel phases are pure and almost tally with the theoretical predictions. No other impure phase could be detected in the XRD patterns of the sample.

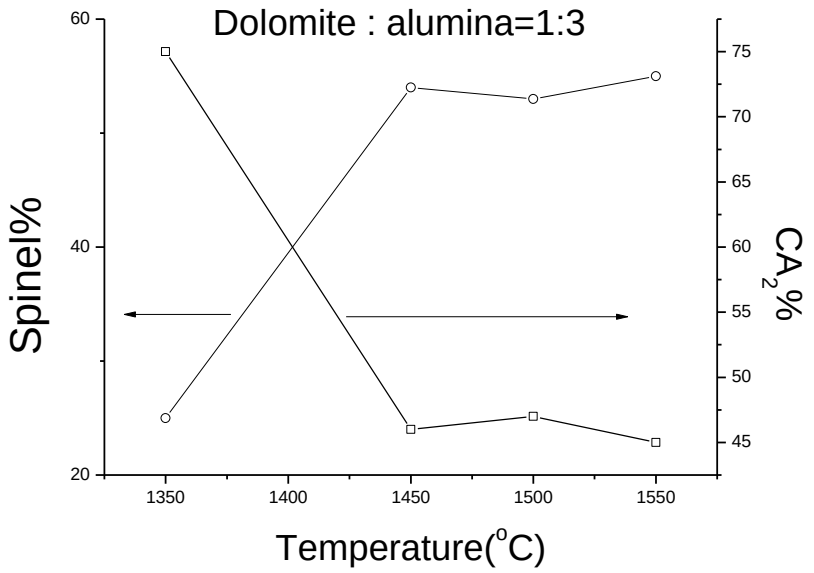

Fig.4.5 Phase analysis of calcium aluminate spinel synthetic aggregate prepared with molar ratio of dolomite to alumina 1:3cas a function of temperature

The amount of different phase present in the sample has also been calculated from the XRD patterns using intensity ratio of the phases present as a function of firing temperature. The results have been presented in Fig. 4.5. At low temperature of 1350^0C, spinel ($MgAl_2O_4$) amount is less as compared to CA_2 ($CaAl_4O_7$) this is due to slow rate of spinalization reaction i.e., MgO reaction with alumina is very slow and CA_2 phase is more because of CA_2 phase form easily i.e., CaO reacts easily with the alumina but there is no impure phase was found at 1350^oC. Same aggregate sample was fired at the temperature of 1450^oC spinel phase is rapidly increase due to MgO react with alumina. Again mixed Sample was fired at 1500^0C showed spinel ($MgAl_2O_4$) and CA_2 ($CaAl_4O_7$) phases and no other impurity phases was found. Sample fired at 1550^0C also showed spinel ($MgAl_2O_4$) and CA_2 ($CaAl_4O_7$) phase coexists together and no other impurity phases was observed. Sample fired at 1600^0C was melted to liquid. In the case of 1:3 ratio, pure spinel and CA_2 phases were found upto1550^0C. The different phases present as a function of firing temperature in the sample has been shown in Table 4.2.

File name	Temperature (^{0}C)	Time (hour)	Dolomite (mol%)	Alumina (mol%)	Spinel (percent)	CA2 (percent)	Other phases
145CA13	1450	4	1	3	54	46	nil
150CA13	1500	4	1	3	53	47	nil
CA1013	1550	4	1	3	55	45	nil
CA13	1350	4	1	3	25	75	nil

Table.4.2 Phase analysis of calcium aluminate aggregate prepared with ESP dolomite dust to calcined alumina ratio 1:3

(c) HIBONITE-SPINEL PHASE (CA_6-SPINEL)

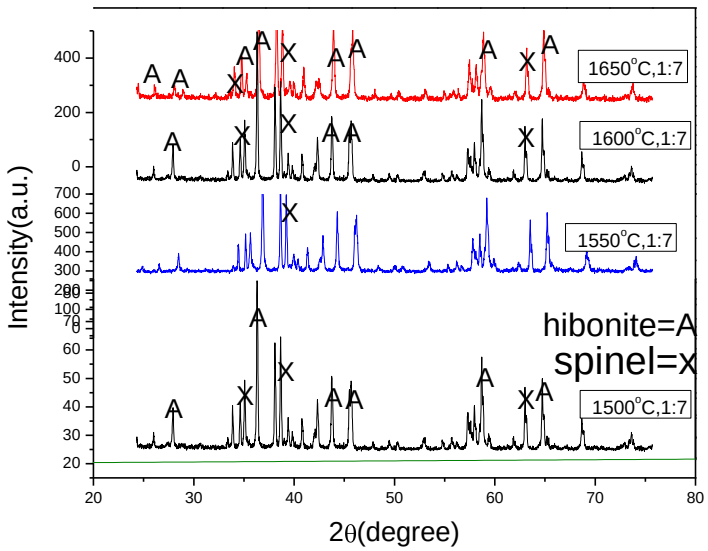

Fig.4.6 XRD Patterns of calcium aluminate spinel aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:7

The XRD patterns of samples prepared with ESP dolomite dust to calcined alumina molar ratio 1:7 as a function of firing temperature has been presented in Fig.4.3 It could be seen that samples calcined at 1500^{o}C contains spinel ($MgAl_2O_4$), hibonite ($CaAl_{12}O_{19}$) and CA_2 ($CaAl_4O_7$) phases. The sample fired at 1550^{o}C, showed the presence of hibonite phase, spinel phase and some CA_2 phases. Sample fired at 1600^{o}C and 1650^{o}C, showed only spinel ($MgAl_2O_4$) and hibonite ($CaAl_{12}O_{19}$) phases and no CA_2 ($CaAl_4O_7$) phase could be detected in the X-ray diffractogram. In the case 1:7 ratio of ESP dolomite dust and calcined alumina samples CA_2 ($CaAl_4O_7$) phase is impurity and spinel and hibonite phases are stoichiometric ones. The study showed that at low temperatures upto 1550^{o}C, CA_2 ($CaAl_4O_7$) impurities

phase present. At higher temperature no impurity phases like CA_2 ($CaAl_4O_7$) could be detected.

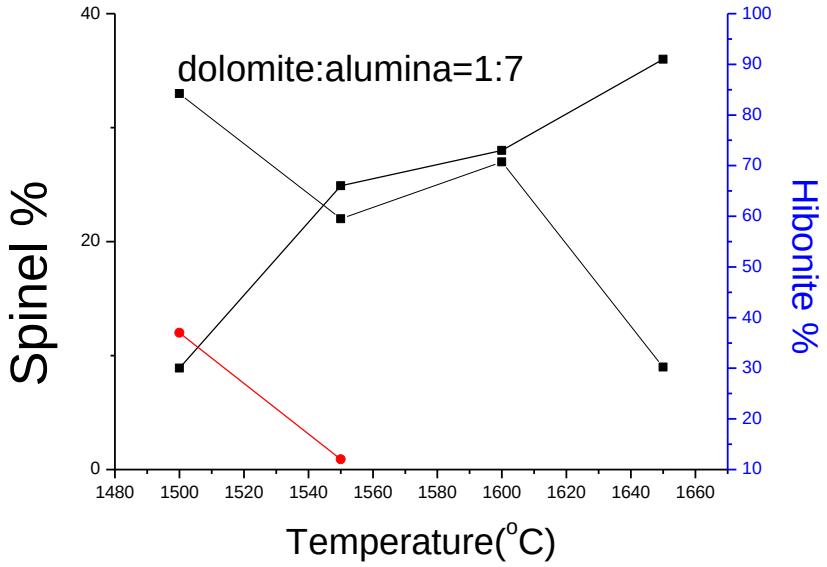

Fig.4.7 Phase analysis of calcium aluminate spinel synthetic aggregate prepared with molar ratio of dolomite to alumina 1:7 as a function of temperature.

The amount of different phase present in the sample has also been calculated from the XRD patterns using intensity ratio of the phases present as a function of firing temperature. The results have been presented in Fig. 4.7. The sample fired at low temperature contains spinel, CA_6 and CA_2 phases. The amount of spinel phase gradually decreases with increase in firing temperature, whereas the CA_6 phases gradually increases. The impurity intermediate CA_2 phase dissociated at temperature on an above 1600°C. Thus the study suggests that the formation of CA_6 phase in this system involves formation and subsequent dissolution of intermediate phases like CA_2. The amount of different phases calculated from the XRD patterns has been tabulated in Table 4.3

File name	Temperature (^{0}C)	Time (hour)	Dolomite (mol %)	Alumina (mol %)	Spinel (percent)	Hibonite (percent)	Other phases
150CA17	1500	4	1	7	33	30	37(CA2)
CA1017	1550	4	1	7	22	66	12(CA2)
1600CA17	1600	4	1	7	27	73	nil
1650CA17	1650	4	1	7	9	91	nil

Table.4.3 1Phase analysis of calcium aluminate aggregate prepared with ESP dolomite dust to calcined alumina ratio 1:7

4.3 PHYSICAL PROPERTY

(a)Apparent porosity and bulk density:

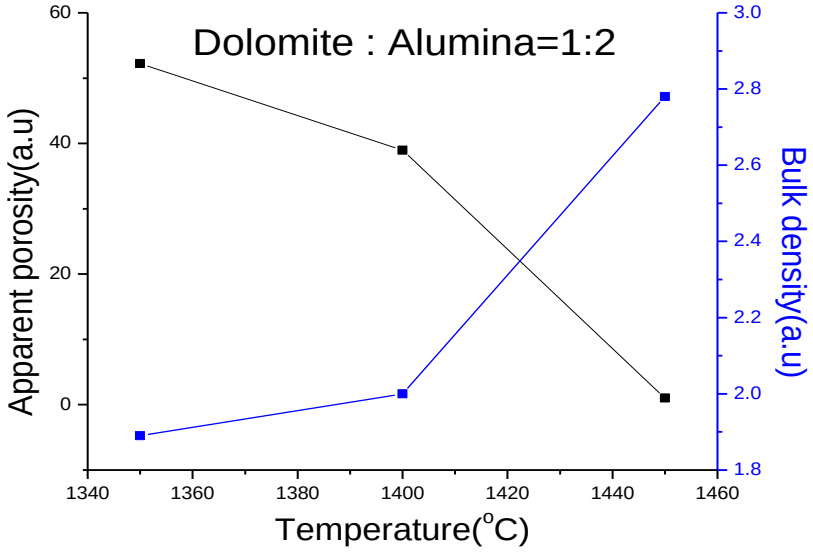

Fig.4.8 Apparent porosity and bulk density of calcium aluminate spinel synthetic aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:2 as a function of temperature.

The bulk density and apparent porosity of the sample prepared with ESP dolomite dust and calcined alumina ratio1:2 have been shown in the Fig.4.8. It could be seen from the Figure 4.8 that the bulk density of the sample is increase with increase in temperature due to the increase density of the sample. The apparent porosity has a function of temperature shows reverse trend which is quite obvious. The BD and AP data for the sample has a function of temperature has been provided in Fig.4.8

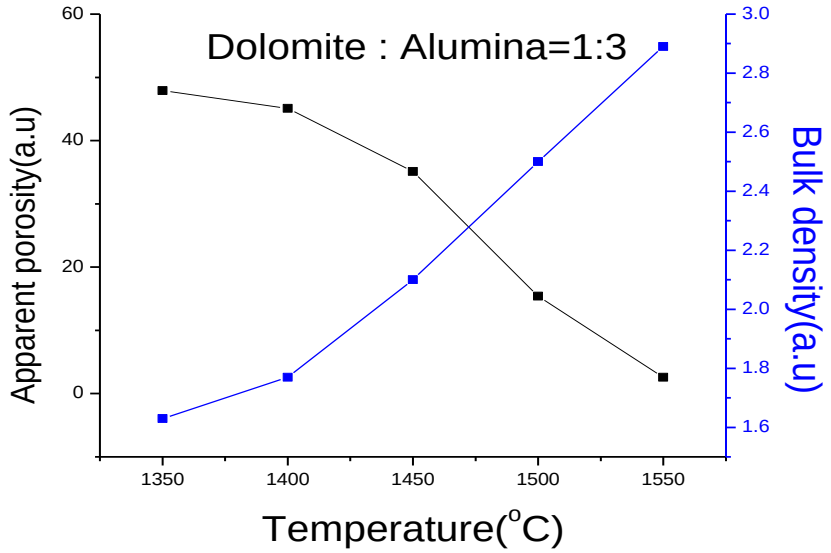

Fig.4.9 Apparent porosity and bulk density of calcium aluminate spinel synthetic aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:3 as a function of temperature.

Apparent porosity and bulk density:

Dolomite-Alumina ratio 1:3

Apparent porosity of the aggregate sample prepared with ESP dolomite dust to calcined alumina molar ratio 1:3 fired in the temperatures range 1350^{o} - 1550^{o}C has been shown in Fig. 4.9. It could be seen from Fig.4.9 that sample fired at 1350^{o}C showed high porosity around 47%. However the porosity decreases with increase in firing temperature. Samples fired at 1550^{o}C showed porosity less than 2%.

Bulk density of the aggregate materials is also varies with the temperature. At the lower temperature bulk density was very low around 1.6 gm/cc and as the firing temperature increases the bulk density increase sharply. It could be seen from the Fig.4.9 that the bulk density is very low at low temperature. At 1350^{o}C fired samples the bulk density is very less as compare to that fired at 1550^{o}C. This is due to the enhanced densification of the samples with increase in firing temperature.

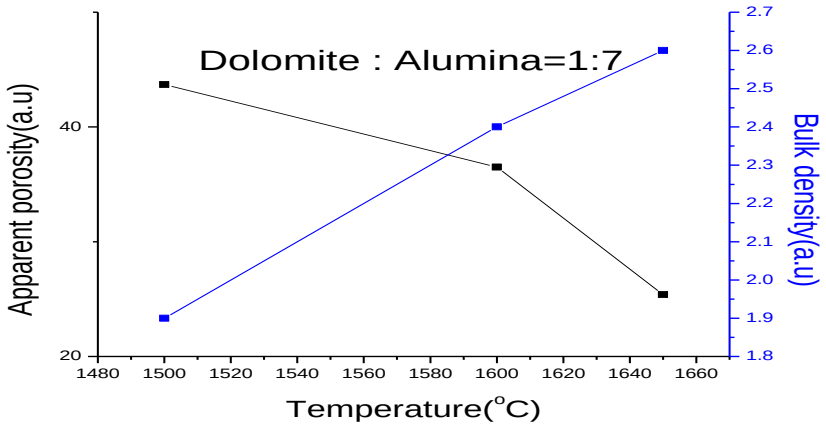

Fig.4.10 Apparent porosity and bulk density of calcium aluminate spinel synthetic aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:7 as a function of temperature.

Apparent porosity and bulk density of dolomite alumina ratio 1:7

Apparent porosity and bulk density of the samples prepared with ESP dolomite and alumina molar ratio1:7 has been shown in Fig. 4.10 as a function of firing temperature. With increase in temperature bulk density is increase but apparent porosity showed a reversed trend. At the lower temperature porosity is very high and bulk density is very low, which could be explained in the same line as discussed in the earlier sections.

(b) Cold crushing strength

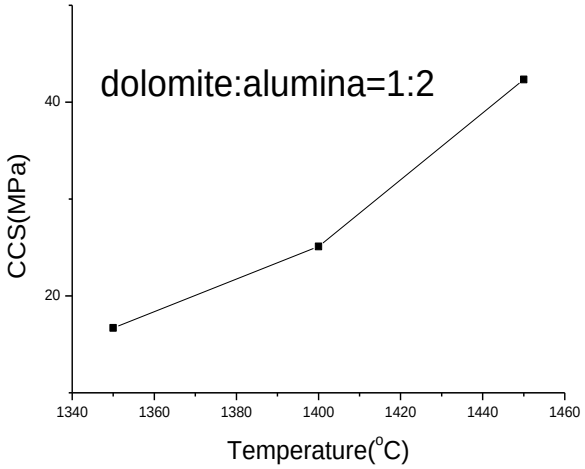

Fig.4.11 Cold crushing strength of calcium aluminate spinel aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:2 as a function of temperature

CCS of the sample prepared with ESP dolomite to calcined alumina molar ratio 1:2 has been shown in the Fig.4.11. It could be seen from the figure that CCS increases with increase in temperature. Increase strength with temperature could be attributing with decrease in porosity in the sample. The decrease in porosity causes a better particle-particle bonding is result in increase strength in the sample.

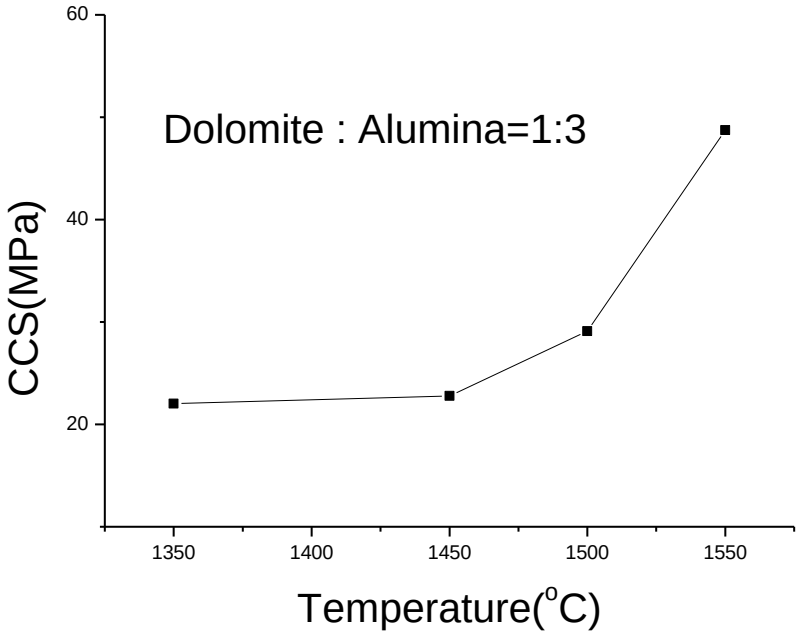

Fig.4.12 Cold crushing strength of calcium aluminate spinel aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:3 as a function of temperature.

CCS of the sample prepared with ESP dolomite to calcined alumina molar ratio 1:3 has been shown in the Fig.4.12. It could also be seen from the figure that CCS increases with increase in temperature. Increase strength with temperature could be attributing with decrease in porosity in the sample. The decrease in porosity causes a better particle-particle bonding is result in increase strength in the sample.

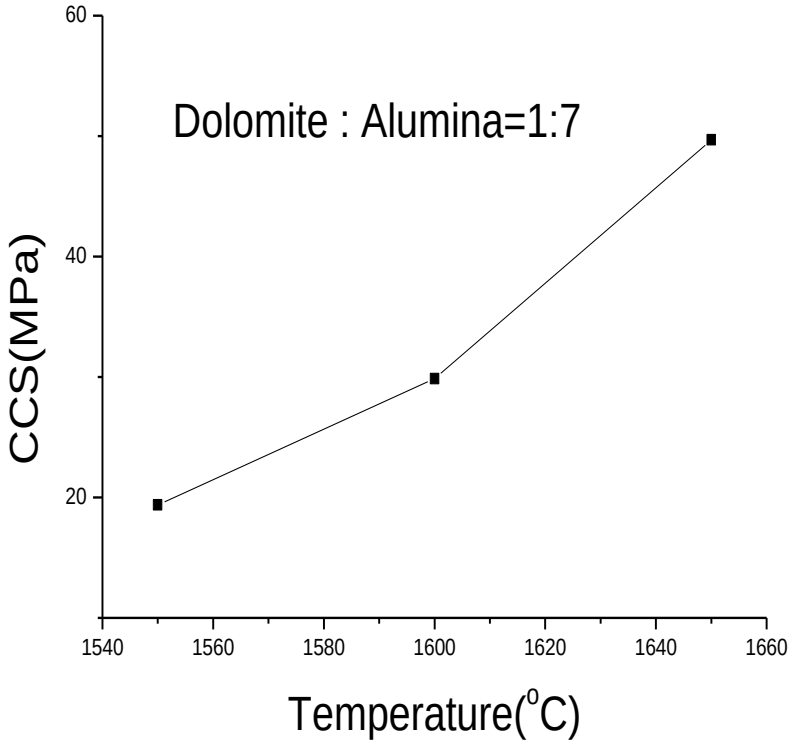

Fig.4.13 Cold crushing strength of calcium aluminate spinel aggregate prepared with molar ratio of ESP dolomite dust to calcined alumina 1:7 as a function of temperature .

Cold crushing strength is varies with the temperature. At the lower temperature strength values are very low as compared to higher temperature. It seems increase temperature lead to increase of strength and decrease of porosity. At higher temperature strength value is high and porosity is very low and density value is also high.

Chapter-5
Conclusion

The following conclusions could be achieved from the present study:

1. Formation of CA and spinel phase occurs at a low temperature. Formation of CA_2 phase occurs at an intermediate temperature whereas formation of CA_6 phase required high temperature.
2. Formation of CA_6 phase undergoes formation and subsequent dissolution of some intermediate phase like CA_2
3. Strength of calcium aluminate–spinel composite is strongly dependent on the porosity of the matrix and type of calcium aluminate phase formed.

Chapter-6

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