DEVELOPMENT OF DOLOMITE BRICKS WITH POSITIVE PLC

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

Master of Technology

In

Ceramic Engineering

By

PRIYA PRASAD

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Department of Ceramic Engineering
National Institute of Technology

Rourkela

MAY 2014

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Under the Guidance of

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CERTIFICATE

This is to certify that the thesis entitled, "**DEVELOPMENT OF DOLOMITE BRICKS WITH POSITIVE PLC**", submitted by **Ms. PRIYA PRASAD** carried out in **TRL Krosaki RefractoriesLimited**, Belpahar, in partial fulfilment of the requirements for the award of Master of Technology Degree in **Ceramic Engineering** at the National Institute of Technology, Rourkela is an authentic work carried out by her 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.I wish her all the success for her future.

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Date:.05.2014 **PRIYA PRASAD**

ABSTACT

Dolomite brick is the most important stable refractory under the working conditions of Argon Oxygen De-carbonization (AOD). For AOD applications, the Dolomite bricks should have positive Permanent Linear Change (PLC) on re-heating. A positive PLC dolomite brick has higher life and most suitable for joint less refractory lining with no cobble stoning defect. So the development of dolomite bricks having positive PLC during applications is a challenge for refractory manufacturing industry. In the present investigation, dolomite refractory bricks were prepared by varying different additive with an intention to get the positive PLC of the brick. It is well known that Iron Oxide is a good additive for dolomite brick sintering. It has also been reported that monoclinic zirconia (m-ZrO_2) additive improves the BD, CCS and PLC of dolomite brick. In this background, first trial composition was containing a fixed amount of 1% m-ZrO_2 and different concentration and types of iron oxide. Mill scale containing Fe_2O_3 was added in two different concentrations 0.5%, 1% and in another trial 0.25% of nano Fe_2O_3 was added. Fe_2O_3 containing bricks showed a good improvement in BD and CCS due to the better sintering of dolomite grains in presence of liquid formation during sintering by the presence of Fe_2O_3.The CCS value was in the range 750-800 kg/cm^2. However, the PLC value was negative in the range of -0.2 to -0.35%. Depending on this result, new additive, Chrome Green oxide was then used. It has been found that the PLC tends to be positive with increase in Cr_2O_3 content. However, in presence of Cr_2O_3 the m-ZrO_2 it was not performing well. Finally m-ZrO_2 was removed and a higher percentage of Cr_2O_3 additive showed the positive PLC (+ 0.12%) of the dolomite brick. The brick showed a CCS value of 650 kg/cm^2. This is in the acceptable limit.

INTRODUCTION

INTRODUCTION

Technological improvement in the manufacturing of iron and steel has changed the operating practice significantly. Increase in furnace capacity, operating temperature, hot-metal temperature and throughput are common to all units. These radical changes along with the need of improved practices for better manufacturing and application environment are demanding a new generation of refractory material with improved properties, performance and life with eco-friendliness.

Refractories play an important role in metallurgical, glassmaking and ceramicindustries, where they are formed into a variety of shapes to line the interiors of furnacesor kilns or other devices for processing the materials at high temperatures [1-2]. Many ofthe scientific and technological inventions and developments would not have beenpossible without refractory materials. Dreaming about producing one kilogram of anymetal without the use of refractory is almost quite impossible. The ASTM C71 definesthe refractories as "nonmetallic materials having those chemical and physical propertiesthat make them applicable for structures or as components of systems that are exposed toenvironments above 1000 °F (538°C) [3].In tune with the changing trends in steelmaking, especially in ladle metallurgy, the high performing shaped refractories are on an increasing demand in recent years. The higher campaign lives and the variability of the newer steelmaking operations are decided by the availability and performance of such shaped refractories with superior high temperature mechanical strength, erosion and corrosion resistance [4, 5].

Initially, the ladles were used only to transport the steel from steel making unit to casting bay, but now-a-days the refining process is also carried out in the same. Thus, steel producers throughout the world have been putting on a continuous effort to improve the ladle life in order to increase the performance of ladles as well as reduce the specific consumption of refractories so as to have a strong grip over cost and quality of steel and also to increase the ladle availability with lesser number of ladles relining per day. Due to the above said reasons, there had been a great technological evolution in ladle lining concept such as: Zonal lining concept, which deals with both selection of refractory quality and refractory lining thickness [6-9].

The type of refractories to be used is often dictated by the conditions prevailing in the application area. Generally, refractories are classified into two different groups [10]:

(a) Based on raw materials, the refractories are subdivided into three categories such asacidic (zircon, fireclay and silica), basic (dolomite, magnesite, magnesia-carbon, chromemagnesiteand magnesite-chrome) and neutral (alumina, chromite, silicon carbide, carbonand mullite) and

(b) Based on manufacturing process, the refractories are subdivided intotwo categories such as shaped refractories (available in the form of different brick shapes, and includes the oxide and non-oxide systems) and unshaped refractories (which includesmortars, castables and monolithic).

Dolomite is a double carbonate of calcium and magnesium ($CaCO_3$, $MgCO_3$). It is one of the important raw material used in iron & steel, ferroalloys, glass, alloy steels, fertilizer industry etc. Dolomite chips are also used in flooring tiles.There are a number of unique properties in dolomite brick that make dolomite well suited for use as a refractory lining in a cement rotary kiln. A high degree of refractoriness allows the dolomite brick to withstand the temperatures and stresses involved in the burning zone, the corrosion resistance to alkalis and a reducing atmosphere, as well as excellent coatability [11-14]. Finally, the environmental safety of the used materials is outstanding properties of the dolomite brick. Dolomite is a magnesium limestone ($CaMgCO_3$). It occurs in nature. Calcined dolomite brick particles are united with the help of silicate bindersand wax. Mixture is then molded to bricks which are air dried and burnt to temperature ranging between 1200 to 1560°C for about one day which gives stabilized dolomite bricks. Such bricks are quite stable towards basic slag [15, 16].

Fig .1 Dolomite refractory

Properties:

- Dolomite bricks are more porous, softer and less strong than magnesia bricks.
- They can be used up to 2300°C without load and up to 1650°C with load.

A good coating formation is the most important property of a basic brick. In practice, a coating will form if the conditions in the kiln are appropriate. The biggest difference between different types of brick used in this context is how well they will hold onto the coating once it is formed. In practice, the clinker coating on the refractory lining is not always present during the campaign. Some or all coating loss may be caused by thermal shock. When the coating on the lining is de stabilized, the brick underneath are subject to a sudden temperature change, which will expose the brick to severe thermal shock [17]. For a long period of time, standard dolomite was limited to the area where stable coating existed over the refractory lining, and shutdowns were minimal. However, the thermal shock resistance of the dolomite brick has been improved significantly by the development of zirconia enriched grades. Zirconia was chosen because it is relatively non-reactive with dolomite.

Zirconia has a high refractoriness and is corrosion resistant to clinker minerals found in cement kilns. Thus the respective zirconia enriched dolomite grades have a high thermal elasticity and excellent thermal shock resistance. In conclusion, the most important requirement on a refractory lining material used in the burning zone of a cement rotary kiln, the zone of the highest temperatures, is its resistance against chemical reactions.

Dolomite bricks do meet these conditions best. The melting phases of the clinker amounting to between 20% and 30% will react with the lime of the refractory brick material at a temperature of about 1450° C forming the minerals alite and belite which are both characterized by very high melting temperatures (2000 and 2130° C). Due to this reaction, a solid and stable coating is formed on the surface of the dolomite bricks. The wear of the brick surface will be reduced by the formation of the coating. Further, the coating forms a protection against temperature losses of the clinker burden in the kiln, i.e. reduced heat losses through the shell. The thermal losses particularly in the hottest Zone, the burning zone, will be reduced considerably. Therefore, dolomite brick are the most suitable brick for the burning zone of the cement rotary kiln.

Dolomite is generally used as a repairing material rather than as a direct refractory because of its defects like porosity, shrinkage and softness. However stabilized dolomites are used in electric furnaces, Bessemer converters, open hearth furnaces etc., cheap substitute for magnesia bricks. Dolomite as a mineral has very few uses. However, dolo-stone has an enormous number of uses because it occurs in deposits that are large enough to mine. The most common use for dolo-stone is in the construction industry. It is crushed and sized for use as a road base material, an aggregate in concrete and asphalt, railroad ballast, rip-rap or fill. It is also calcined in the production of cement and cut into blocks of specific size known as "dimensionstone".

Dolomite's reaction with acid also makes it useful. It is used for acid neutralization in the chemical industry, in stream restoration projects and as a soil conditioner.

Dolomite is used as a source of magnesia (MgO), a feed additive for livestock, a sintering agent and flux in metal processing and as an ingredient in the production of glass, bricks and ceramics [18-20].Dolomite serves as the host rock for many lead, zinc andcopper deposits. These deposits form when hot, acidic hydrothermal solutions move upward from depth through a fracture system that encounters a dolomitic rock unit. These solutions react with the dolomite which causes a drop in pH that triggers the precipitation of metals from solution. Dolomite also serves as an oil and gas reservoir rock. During the conversion of calcite to dolomite a volume reduction occurs. This can produce pore spaces in the rock that can be filled with oil or natural gas that migrate in as they are released from other rock units. This makes the dolomite a reservoir rock and a target of oil and gas drilling [21].

LITERATURE SURVEY

LITERATURE SURVEY

Refractories are in use since mankind began to develop metallurgical process, being clay the first refractory raw material ever used. This traces refractory development back to years 3500-3000 BC, and at around 1500 BC furnaces made of refractory bricks have started to be developed for the production of metals and glass. Up to the 19th century, refractories were composed of natural ores, such as dolomite stones and clay, because the temperatures required for ore beneficiation, as well as the aggressiveness of the industrial slags, were not as demanding as those of modern industry. It was in the end of the 18th and beginning of 19th century that the foundations of modern metal beneficiation, the development of Portland cement and of modern glass processes started to impose higher requirements to the refractory industry. The new processes demanded higher quality refractory linings, which brought the need to use higher quality raw materials. Silica, zircon sand, chrome ore, magnesite, dolomite and fireclay started to be used according to the particularities of the process for which the refractory was needed. Schaefer rediscovered monolithic linings at 1914 [22, 23], which were pliable in the beginning, but evolved to cement-bonded powdery concretes in the 1930's. In the 1960's, calcium-aluminate cements, more specifically Cement Fondue started to be used for refractory applications, followed by higher-quality 70% and 80% cements in the end of 1970's and beginning of 1980's. Concomitantly, the difference between mechanical and corrosion resistance of castables, when compared to bricks, started to be diminished, due to the introduction of super-fine raw materials and dispersing aids to castables, which enabled the reduction of cement and water content, creating a more compact macrostructure with enhanced properties.

In the beginning of the 1990's, pumping was adapted from the building to the refractory industry, which enabled very high installation rates, and also reduced the material losses and environmental problems associated to dry gunning.

Dolomite And Its Specification For Some Industries

Dolomite is a double carbonate of calcium and magnesium ($CaCO_3$, $MgCO_3$). It is one of the important raw material used in iron & steel, ferroalloys, glass, alloy steels, fertilizer industry etc. Dolomite chips are also used in flooring tiles [24].

The specifications of dolomite required for different industries are given below:

1. Iron and Steel Industry: Dolomite is used in iron and steel industry as refractory raw material and as a flux. The ISI (Is 10346&1982) has prescribed the following specifications of dolomite for use in the manufacture of refractory bricks, fettling material and for the blast furnace and sintering plants.The type of dolomite used in blast furnace, sinter, and pellet plants is of same quality but it is of inferior grade as compared to that used in steel melting shop. The ISI stipulates that dolomite for use in BF /SP should contain MgO 18% (min), CaO 28% (min) and acid insoluble 8% (max), whereas steel plants in practice, consume dolomite with MgO 18 to 19.5%, CaO 29 to 30% and acid insoluble 6 to 10%. The steel melting shop requires superior quality dolomite for fluxing purposes. The total insoluble should be below 4%. The silica content should be as low as possible but in no case above 2.5%. The steel plants however, use dolomite with acid insolubleup to 6 and in the case of TISCO it is as high as 8.7%.

2. Ferro-Manganese Industry: The specifications of dolomite for use in ferromanganese are more or less similar to SMS grade dolomite. Physically dolomite should be hard and fine grained because crystalline dolomite gives fritting effect in the furnace. Ferro alloy industry actually consumes dolomite with MgO 19 to 20%, CaO 28 to 30% $Si0_2$ 2 to 5%, and Al_20_3 2 to 2.5%.

3. Glass Industry: High grade dolomite with as low iron content as possible is required by the glass industry. Glass grade dolomite is typified by its purity and consistency. The MgO and CaO content should not very by more than 0.5%. The chief undesirable impurities are iron followed by chromium, manganese, vanadium, lead, all of which colour the glass or they may cause defects in the glass. For certain commercial colorless glass, the Fe_2O_3 content up to 0.25% is permissible, but for truly colourless glass, Fe_2O_3 content of 0.04% (max) is sometimes specified.The ISI (IS:997-1937) has prescribed specifications for limestone and dolomite for glass industry as given below. In case of dolomitic limestone or dolomite, requirement of lime and CaO may be fixed by mutual agreement between purchaser and the supplier.When the material is supplied in powder form, the grain size distribution of the material shall be between the following limits:(a) Material retained on 2.00 mm sieve - Nil.(b) Material passing 125 micron IS sieve - 25%

4. Fertilizer Industry: Dolomite for use in fertilizer industry must have $CaCO_3$ +$MgCO_3$ 90% (min) and SiO_2 5% (max).Inferior grade dolomitic limestone of 15-20% MgO can be used as soil conditioner. Ground dolomite, 50% of which must be 100 BS mesh size be considered suitable as a soil conditioner if it is applied at the rate of 2-3 ton per acre.The ISI (rs: 5407 - Part 2-1985) has prescribed the specifications of limestone and dolomite to be used as soil amendments. According to this specification, 90%, by mass of the material should pass through 2 mm (10 mesh) sieve and 50% by mass of material to pass through 205 micron (60 mesh) sieve. The neutralizing value (express as $CaCO_3$) percent by mass shall not be less than 70%. The total lime and magnesia (as CaO + MgO) shall not be less than 50% by mass and the material shall not contain more than 5% moisture by mass.

5. Lime: The dolomite for the manufacture of lime should contain $CaCO_3$ 58-75%, $MgCO_3$ 28-48% and other constituents should be less than 3%. .

6. Magnesium Metal: Calcined dolomite of 200 mesh size is used in the extraction of magnesium metal.

7. Filler/Extender: For this purpose, dolomite must be very pure and in particular be free from colouring impurities such as oxides of iron, chromium, manganese etc.

8. Coal Mining Industry: Dolomite for this purpose must be finely powdered to a carefully controlled grading with at least 50% passing 200 mesh sieves. Silica content should not exceed 5% as to minimize any risk of silicosis through inhalation by miners.

9. Sea -Water - Magnesia: The essential requirements of dolomite raw material for this purpose are that impurities like iron oxide and alumina in particular are kept to a minimum.

Industrial Applications

Dolomite is chiefly used as refractory, ramming, and fettling material in steel melting shop, and as fluxing material in blast furnace operation in secondary steel and ferromanganese manufacture. To a lesser extent, it is used in the glass industry especially in sheet-glass manufacture. It also finds use in the manufacture of mineral wool [25].In England, dolomite has become a useful source for the production of magnesite by reacting calcined dolomite with sea-water. The UK is meeting nearly 50% of her magnesite requirements by this method. Dolomite is also a good source of magnesium metal. The magnesium metal is extracted from dolomite by the well-known Ferro-silicon process.Dolomite decomposes completely above 900ºC. The product resulting from this relatively low-temperature calcination is highly porous and reactive and is known as 'calcinated dolomite'. Dolomite is sometimes used both in the raw and calcined form as refractory material for hearth maintenance and for banking door in open hearth furnace [26, 27].

For most refractory uses, it is desirable to subject the dolomite to a heat treatment at a high temperature of the order of 1700ºC, to shrink the material thoroughly and render it less reactive. Dead burnt (D.B.) dolomite is the term generally used for the refractory made by firing dolomite, with or without additives, at high temperature to produce well shrunkparticles.

In basic converters, the bricks employed are generally of D.B. dolomite and sometimes also of D.B. magnesite. Dolomite bricks are kept in the outer lining because it has lower thermal conductivity than magnesite.

Manufacturing Process:

Dead burnt refractory dolomite is produced in rotary kilns. Generally high-grade dolomite, containing combined impurities less than 3%, is selected for dead burning. As it is difficult to densify high purity dolomite in a rotary kiln, it is customary to use some mineralizers to facilitate dead burning. Iron oxide is a common additive. The manufacturing process varies with the grade of D.B. dolomite desired to be produced. In most of the plants in European countries a typical operation, employing rotary kilns lined in the hot zone with basic bricks and fired with powdered coal, is used. The temperature reached in the hot zone is of the order of 1760ºC. The kilns have continuous gas sampling equipment which measures and records the oxygen, combustibles, and carbon dioxide contents of the kiln exit gases for combustion control. The latter is particularly important in achieving a uniform quality of the product, effective use of dead burning agents and efficient use of fuel in the manufacture of dead burnt dolomite.

The dolomite after dead burning is cooled in either rotary or reciprocating recuperative coolers. The air used for cooling gets heated and is again used as secondary air for combustion in thekilns. When D.B. dolomite is manufactured with an additive, it is necessary to use somewhat higher firing temperature in order to shrink the dolomite in a reasonable time-cycle in the kiln. This has been accomplished by improved thermal efficiency in the kiln. Some of the means to attain higher efficiency have been the use of insulating brick-back of the basic lining in the hot zone and the optimum utilization of secondary air from the recuperative coolers, in order to pick up as much of the available heat as is possible from the cooling of the product.There is another product known as 'stabilized' refractory dolomite. It is manufactured by the process similar to that of Portland clinker. Dolomite and serpentine with small amounts of suitable stabilizing agents are ground to slurry in a ball mill. The slurry is fired to a dense mature clinker in a rotary kiln having a temperature of the order of 1760ºC. The optimum capacity of vertical or shaft kiln using coke admixed with dolomite for fuel is kept at a minimum of 100 tons a day. Such kilns are widely used in the USA and the UK, Scandinavia and other European countries. Great progress has been made in the automation of kilns in the steel-producing countries. D.B. dolomite can withstand temperatures upto 2300ºC. It is widely used as a refractory material wherever steel is refined using basic slag. It is used for original hearth installations in the open hearth furnaces as well as for hearth maintenance. These hearths are installed using tar-dolomite ramming mixes and rammed dolomite. Dolomite refractories are also used in electrical furnaces and in cement industry during clinker manufacture.

SPECIFICATIONS

Steel manufacturers prefer dolomite of the following composition for dead burning:

$MgCO_3$ - 35% Min.
SiO_2 - 1% Max.
$Fe_2O_3+Al_2O_3$ - 1.5% Max.
$CaCO_3$ - Remainder

The dolomite containing insoluble ($Al_2O_3+Fe_2O_3+SiO_2$)up to 7%, is used in the blast furnace by most of the steel manufacturers in the country but the dolomite containing a maximum of

4 to 5% insoluble is preferred. Silica and alumina contents in dolomite are not regarded deleterious for blast furnaces. They only cause unnecessary increase in the slag. Dolomite has been found as a useful support to limestone in removing sulphur from the iron ore. It also reduces the viscosity of the slag, thus chemical reactions in the furnace. For the steel melting shop the total insoluble below 4% are preferred.

DOLOMITE QUALITIES

S-DOL:*S-DOL* is a high purity sintered dolomite that is sized, blended and pressed into a brick shape for rotary kilns. It is then fired in a high temperature tunnel kiln to create a strong ceramic ally bonded brick. This is the standard brand of fired, direct bonded dolomite. It is the standard recommendation and most cost effective solution for the center of the coating zone.

Z-DOL:*Z-DOL* is a zirconia enriched version of *S-DOL*. *Z-DOL* is the premium quality, spalling resistance refractory for use in the burning zone of a rotary kiln. It is designed for burning zones where coatings may be unstable or thin, or where thermal fluctuations are more significant. The thermal shock resistance is greatly increased by small additions of zirconia to the mix.

ZLP-DOL: *ZLP-DOL* is the newest upgrade from *Z-DOL*. *ZLP-DOL* is critically sized, blended, and burned at a higher temperature to obtain a low permeable property. ZLP-DOL is designed to minimize penetration of gaseous components into the surface which could condense inside the brick. *ZLP-DOL* was developed for burning zones which experience abnormal chemical attack from burning industrial waste fuels.

TZ40-DOL: *TZ4O-DOL* is a magnesite enriched dolomite with zirconia additions. This product has been developed for burning zones with extremely unstable coatings. The magnesite enrichment in the fine fraction of the brick is designed to insulate the free lime by coating and protect the lime against reaction with sulphur containing volatiles in the kiln atmosphere. This product also contains a zirconia enrichment to improve its resistance to thermal shock [28].

EFFECT OF IRON OXIDE ADDITION ON THE HYDRATION RESISTANCE AND BULK DENSITY OF DOLOMA

Here in this study without any additives and mill scale (98.6 wt.% Fe_2O_3 content) added with natural dolomite and firing is done at 1650°C for 24 hours.Here hydration resistance was little better. Doloma ($MgCaO_2$) is the semi product used to produce dolomite refractory. They have extremely high melting point as the eutectic for the CaO-MgO binary system occurs at 2370^o C.Doloma is a material that is susceptible to hydration and thus its free lime ratio must be lower than a critical value. The main impurities present in Doloma are SiO2,Al_2O_3,and Fe_2O_3.Sintering occurs through liquid phase mechanism. Doloma is one of the attractive steel making refractories because of its potential cost effectiveness and worldwide abundance [29-33].

ROOT CAUSES OF HYDRATION

- Quality of Dolo Sinter
- High moisture content in Resin
- Amount of Dolo dust in mix and LOI of dolo dust
- Improper Tar coating
- Tempering kiln parameters
- Packaging

RESOURCES: Dolomite occurrences are widespread in the country. As per UNFC system, as on 1.4.2010 total resources of dolomite are placed at 7,730 million tones, out of which 738 million tones are placed under reserves category and the balance 6,992 million tones under remaining resources category.Gradewise, BF/sintering grade accounts for 26% resources followed by SMS (17%), refractory (9%), BF & SMS mixed (4%) and glass (3%). Others, unclassified, not-known and BF, SMS & refractory mixed grades together account for the remaining 38% resources. Major share of about 91% resources was distributed in eight states: namely, Madhya Pradesh (29%), Andhra Pradesh (15%), and Chhattisgarh (11%) Orissa and Karnataka (9% each), Gujarat (7%), Rajasthan (6%) and Maharashtra (5%). The remaining 9% resources are distributed in Arunachal Pradesh, Jharkhand, Haryana, Sikkim, Tamil Nadu, Uttarakhand, Uttar Pradesh and West Bengal.

MINING AND MARKETING

Dolomite mines are generally worked by opencast method of mining. Manual working is in vogue in most mines. However, a few mines are semi-mechanized. Steel plants draw major supplies of dolomite for use as a flux and also as a refractory material. The requirement of low silica dolomite is increasing in steel plants at Bhilai, Rourkela, Visakhapatnam and Jamshedpur. However, the supply of such materials from indigenous sources is posing a problem. Therefore, Bokaro, Rourkela, Durgapur and Jamshedpur steel plants are drawing supplies of low silica dolomite from Bhutan for use in tar-bonded refractory bricks required for lining of LD furnaces and also for fluxing purposes. Bhilai, Bokaro, Rourkela, Jamshedpur, Visakhapatnam and Bhadravati steel plants have captive mines. Besides, these plants drawsupplies from private parties. Dolomite produced from Tulsidamar mine in Garhwa district, Jharkhand, is used mainly by Bokaro Steel Plant. Dolomite produced in Tumkur district of Karnataka is supplied to the Ferro-manganese plants at Dandeli, Uttar Kannad district. The VISP's steel plant at Bhadravati receives its supplies from Nerelekere mine in Bagalkot, Karnataka. Dolomite of Baradwar and Hirri areas in Chhattisgarh is supplied to the steel plants at Bhilai, Bokaro and Rourkela besides foundry and glassmanufacturing units. Birmitrapur, Panposh and Gomardih areas of Sundergarh district, Odisha,supplied dolomite to iron and steel plants at Durgapur, Rourkela, Burnpur and Jamshedpur.

Dolomite from this region is also used by the ferromanganese plants at Joda and Rayagada in Odisha.Low-silica dolomite from Jayanti area in Jalpaiguri district of West Bengal is supplied mainly to steelplants at Durgapur and Jamshedpur. In Odisha and Rajasthan dolomite is supplied to the foundry and grinding units. The production from Vadodara district, Gujarat, is used for making chips and tiles. In Gujarat and Maharashtra, dolomite is used for making potteries and in ferroalloys industry.Dolomite produced in Jhabua district, Madhya Pradesh, is utilized by fertilizer, tile-making and grinding units. Dolomite of Jabalpur and Mandla districts is supplied to chips manufacturing units at Katni and Bhilai, respectively.

USES

Dolomite as a mineral has very few uses. However, dolostone has an enormous number of uses because it occurs in deposits that are large enough to mine. The most common use for dolostone is in the construction industry. It is crushed and sized for use as a road base material, an aggregate in concrete and asphalt, railroad ballast, rip-rap or fill. It is also calcined in the production of cement and cut into blocks of specific size known as "dimension stone". Dolomite's reaction with acid also makes it useful. It is used for acid neutralization in the chemical industry, in stream restoration projects and as a soil conditioner. Dolomite is used as a source of magnesia (MgO), a feed additive for livestock, a sintering agent and flux in metal processing and as an ingredient in the production of glass, bricks and ceramics[34, 35]. Dolomite serves as the host rock for many lead, zinc andcopper deposits. These deposits form when hot, acidic hydrothermal solutions move upward from depth through a fracture system that encounters a dolomitic rock unit. These solutions react with the dolomite which causes a drop in pH that triggers the precipitation of metals from solution. Dolomite also serves as an oil and gas reservoir rock. During the conversion of calcite to dolomite a volume reduction occurs.

This can produce pore spaces in the rock that can be filled with oil or natural gas that migrate in as they are released from other rock units. This makes the dolomite a reservoir rock and a target of oil and gas drilling.Dolomite after calcination is used for refractorypurposes (as a substitute of magnesite refractories) inlinings of furnaces like basic open-hearth steel furnacesand basic Bessemer converters.High purity dead-burnt dolomite bricks are requiredfor lining LD furnaces while mini-steel plants generallyrequire dolomite for fettling and refractory purposes.Like limestone, dolomite is used as a flux in iron &steel, Ferro-alloys and glass works. A few steel plantshave dispensed with the use of dolomite in blastfurnaces and its use in the preparation of self-fluxingsinters is found adequate for blast-furnace charge.It is useful in the recovery of magnesia andalso in the manufacture of magnesium metal; for the manufacture of basic magnesium carbonate (termed'technical carbonate'), 'block magnesia' or 'magnesia alba' used in pipe and boiler coverings and for otherheat insulation, in pharmaceutical, rubber andchemical industries, and in the manufacture of paper,leather, glass, potteries and high-magnesium limes.In agriculture, it is used as a soil conditioner tocorrect acidity. It finds use as a filler in fertilizers,paints & varnishes, for suppression of dust in coalmines. It is not also as a building stone and in themaking of flooring tiles as chips & powder [36 – 39].

SPECIFICATIONS

Generally, insoluble like SiO_2, Fe_2O_3 and Al_2O_3 areconsidered deleterious constituents of dolomite for anyindustrial use. It is essential that these insoluble should beas low as possible. High purity dolomite with less than oneper cent insoluble is preferred for making refractory brickswhich are used in the lining of LD furnaces. Similarly, high-grade dolomite containing as low iron aspossible (less than 0.15%) is required in glass industry.

Specifications forflux grade dolomite for use in iron & steel industry have been revised and are prescribed in IS: 10346 - 2004 (second revision,Reaffirmed 2009) while specification of dolomite for refractory industry are prescribed in IS: 14296 - 1995 (Reaffirmed 2010).IS: 15366 - 2003 (Reaffirmed 2009) lays down the specifications of dolomite for paint industry[40-42].

FUTURE OUTLOOK

Over 95% of the total production of dolomite finds outlet mainly in iron and steel and allied industries. The importance of high purity deadburntdolomite bricks for lining LD furnaces has gained ground due to LD process of steelmaking. At the same time, a few of the steel plants have dispensed with the use of dolomite in blast furnace. Dolomite used in the preparation of self-fluxing sinters is found adequate for the blast furnace charge. Ministeel plants generally require dolomite for fettling and refractory purposes only. The resources of the refractory grade dolomite in the country are meager and this type of material is in short supply but very much required for making tar-bonded dolomite bricks. Therefore, intensive search is needed in non-Himalayan regions for locating deposits of massive non-crystalline dolomite, containing less than 2.5% R2O3 for use in tar-dolomite bricks required for lining of LD steel furnaces. The Sub-Group - II of the Working Group on Minerals forth 12th Plan has recommended the exploration of low silica dolomite in the states of Andhra Pradesh and Odisha may be initiated by the State DGMs.The Sub-Group has estimated the apparent domestic demand of dolomite at 6.15 million tonsby 2011-12 and at 9.46 million tons by 2016-17at 9% growth rate [43-45].

THE TRANSITION ZONES

Various cement plants have made industrial wastes a substitute part of their conventional fuel (gas, oil, coal) and raw materials. The cement kiln is very efficient in waste disposal due to inherent high processing temperatures and long residence time for gases and material. In particular, fluctuations in the operation of the kiln, which often arise when using waste fuel, will ultimately affect the performance life of the kiln refractories. As this effective way of industrial and municipal waste disposal has an economic benefit to the cement producer, the refractory industry has to look for means to cope with the different conditions in the cement kiln.

The main attack phenomena resulting from burning waste in cement kilns are; increased refractory wear due to corrosion by liquid clinker phases, thermal shock, abrasion, and salt infiltration causing chemical corrosion. The effect of increased levels of alkali, SO_3 and chlorine on basic bricks is their structural densification on the hot face as a result of the infiltration of liquid phases. This structural change will make bricks more susceptible to damage by thermo cycling.

In order to improve refractory life, it is often necessary to use a combination of basic brick types. The refractory market offers a number of chrome-free brick grades which can be used to cope up with varying kiln conditions. As far as development and research in basic bricks is concerned, new means had to be considered to achieve chemical stability, both against corroding liquid phases from the clinker components, as well as from components contained in the kiln atmosphere in a vaporized stage which are able to condense within the brick lining.

Therefore, research and development has focused on dolomite-based bricks with low permeability. The targeted performance life improvement by MgO-enrichment and reduction of permeability to a minimum would increase brick density, which would be diametrical to the required high thermal shock resistance. Therefore, the thermal elasticity of such brick had simultaneously to be improved to avoid spalling and cracking, which would be caused by thermal variation. The developed possess [46- 48].

- To insulate the accessible free lime by coating and to protect the lime against reaction with sulfur containing volatile constituents in the kiln atmosphere.
- To lower permeability against standard burnt dolomite bricks and thereby minimize penetration of gaseous components into the surface, which could condense inside the brick.
- To achieve good thermal shock resistance by Zirconia additions.

TZ40-DOL is a low-priced alternative for the upper transition zones and can be a substitute for spinel bricks. It can even be installed in the transition zone when the lower limiting value of the alkali-sulfate relation is falling short of (<0.8), according to the Holder bank formula [49, 50].

1. OUTLET ZONE
2. LOWER TRANSITION ZONE
3. SINTERING ZONE
4. UPPER TRANSITION ZONE
5. SAFETY ZONE
6. INLET ZONE

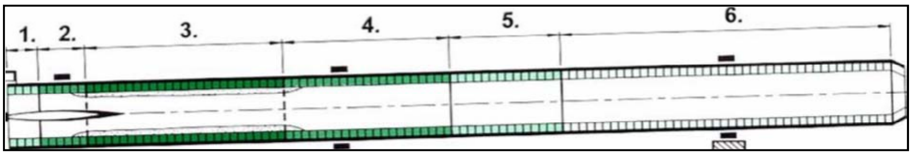


Fig 2:CONSTRUCTION OF A CEMENT KILN

Microstructure development in ceramic systemhas attracted a great deal of attention, determined either for theoretical or practical reasons. The balance between densification and grain growth has long been recognized as the main factor that determines the microstructure of the materials. Existing grain growth models, which are usually applied to single-phase ceramic systems, involve assumptions regarding interfacial behavior, grain shape and grain-boundary mobility, but they generally ignore the topological constraints of the systems. From those, the stated models frequently predict kinetic relationships that do not well to the experimentalresults. The effect of topological constraints on coarsening of biphasic ceramic systems with low mutual solid solubility has been investigated, making evident that the second phase particles are effective against grain growth [51– 55]. However, in those systems that use either solid-solution or second phase additives to prevent abnormal graingrowth, the effect of second phase particles depends on the dispersion degree achieved during Powder processing.

Dolomite zircon mixtures have become interesting for finding alternate sources to improve the production of high magnesiarefractories. To asses this option, two minerals, dolomite and zircon were selected, as economically raw materials, to produce$MgO \pm CaZrO3 \pm Ca_2SiO_4$ materials. The reaction sintering mechanism of zircon dolomite mixtures were investigated using only ground Spanish dolomite and zircon powders as starting materials. During the heat treatment decomposed dolomite (CaO+MgO) reacts with zircon, from 1000 to 1200^{o}C, through a series of reactions before the stable compounds are formed. From the results obtained the reaction occurs prior to sintering in the presence of an amorphous transitory phase, magnesium calcium silicate phase and the limiting process during the reaction is the formation of Ca_2SiO_4. The sintering occurs after the end of the reaction so by controlling the whole process it is possible to obtain materials with controlled porosity [56,57].

EXPERIMENTAL

EXPERIMENTAL

PLC specimen samples were made with following raw materials, composition and experimental conditions as shown in the Table 1 to Table 7.

Raw materials used for this study: Calcined Dolomite, Fused magnesia large crystal (FMLC), Chrome Oxide green, Mill Scale, Zirconia, Nano Iron Oxide, Wax andStearic Acid.

Table 1: Experimental conditions

BATCH SIZE	**1 KG**
GRAIN HEATING	Yes
DIMENSION	Ht: 50MM Dia : 50MM
AMOUNT OF MIXTURE FOR PRESSING	~300 gm
PRESSING	1.8 T/cm^2
FIRING	1650 ± 10 º C SOAKING – 2 HOURS

Batch compositionT1, to T6 are mentioned on Tables T2 to T7 below:

Table 2: Composition of T 1

T1		
Raw Materials	Granulometry (mm)	% Addition
Dolomite	(3-5)	10
	(1.6-3)	45
	(0.3-1.6)	10
	(0-0.3)	15
	Dust	5
FMLC 97	(0-1)	10
FMLC 97	Dust	5
Mill Scale	Dust	0.5
m-ZrO_2	Dust	1
Wax	-	2.2
Stearic Acid	-	0.05

Table 3: Composition of T2

T2		
Raw Materials	Granulometry (mm)	% Addition
Dolomite	(3-5)	10
	(1.6-3)	45
	(0.3-1.6)	10
	(0-0.3)	15
	Dust	5
FMLC 97	(0-1)	10
FMLC 97	Dust	5
Mill Scale	Dust	1
m-ZrO_2	Dust	1
Wax	-	2.2
Stearic Acid	-	0.05

Table 4:Composition of T3

T3		
Raw Materials	Granulometry (mm)	% Addition
Dolomite	(3-5)	10
	(1.6-3)	45
	(0.3-1.6)	10
	(0-0.3)	15
	Dust	5
FMLC 97	(0-1)	10
FMLC 97	Dust	5
Nano Fe_2O_3	Dust	0.25
m-ZrO_2	Dust	1
Wax	-	2.2
Stearic Acid	-	0.05

Table 5: composition of T4

T4		
Raw Material	Granulometry (mm)	% Addition
Dolomite	(3-5)	10
	(1.6-3)	45
	(0.3-1.6)	10
	(0-0.3)	15
	Dust	4
FMLC 97	(0-1)	10
FMLC 97	Dust	5
Cr_2O_3 Green	Dust	X1
m-ZrO_2	Dust	1
Wax	-	2.2
Stearic Acid	-	0.05

Table 6:Composition of T5

T5		
Raw Materials	Granulometry (mm)	% Addition
Dolomite	(3-5)	10
	(1.6-3)	45
	(0.3-1.6)	10
	(0-0.3)	15
	Dust	5
FMLC 97	(0-1)	10
FMLC 97	Dust	5
Cr_2O_3Green	Dust	X2
Wax	-	2.2
Stearic Acid	-	0.05

Table 7:Composition of T6

T6		
Raw Materials	Granulometry (mm)	% Addition
Dolomite	(3-5)	10
	(1.6-3)	45
	(0.3-1.6)	10
	(0-0.3)	15
	Dust	5
FMLC 97	(0-1)	10
FMLC 97	Dust	5
Cr_2O_3Green	Dust	X3
Wax	-	2.2
Stearic Acid	-	0.05

Chemical analysis of all raw materials are supplied by the industry and shown in Table 8.

Table 8: Chemical analysis of raw materials

CONSTITUENT	%			
	FMLC 97	DOLOMITE	Cr_2O_3 GREEN	MILLSCALE
MgO	97.3	39.33	-	-
Fe_2O_3	0.5	1.0	-	97
Al_2O_3	0.2	-	-	-
SiO_2	0.5	1.0	-	-
CaO	1.5	57.9	-	-
Cr_2O_3green	-	99	-	-

BRIEF DESCRIPTION ABOUT RAW MATERIALS

CALCINED DOLOMITE: Dolomite is an anhydrous carbonate mineral composed of calcium magnesium carbonate $CaMg(CO_3)_2$. The word dolomite is also used to describe the sedimentary carbonate rock, which is composed predominantly of the mineral dolomite also (also known as dolostone).Solid solution exists between dolomite, iron rich ankerite and the manganese rich kutnohorite. Small amounts of iron in the structure give the crystals a yellow to brown tint. Manganese substitutes in the structure also up to about three percent MnO. High manganese content gives the crystals a rosy pink color. Lead, zinc, and cobalt also substitute in the structure for magnesium. The mineral dolomite is closely related to huntite $Mg_3Ca(CO_3)_4$ [58 -60].

In the present project, dolomites were used in five different granulometry. Dolomite was taken from source in **Salbari in Bhutan.** Fig. 3 and Fig. 4 shows the XRD pattern and the phases present in dolomite course and dust.

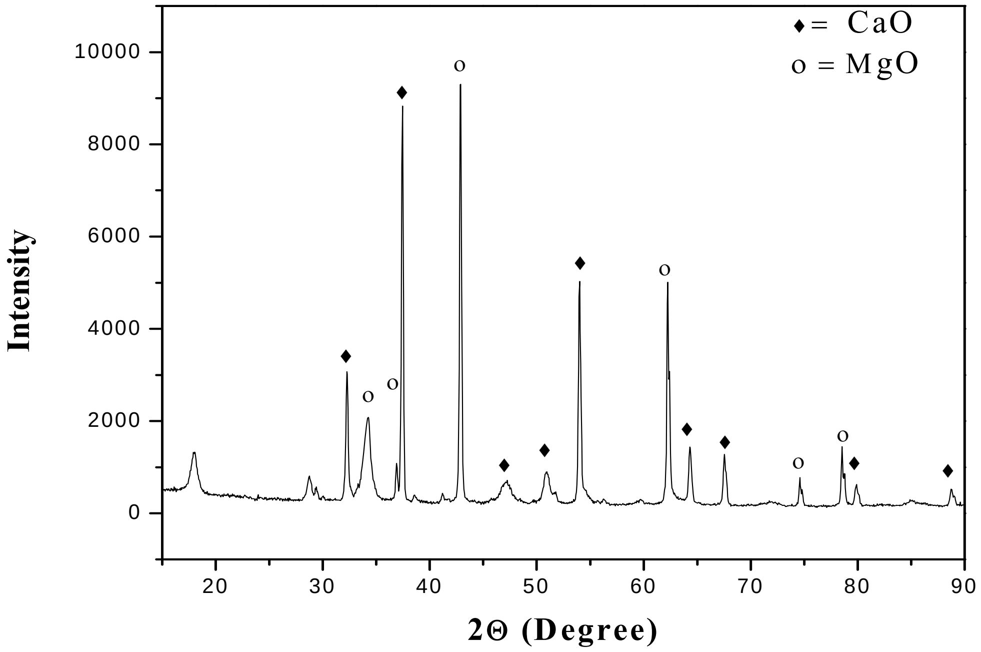


Fig 3: XRD pattern of Dolomite

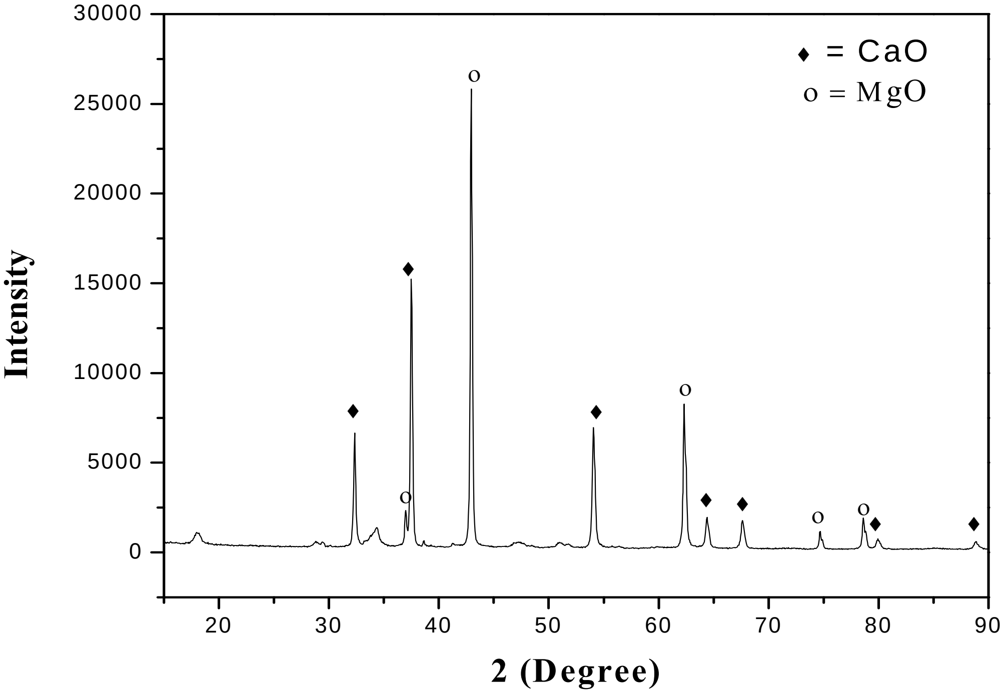


Fig4: XRD pattern of Dolomite dust

FMLC: Fused Magnesia having large crystal size (500 - 1000μm), is an alkaline earth metal and the eighth-most-abundant element in the Earth's crustand ninth in the known universe as a whole. Magnesium is the fourth-most-common element in the Earth as a whole (behind iron, oxygen and silicon), making up 13% of the planet's mass and a large fraction of the planet's mantle. The free element (metal) is not found naturally on Earth, as it is highly reactive (though once produced, it is coated in a thin layer of oxide, which partly masks this reactivity). The free metal burns with a characteristic brilliant-white light, making it a useful ingredient in flares. The metal is now obtained mainly by electrolysis of magnesium salts obtained from brine [61-67].

FMLC was also used in two different granulometry. The XRD pattern (Fig.5) shows the phases present in FMLC.

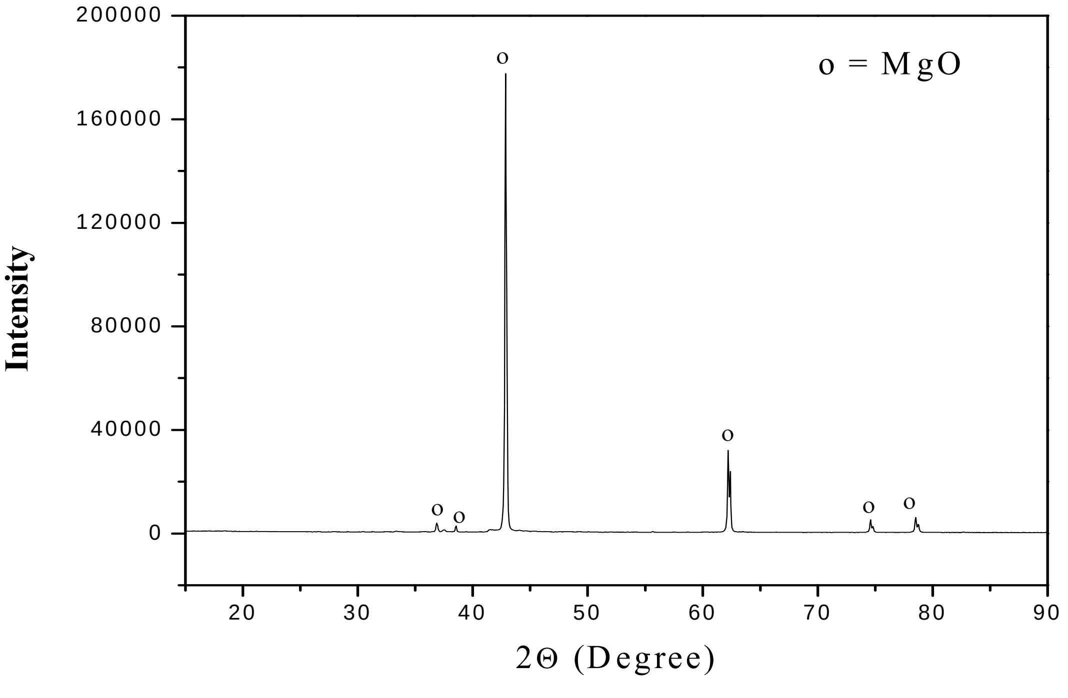


Fig 5: XRD pattern of FMLC

CHROME OXIDE:Cr_2O_3 adopts the corundum structure, consisting of a hexagonal close packed array of oxide anions with 2/3 of the octahedral holes occupied by chromium. Similar to corundum, Cr_2O_3 is a hard, brittle material (Mohr hardness 8-8.5). It is antiferromagnetic up to 307 K, the Neel temperature. It is not readily attacked by acids or bases. It turns brown when heated, but reverts to its dark green color when cooled. It is also hygroscopic.Chromium (III) oxide is amphoteric. Although insoluble in water, it dissolves in acid to produce hydrated chromium ions, [Cr $(H_2O)_6]^{3+}$ which react with base to give salts of $[Cr(OH)_6]^{3-}$. It dissolves in concentrated alkali to yield chromite ions [68-71]. When heated with finely divided carbon it can be reduced to chromium metal with release of carbon dioxide. When heated with finely divided aluminum it is reduced to chromium metal and aluminum oxide.**Cr_2O_3 + 2 Al → 2 Cr + Al_2O_3**, Unlike the classic thermite reaction involving iron oxides, the chromium oxide thermite creates few or no sparks, smoke or sound, but glows brightly. Because of the very high melting point of chromium, chromium thermite casting is impractical [72 -74]. The XRD pattern (Fig 6) shows the phases present.

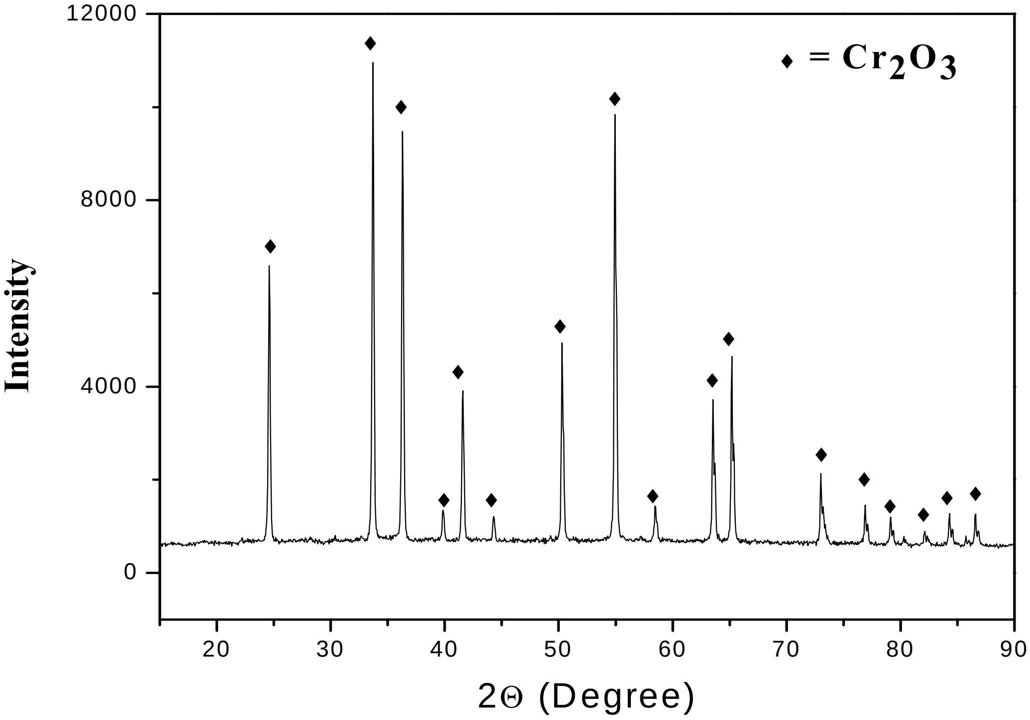


Fig 6: XRD pattern of Chrome oxide green powder

MILL SCALE: Mill scale, often shortened to just scale, is the flaky surface of hot rolled steel, iron oxides consisting of iron(II) oxide (FeO), iron(III) oxide (Fe_2O_3), and iron (II,III) oxide (Fe_3O_4, magnetite).Mill scale is formed on the outer surfaces of plates, sheets or profiles when they are being produced by rolling red hot iron or steel billets in rolling mills. Mill scale is composed of iron oxides mostly ferric and is bluish black in color. It is usually less than 1 mm (0.039 in) thick and initially adheres to the steel surface and protects it from atmospheric corrosion provided no break occurs in this coating. Because it is electro-chemically cathodic to steel, any break in the mill scale coating will cause accelerated corrosion of steel exposed at the break. Mill scale is thus a boon for a while until its coating breaks due to handling of the steel product or due to any other mechanical cause.Mill scale is a nuisance when the steel is to be processed. Any paint applied over it is wasted since it will come off with the scale as moisture laden air get under it. Thus mill scale can be removed from steel surfaces by flame cleaning, pickling, or abrasive blasting, which are all tedious operations that waste energy. This is why shipbuilders used to leave steel delivered freshly rolled from mills out in the open to allow it to 'weather' until most of the scale fell off due to atmospheric action. The XRD pattern (Fig. 7) shows the phases present.

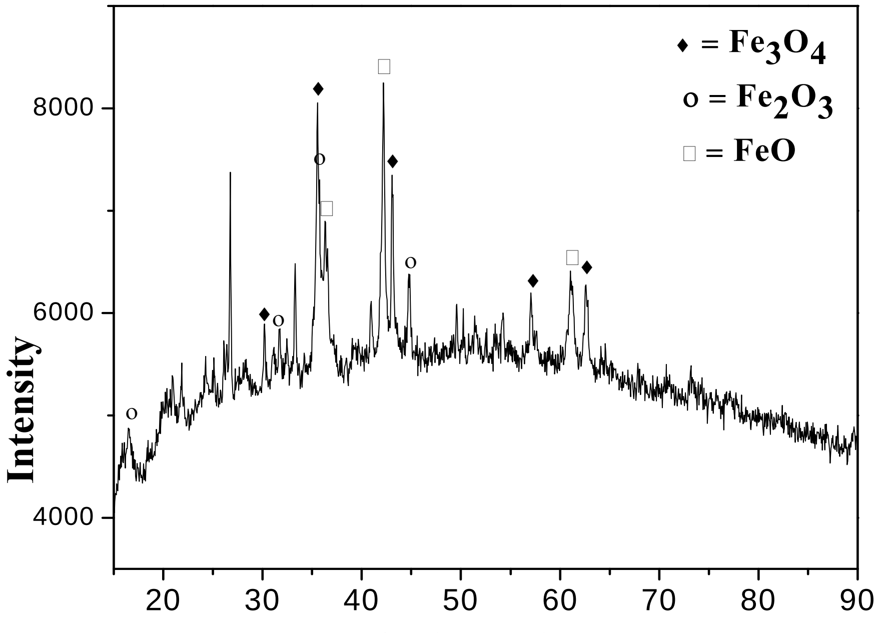


Fig .7 XRD pattern of Mill scale powder

ZIRCONIA: Zirconia is a white crystalline oxide of zirconium. It's most naturally occurring form, with a monoclinic crystalline structure. Three phases are known: monoclinic < 1170°C, tetragonal 1170°C–2370 °C, and cubic >2370 °C. The trend is for higher symmetry at higher temperatures, as is usually the case. A few percentage of the oxides of calcium or yttrium stabilize the cubic phase. The very rare mineral tazheranite (Zr, Ti, Ca) O_2 is cubic. Unlike TiO_2, which features six-coordinate Ti in all phases, monoclinic zirconia consists of seven-coordinate zirconium centers. It is chemically unreactive Zirconia is often more useful in its phase 'stabilized' state. Upon heating, zirconia undergoes disruptive phase changes. By adding small percentages of yttrium, these phase changes are eliminated, and the resulting material has superior thermal, mechanical, and electrical properties. In some cases, the tetragonal phase can be meta-stable. If sufficient quantities of the meta-stable tetragonal phase is present, then an applied stress, magnified by the stress concentration at a crack tip, can cause the tetragonal phase to convert to monoclinic, with the associated volume expansion. This phase transformation can then put the crack into compression, retarding its growth, and enhancing the fracture toughness. This mechanism is known as transformation toughening, and significantly extends the reliability and lifetime of products made with stabilized zirconia. The XRD pattern (Fig.8) shows the phases present.

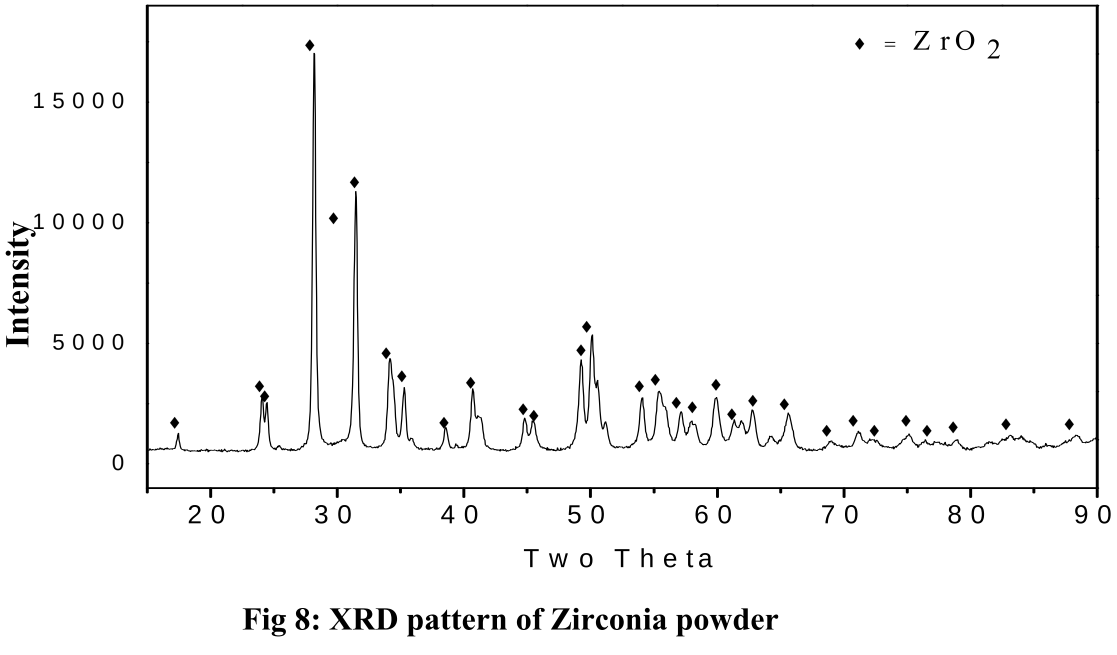


Fig 8: XRD pattern of Zirconia powder

NANO IRON OXIDE: Iron oxide nanoparticles are iron oxide particles with diameters between about 1 and 100 nanometers. The two main forms are magnetite (Fe_3O_4) and its oxidized form maghemite (γ-Fe_2O_3). They have attracted extensive interest due to their super paramagnetic properties and their potential applications in many fields (although Co and Ni are also highly magnetic materials, they are toxic and easily oxidized).Applications of iron oxide nanoparticles include terabit magnetic storage devices, catalysis, sensors, and high-sensitivity bimolecular magnetic resonance imaging(MRI) for medical diagnosis and therapeutics. These applications require coating of the nanoparticles by agents such as long-chain fatty acids, alkyl-substituted amines [83-85].

Wax: Waxes are a class of chemical compounds that are plastic (malleable) near ambient temperatures. They are also a type of lipid. Characteristically, they melt above 45 °C (113 °F) to give a low viscosity liquid. Waxes are insoluble in water but soluble in organic, nonpolar solvents. All waxes are organic compounds, both synthetic and naturally occurring [86 -90].

STEARIC ACID: Stearic acid is the saturated fatty acid with an 18-carbon chain and has the IUPAC name octadecanoic acid. It is a waxy solid, and its chemical formula is $CH_3(CH_2)_{16}CO_2H$. Its name comes from the Greek word στέαρ *"stéar"*, which means tallow. The salts and esters of stearic acid are called stearates. Stearic acid is one of the most common saturated fatty acids found in nature following palmitic acid [91-93].

PROCEDURE OF MAKING THE SPECIMEN

The following points should be carefully followed :

1. The dolomite should be calcined.
2. The coarseand dust particles should be measured in other bowl.
3. Wax and stearic acid should be melted together in a different bowl.
4. While pressing the bricks the material should be warm.
5. The mould should be properly clean.
6. It should be noted that , while giving for firing the brick should be kept properly , so that it does not fell off.
7. After the pressing, the samples were placed for 1st firing at 1650 ºC for 24 hours and the 1st firing data for weight loss measurement and BD were taken. Again the samples were re-fired for PLC at 1650 º C for 24 hours. The PLC fired data for PLC,BD, CCS and Weight Loss were also taken.

8. PHYSICAL PROPERTEIS

9. **APPARENT POROSITY (AP):** The apparent porosity is a measure of the volume of the open pores, into which a liquid can penetrate, as a percentage of the total volume. This is an important property in cases where the refractory is in contact with molten charge and slags. A low apparent porosity is desirable since it would prevent easy penetration of the refractory size and continuity of pores will have important influences on refractory behavior. A large number of small pores is generally preferable to an equivalent number of large pores[94].

Sample preparation flow-chart is shown in Fig. 9.

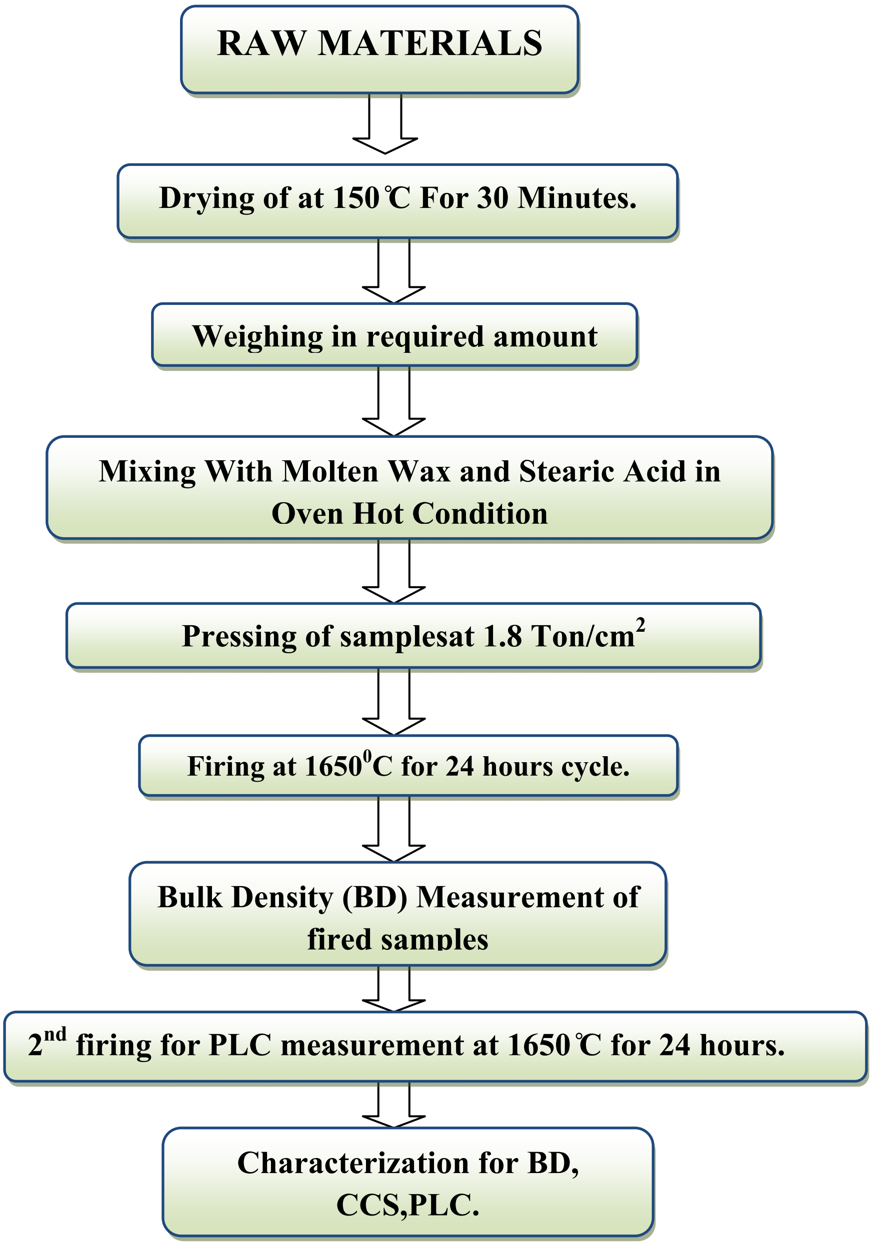


Fig 9: Flow chart of making the dolomite samples for PLC test

BULK DENSITY (BD): The bulk density is generally considered in conjunction with apparent porosity. It is a measure of the weight of a given volume of the refractory. For many refractories, the bulk density provides a general indication of the product quality.It is considered that the refractory with higher bulk density (low porosity) will be better in quality. An increase in bulk density increases the volume stability, the heat capacity, as well as the resistance to abrasion and slag penetration [94].

PERMANENT LINEAR CHANGE (PLC) ON REHEATING

In refractory, certain permanent changes occur during heating and these changes may be due to: • Change in the allotropic form, • Chemical reaction, • Liquid phase formative, • Sintering reactions. PLC was calculated using formule:

PLC (%) linear = (Increase or decrease in length)/Original length × 100
PLC %(volume) = (Increase or decrease in volume)/Original volume ×100
These changes determine the volume stability and expansion and shrinkage of the refractory at high temperatures.

Cold Crushing Strength (CCS):

Cold crushing strength (CCS) of a refractory brick represents its strength. It tells us how much load that refractory can bear in cold conditions. The concept of testing CCS of a refractory material has perhaps, come from metallurgy. This is because for any refractory brick it is rather rare that it would fail simply due to load on it in cold condition. The determination of cold crushing strength does not appear to be important from that point of view. But still testing of this property i.e. knowing the strength of the refractory bricks done to check some other properties which are direct result of strength such as ‘abrasion’. The stronger a material is the greater is the resistance to abrasion. Also stronger refractories are expected to have higher resistance to slag attack. The determination of cold crushing strength (CCS), however, is highly important in case of refractory insulating bricks where bricks have to be porous as well as strong.

Volume stability, expansion and shrinkage at high temperature:

The contraction or expansion of the refractories can take place during service. Such permanent changes in dimensions may be due to:

a) The changes in the allotropic forms which cause a change in specific gravity

b) A chemical reaction which produces a new material of altered specific gravity.

c) The formation of liquid phase.

d) Sintering reactions.

e) It may also happen on account of fluxing with dust and slag or by the action of alkalies on fireclay refractories, to form alkali-alumina silicates, causing expansion and disruption. This is an example which is generally observed in blast furnaces.

While it is desirable that all these changes are effected during manufacturing, it is not possible due to economic reasons, as the process is time dependent. Permanent Linear Change (PLC) on reheating and cooling of the bricks give an indication on the volume stability of the product as well as the adequacy of the processing parameters during manufacture. It is particularly significant as a measure of the degree of conversion achieved in the manufacture of silica bricks.

Results and Discussions

Results and Discussions

Observation OF Iron oxide

It has been reported that Iron Oxide (Fe_2O_3) plays an important role in Dolomite refractories [95]. It is establish that Fe_2O_3 helps in liquid phase sintering of dolomite, which results in a good densification of the brick.For that reason, the CCS increases with Fe_2O_3 addition due to the increase in BD, decrease in AP. This in turn improves the hydration resistance.As well as Fe_2O_3containing liquid, which forms during sintering solidify as a coating upon the Dolomite grains.This coating again improves the hydration resistance. In this background, the first trial composition for the present study was composed of Fe_2O_3containing additives.Our target was to get positive PLC of the brick. The references [96] also stated that the Fe_2O_3 containing dolomite brick will not produce shrinkage during PLC firing because the brick is already highly densified.

ROLE OF ZIRCONIA

It has also been reported that monoclinic Zirconia (m-ZrO_2) additives in Dolomite brick improves the properties like crack arresting[97] by forming $CaZrO_3$ bonded materials. The thermal expansion of $CaZrO_3$ compared to MgO can lead to the formation of gaps between Ca_2SiO_4, $CaZrO_3$ and MgO grains. These discontinuities can increase toughness and thermal shock resistance by stopping crack propagation. On this basis, our first trials composition was based on 1 % monoclinic $ZrO_2$and mill scale additives with 0.5 % and 1 % variation. Mill scale mainly contains Fe_2O_3.

Standard dolomite PLC sample with dimension 50*50 mm (Height * diameter) were fabricated with different additives. The prepared PLC sample were fired at 1650˚C for 24 hours (1st firing) and those fired samples were re-fired at 1650˚C(PLC firing) for 24 hours for PLC measurement .The bulk density of green, 1st fired and PLC fired specimen were measured. The CCS and PLCof samples were also measured. The specimen were characterized using XRD and SEM.

Fig 10 shows the T1 blocks. Figure shows that a typical grayish colour of the iron containing fired specimen. There were very little visible surface defects like crack or big pores.

Fig 10: T1 blocks after PLC firing.

Fig 11 shows that BD of T1 and T2 along with T3 composition. There is no significant difference of green, 1^{st} fired and PLC BD.

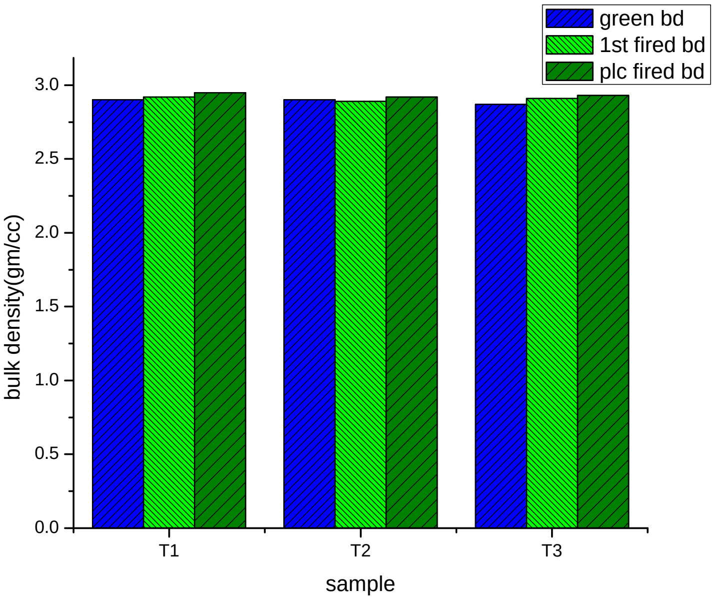


Fig 11: BD of T1, T2,T3 specimens.

Their CCS is also similar as shown in the Fig. 12.

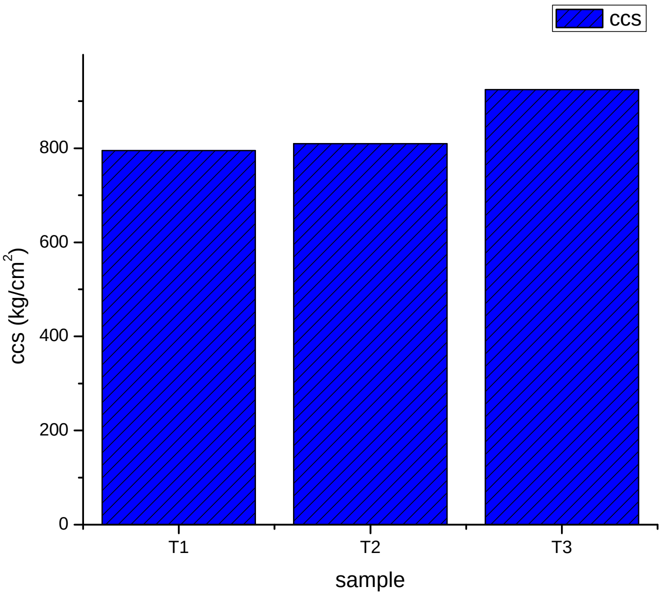


Fig 12: CCS of T1,T2,T3 specimens.

Observation of T1 & T2

Fig 13 AND 14 shows the XRD pattern of T1 and T2 PLC fired specimen powder. The two specimens have almost same XRD pattern indicating similar phases are present in them. They have the following phase composition (Table 9):

Table 9: Percent phase composition of T1 and T2, calculated from XRD.

MgO	(70 -80)%
CaO	(20 – 30)%
$CaZr_2O_3$	3%
CaFeO	(3 -4)%

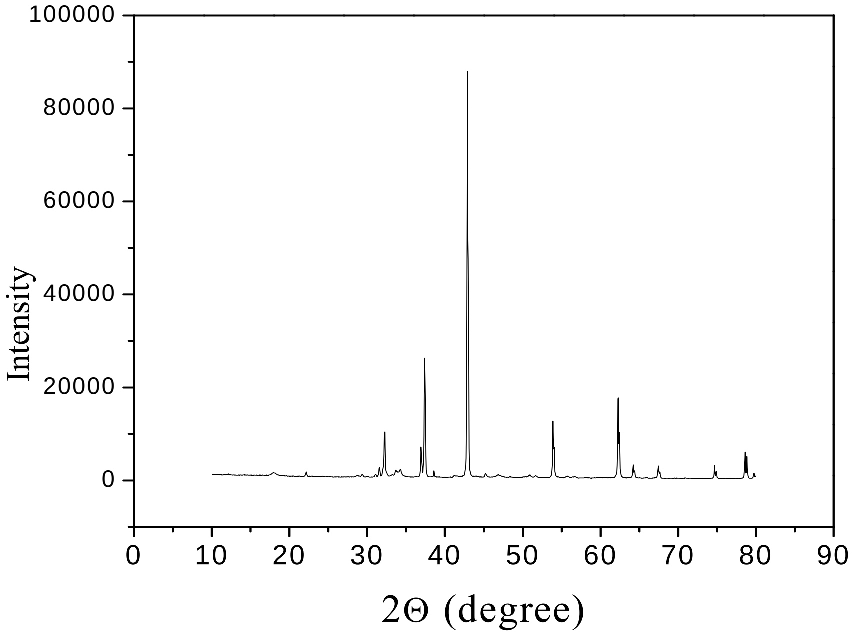


Fig 13: XRD pattern of T1

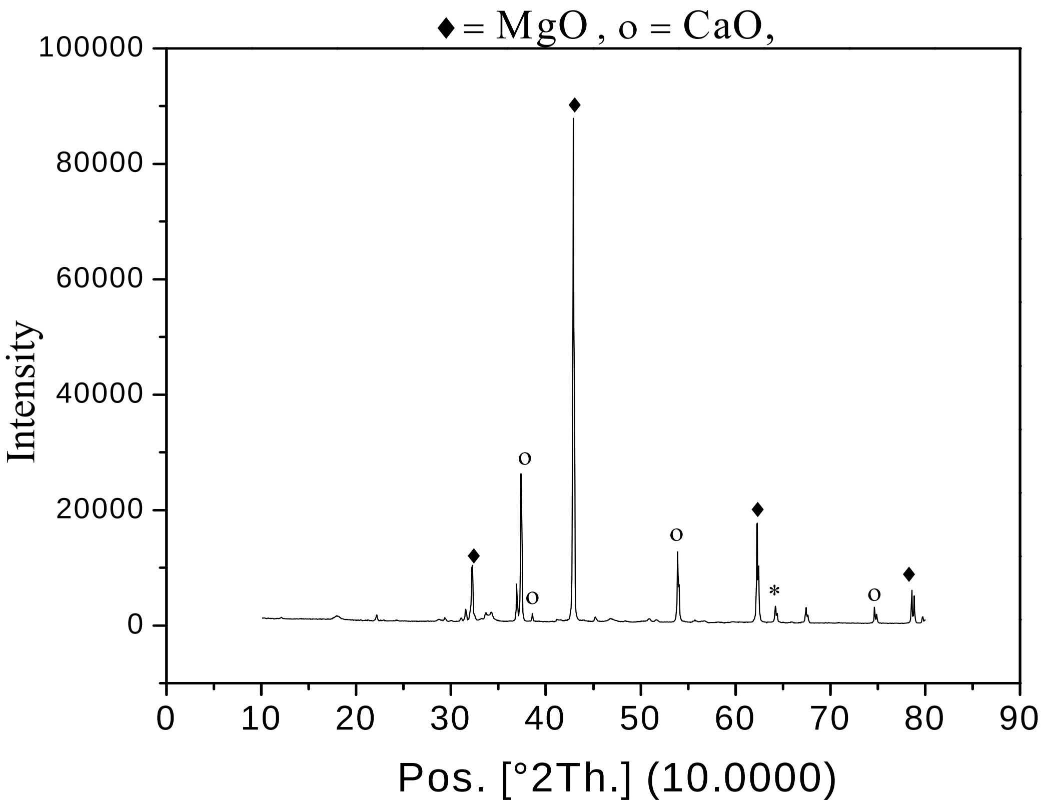
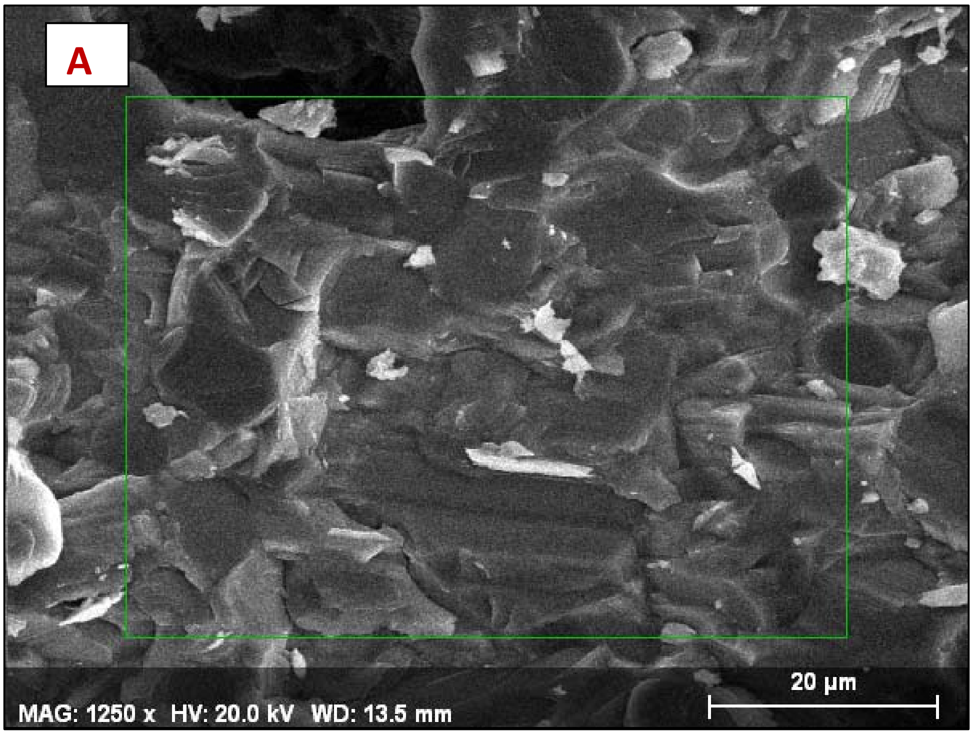


Fig 14: XRD pattern of T2

The phase analysis indicates that ZrO_2 used in the refractory mainly reacts with CaO to form $CaZr_2O_3$ and this $CaZr_2O_3$ protects from hydration. The Fe_2O_3 used also react with CaO, MgO to form calcium magnesium iron oxide phase which also coat CaO and further improves its hydration resistance. So, CaO mainly reacts with Fe_2O_3, $ZrO_2$and even with impurities like SiO_2, Al_2O_3.That iswhy the XRD analysis shows 20-30% CaO in fired sample. MgO present is much higher as it is not reacting with additives or impurities, at the same time MgO also comes from FMLC.

Fig 15(a) shows the SEM microstructure of T1 specimen fracture surface after CCS measurement. The microstructure shows that the ceramics are highly compact and non-porous body. Fig 15(b) shows the elemental mapping of Fig 15(a). The mapping shows that CaO and MgO are present separately.ZrO_2 and $Fe_2O_3$are almost homogeneously distributed in the microstructure. However the percentage of ZrO_2 are more in CaO matrix, this indicates that ZrO_2 mainly reacts with CaO.



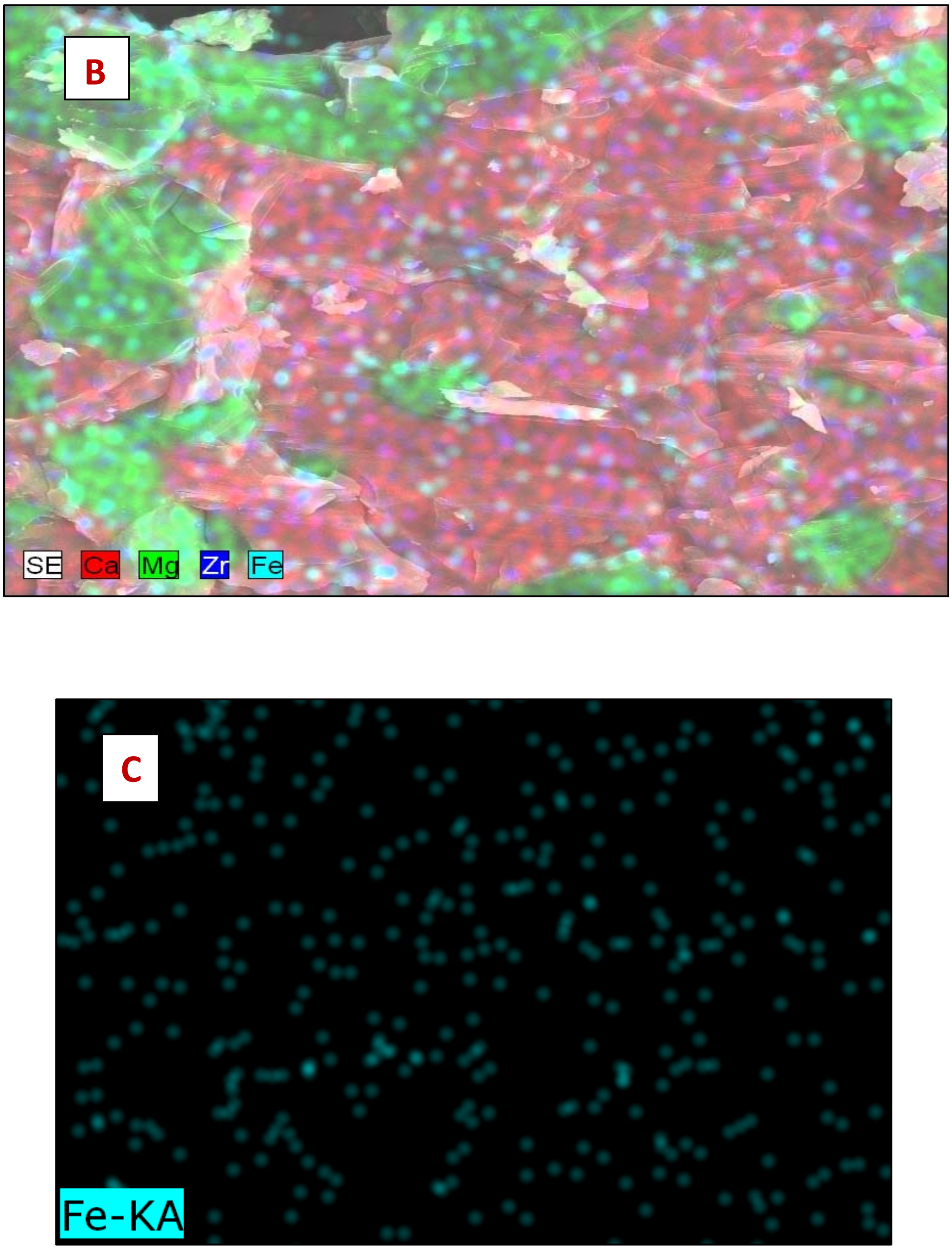


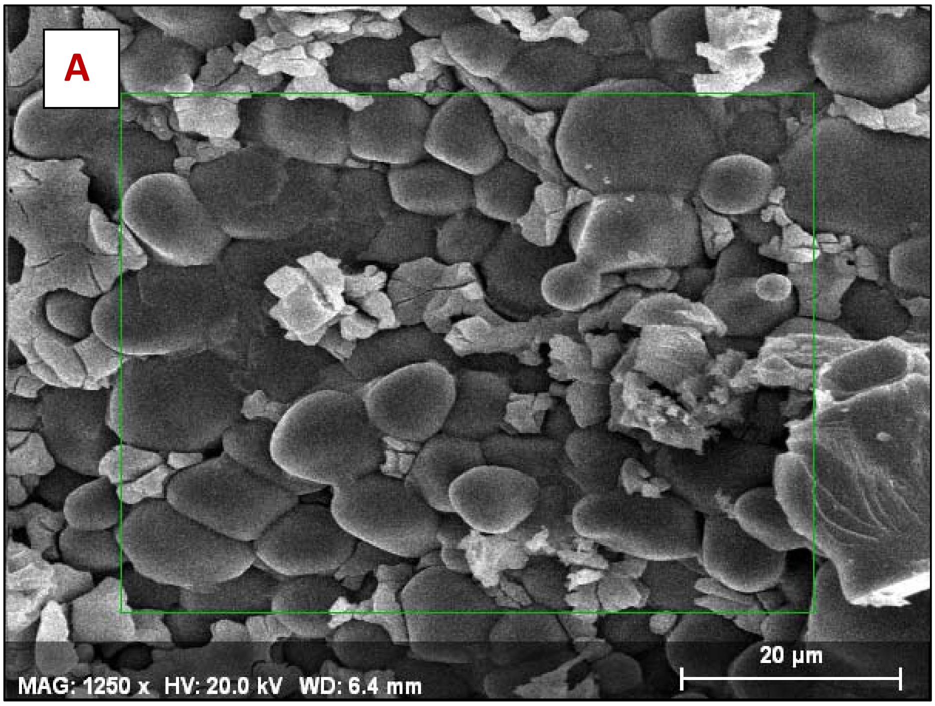
Fig 15 (a) SEM microstructure of T1 specimen, (b) elemental mapping of, and (c) Fe-elemental mapping.

Fig 15 (C) showsFe_2O_3 elemental mapping of Fig. 15 (a). The mapping shows that $Fe_2O_3$is homogeneously distributed in the specimen indicatingan efficient mixing of the material.

Fig 16(a) shows the SEM microstructure of T2 specimen. This microstructure shows the presence of 2 types of grains. The bigger round shaped grains are mainly MgO grain with an average size of 10 micron, which can be easily identified from the elemental mapping fig

16(b), of the same area. The smaller whitish phases present in the microstructure are mainly CaO. The shape of CaO are non-uniform, may be due to hydration of CaO during SEM sample preparation. One important observation is the cracking of the CaO grain due to the expansion created by the hydration. So, it is confirmed that the CaO is the major hydrating phase in Dolomite refractories.

The fig 16(b) and(c) shows that the Zr, Fe are homogeneously distributed throughout the sample.T1 and T2 were evaluated for its PLC. The table 10 shows the PLC values for the two. The values were almost similar and with (-ve) negative PLC.



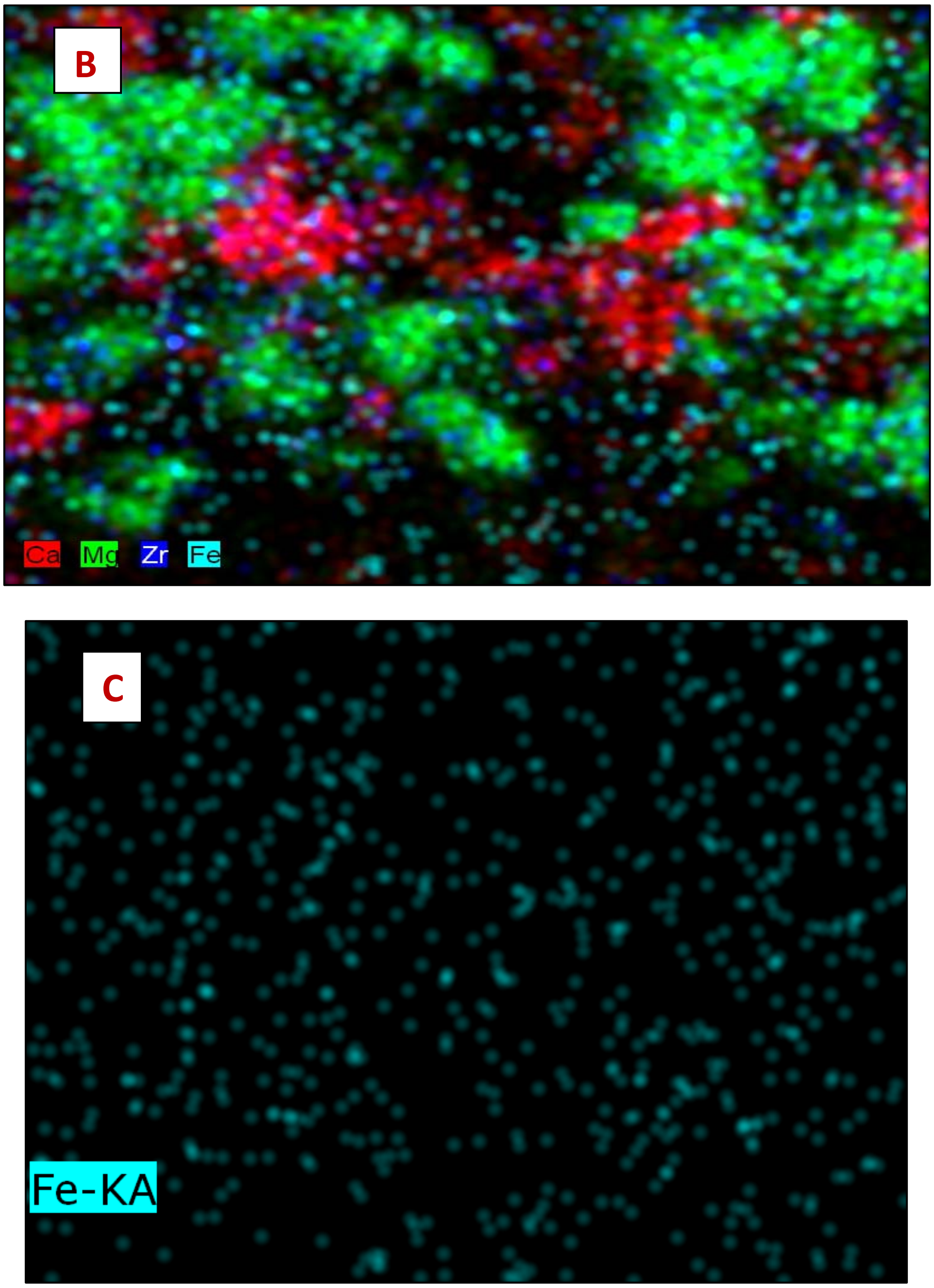


Fig 16: (a) SEM microstructure of T2 specimen, (b) elemental mapping of, and (c) Fe- elemental mapping.

Observation Of Using Iron Oxide(T3)

To study the effect of nano Fe_2O_3, composition T3 was prepared using 0.25 % nano Fe_2O_3. the BD and PLC of T3 specimen almost similar to those of T1 and T2 however on taking the CCS observation T3 increased in spite of using 0.25 wt.% of nano Fe_2O_3 . This indicates nano Fe_2O_3 is very effective in decreasing the sintering temperature and producing better bonding between grains. Fig 17 and 18(a-c) shows the XRD pattern, SEM microstructure and elemental mapping of T3 specimen, depicting almost similar crystalline phases, grain distribution, and elemental distribution of Zr and Fe.

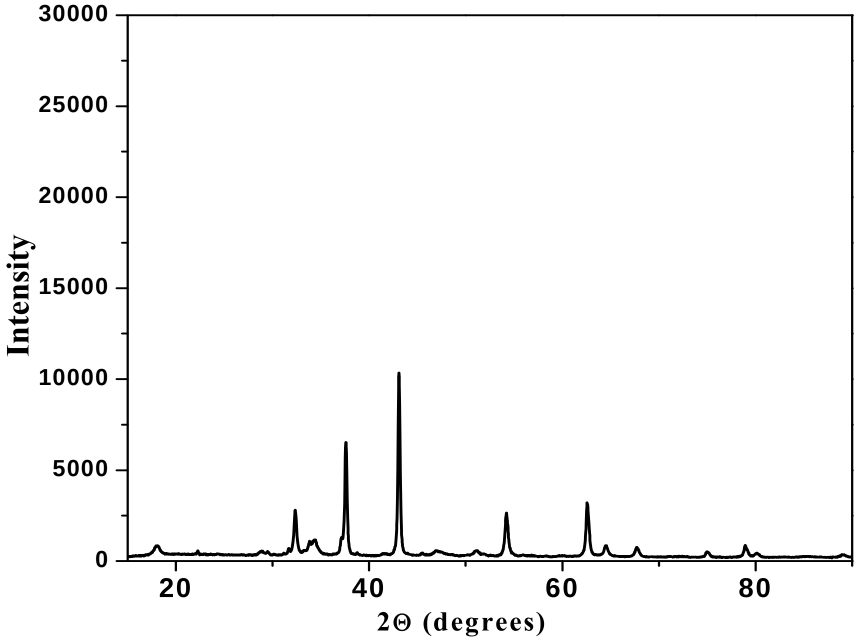
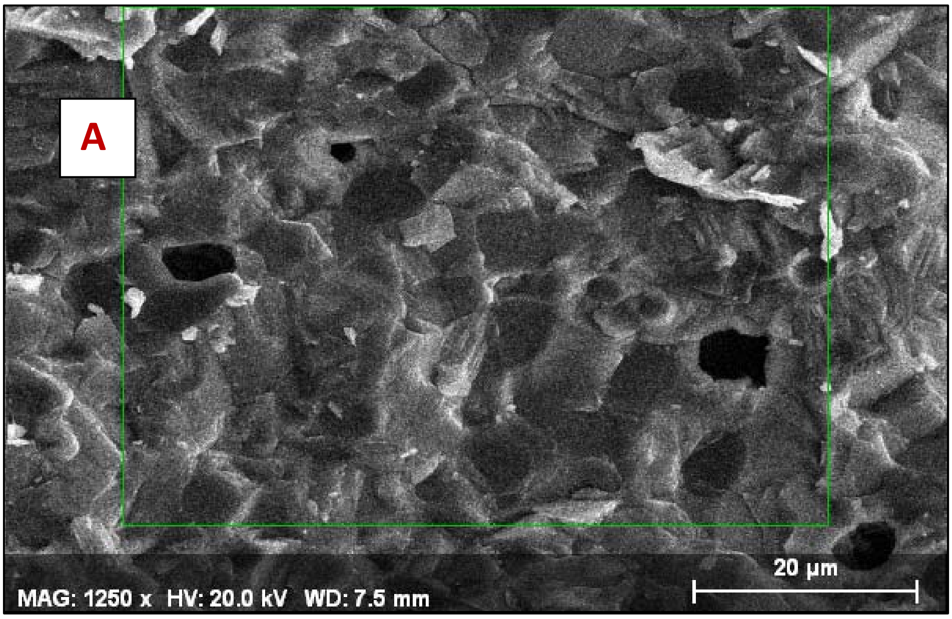


Fig 17: XRD pattern of specimen T3



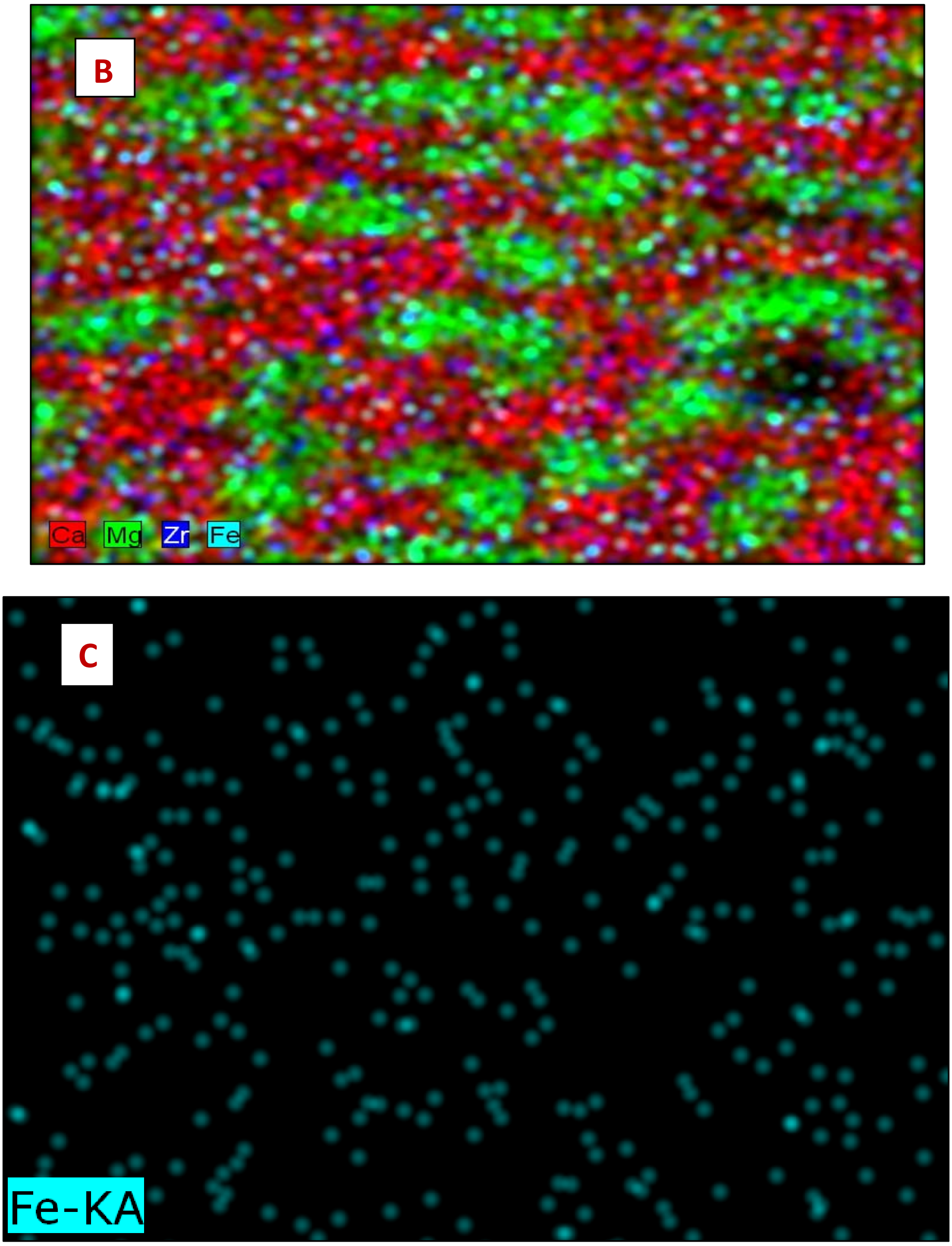


Fig 18: (a) SEM microstructure of T3 specimen, (b) elemental mapping of, and (c) Fe- elemental mapping.

OBSERVATION OF T4

The PLC of T3 sample again shows the negative values. Although these specimen having Fe_2O_3 additives shows a negative PLC for the reason. The next experiment was conducted in a composition without containing any Fe_2O_3 additives.The composition T4 was composed of some % of Cr_2O_3 and ZrO_2, like previous BD of the specimen was similar. But the CCS was slightly lower and PLC was near to zero however negative. Fig 19 and 20 shows the XRD pattern and SEM microstructure of the specimen and BD, CCS and PLC values are shown in table 10.

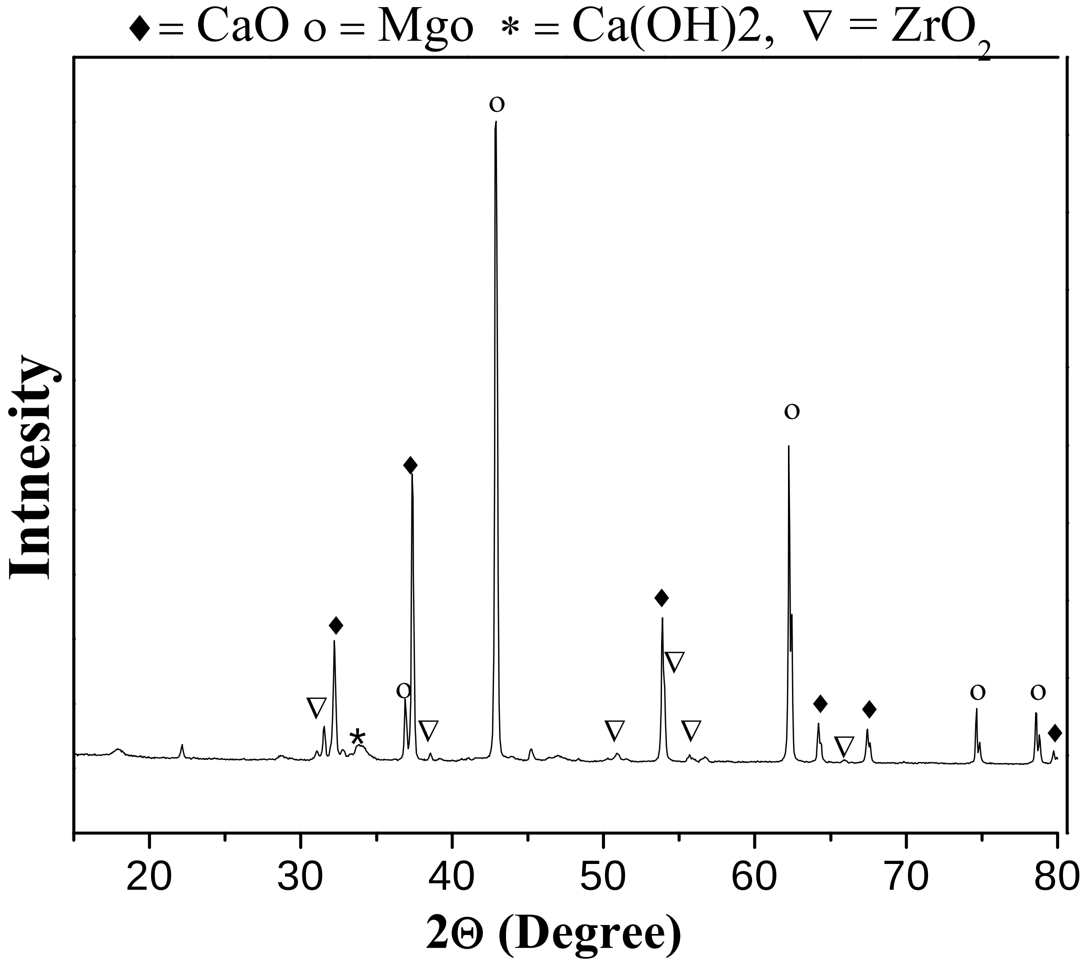


Fig 19:XRD pattern of specimen T4

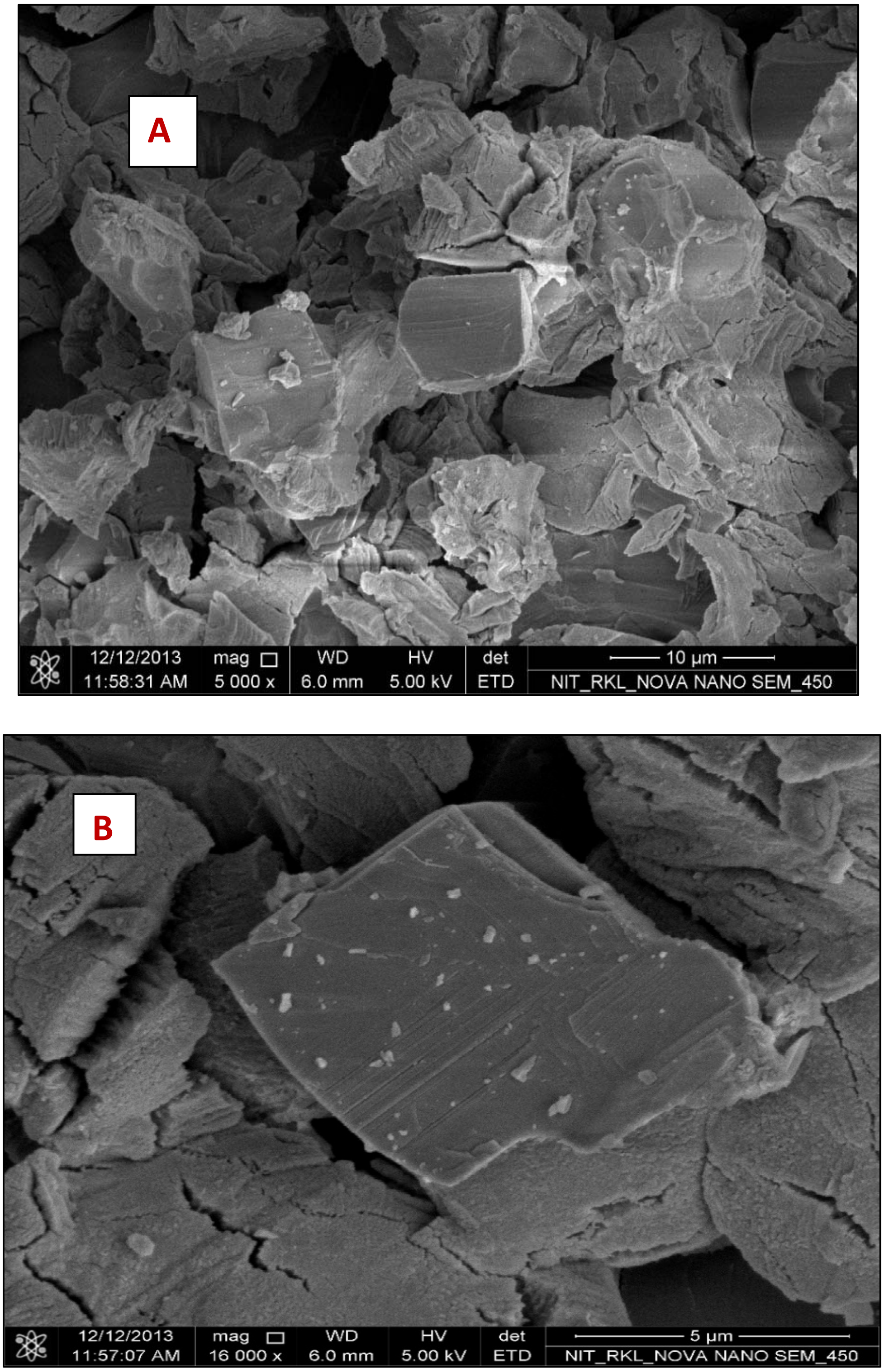


Fig 20 (a & b) SEM images shows the microstructure of specimen T4

The result (Fig 21)of composition T4 indicates that the PLC of the brick decreases that means the Cr_2O_3 is effecting for reduction of negative PLC. With these information the next two composition T5and T6 were formulated in which the Cr_2O_3 were varied, however no Zirconia.

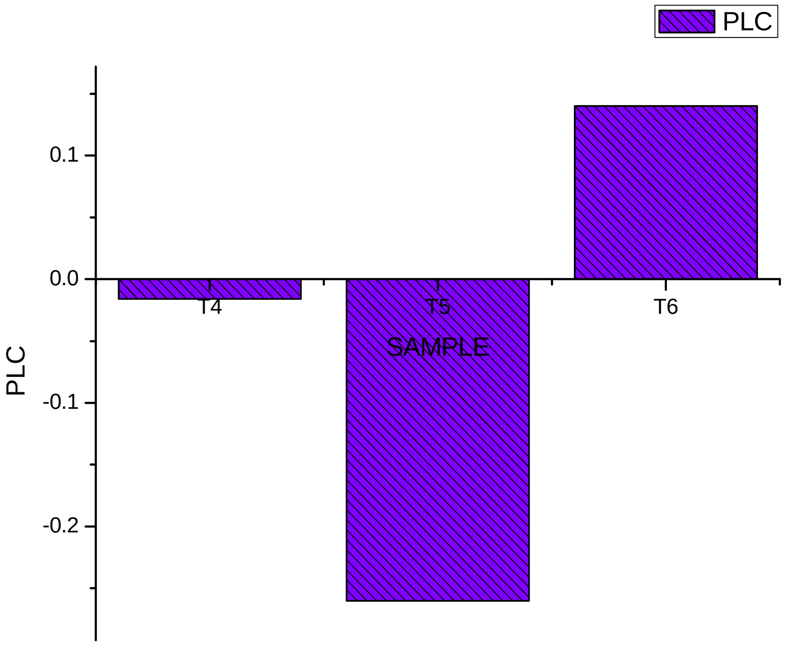


Fig 21: PLC ofspecimen T4,T5,T6

OBSERVATION OF T5 and T6

Fig 22 and 23 shows the XRD pattern of T5 and T6, the specimen were not having zirconia, for that reason there was no diffraction peak for calcium zirconate, other phases were almost similar. There were no diffraction peaks for chromium oxide which indicates that Cr_2O_3 has been observed inCaO or MgO, may be by forming spinel phase.

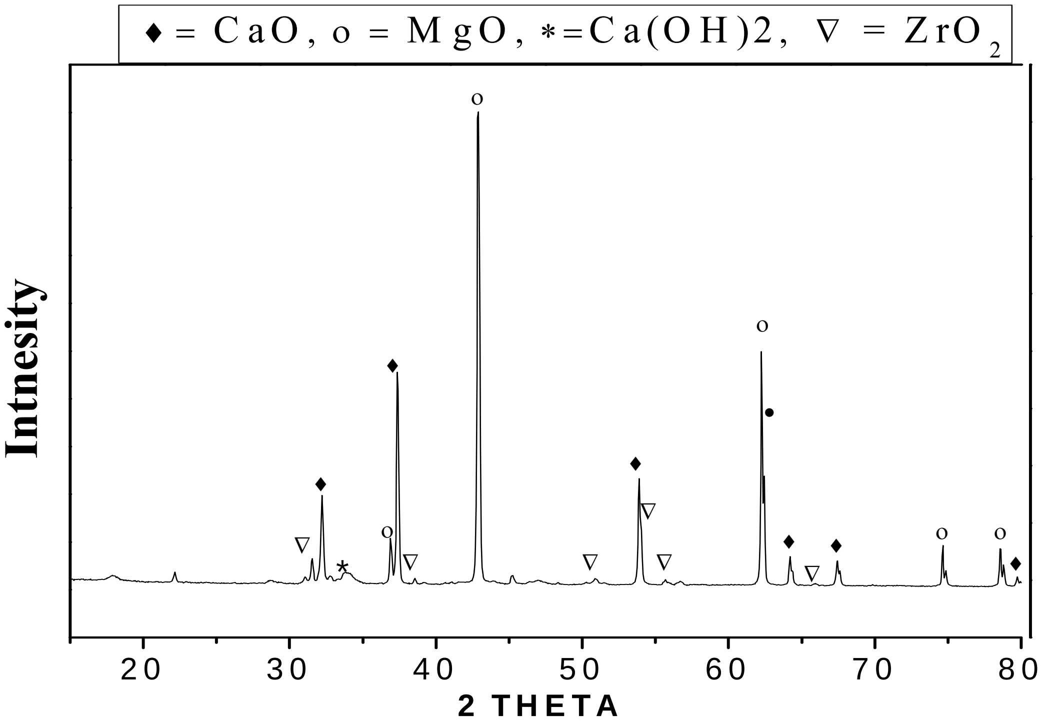


FIG 22: XRD pattern of specimen T5

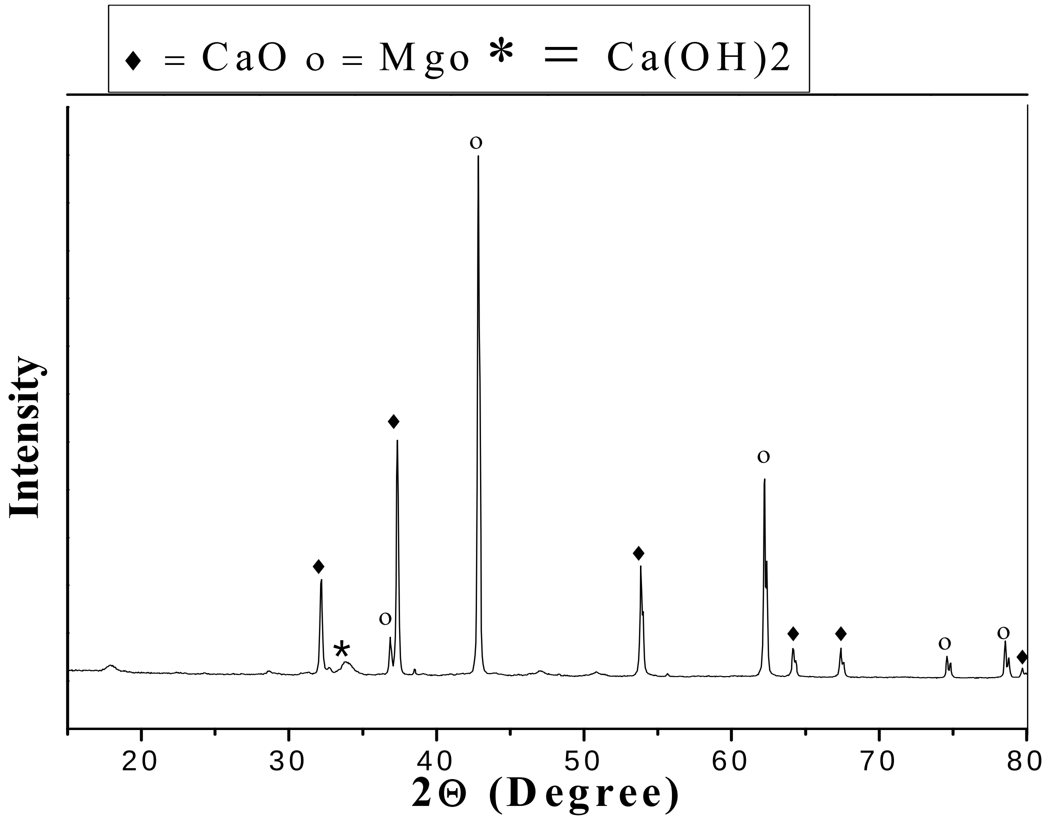
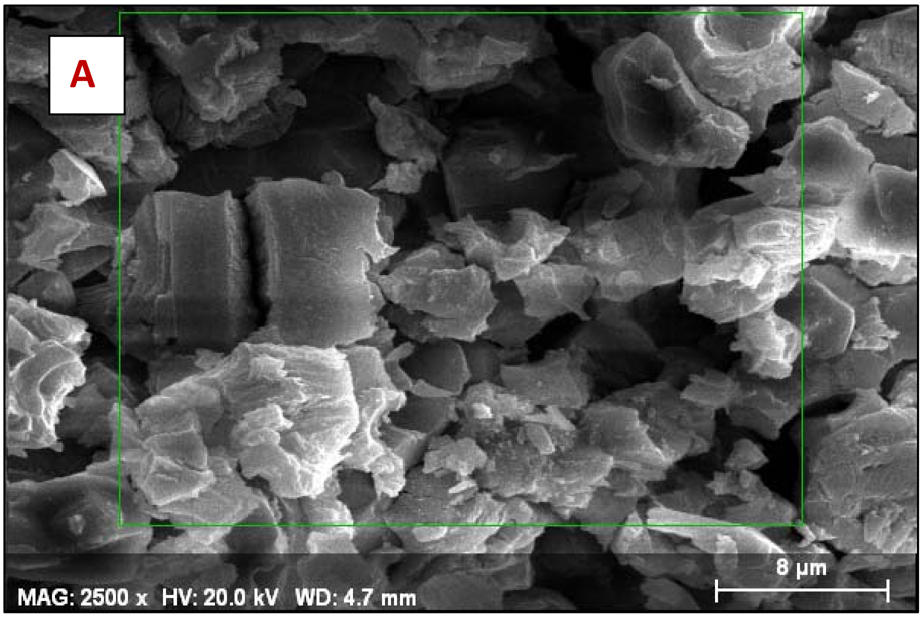
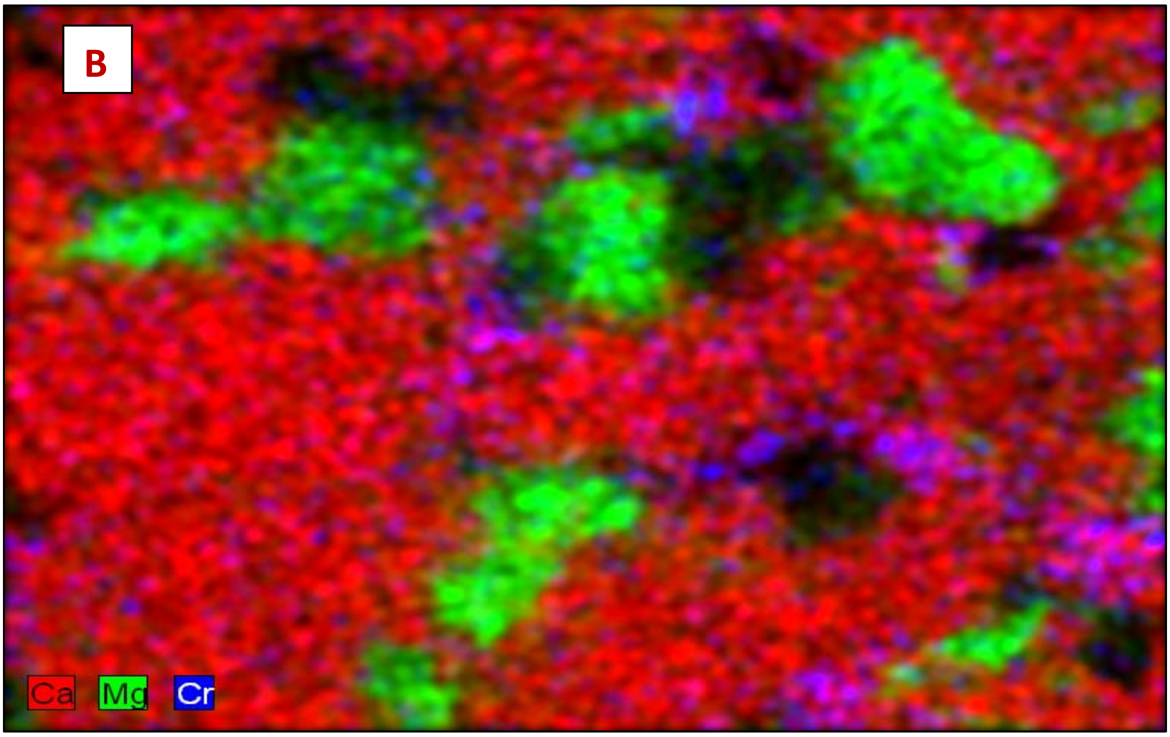


FIG 23: XRD pattern of specimen T6

SEM of T5 and T6 (Fig 24 & 25) shows similar distribution of CaO and MgO. The elemental mapping of both the specimen shows that chromium phase is homogeneously distributed. BD, PLC and CCS results were almost similar as shown in table 10, BD were almost similar to another specimen.





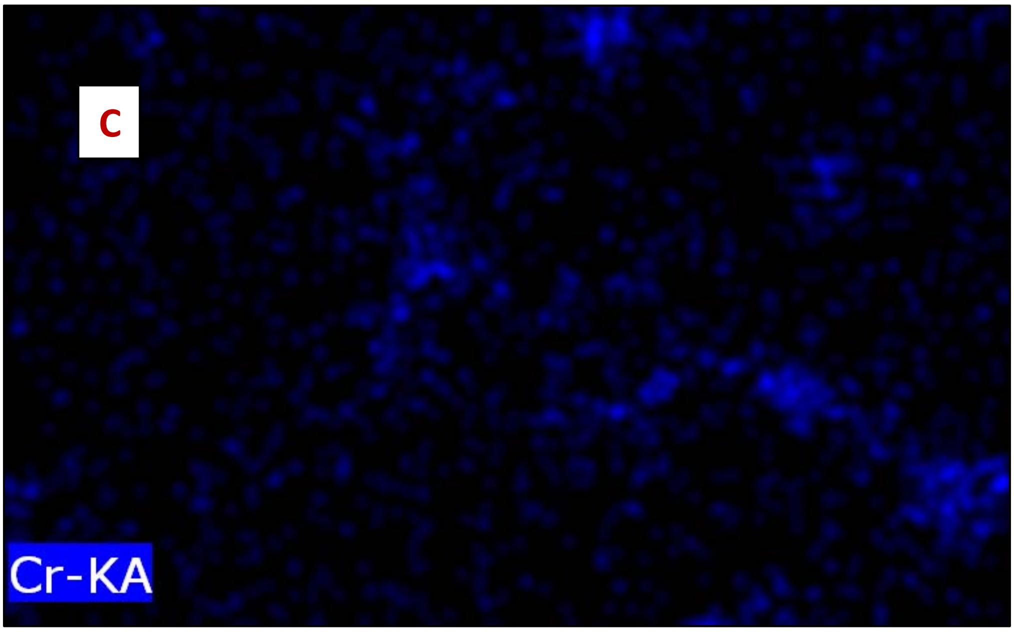
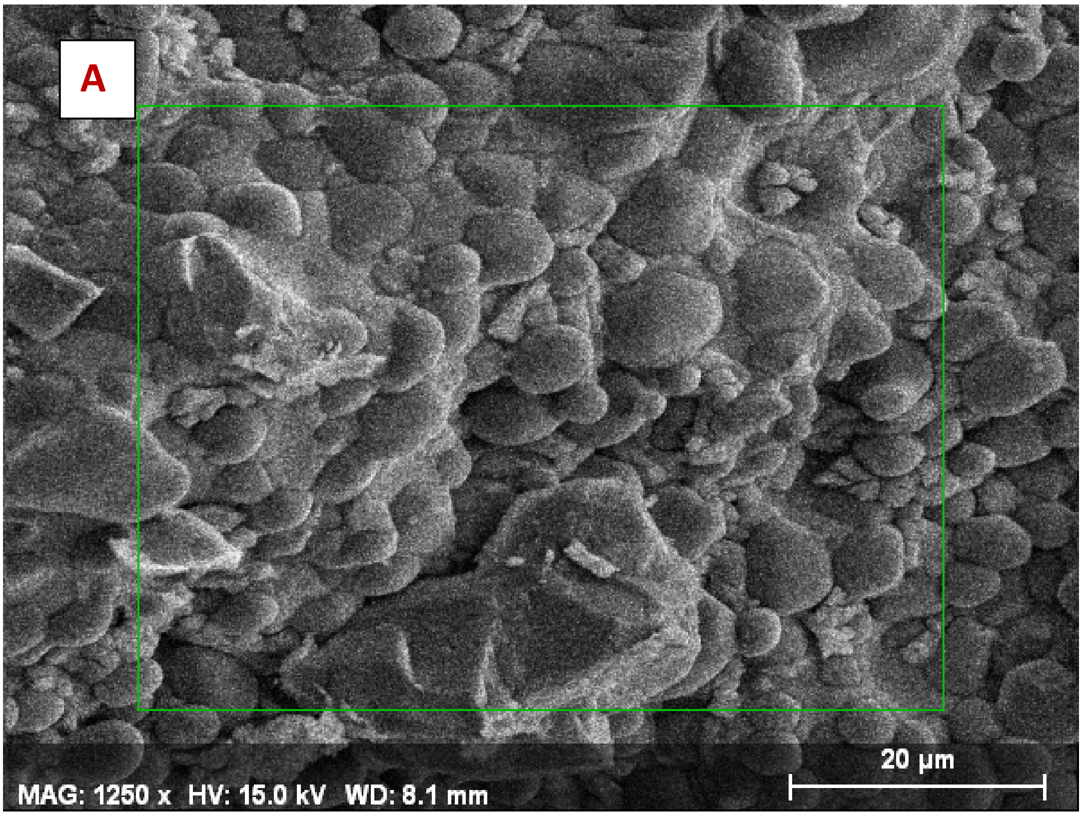


Fig 24(a) SEM microstructure of T5 specimen, (b) elemental mapping of, and (c) Cr-elemental mapping.



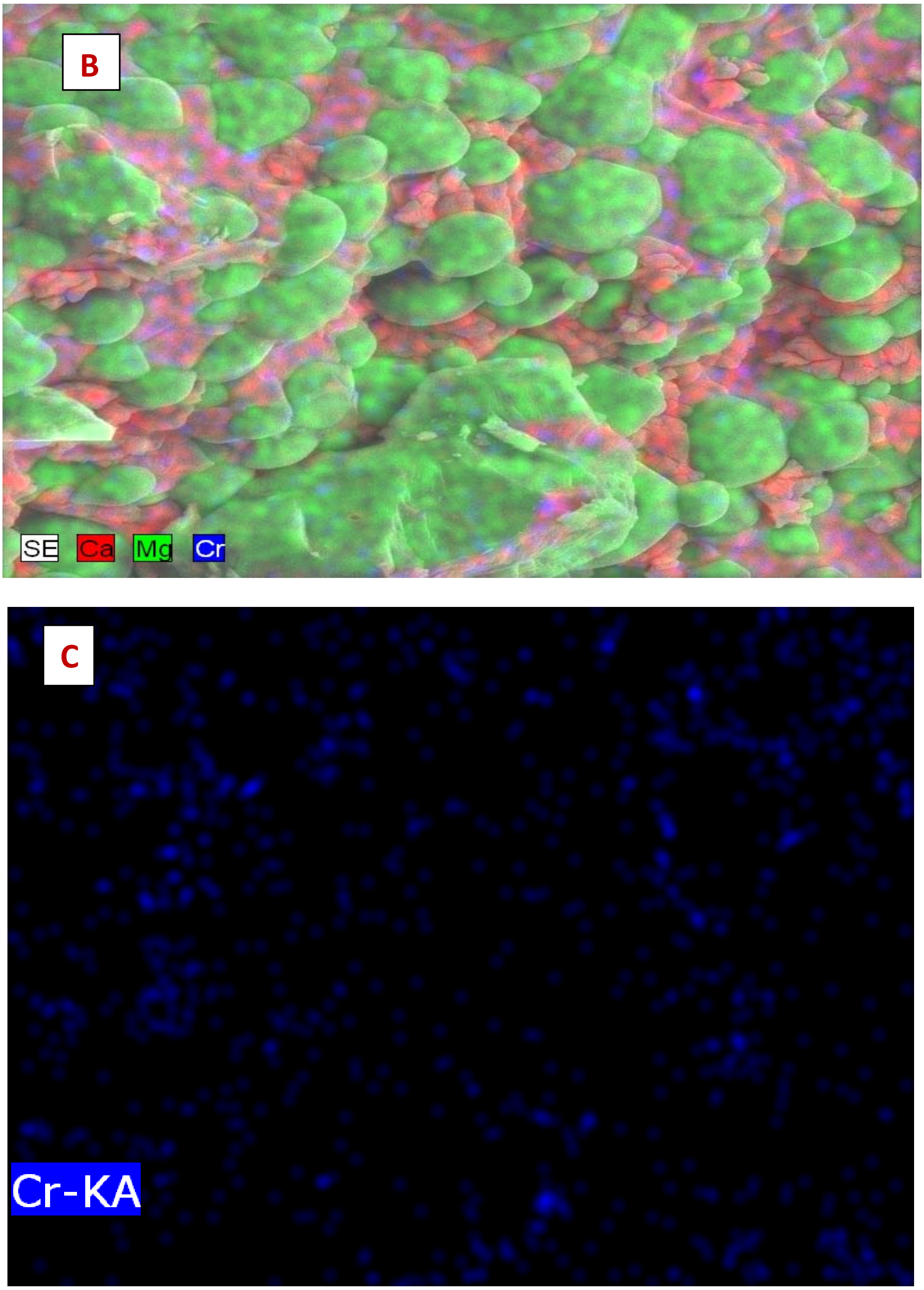


Fig 25 (a) SEM microstructure of T6 specimen, (b) elemental mapping of, and (c) Cr- elemental mapping.

However the CCS of T6 was higher than T5, this may be due to higher percentage of chromium oxide in T6.A significantly improvement in PLC was observed in T6 specimen.

The PLC was positive in T6 which is again due to higher amount of Cr_2O_3 in the dolo magnesite brick. The major reason for the positive PLC is due to the formation of chromate spinel phase. The spinelisation increases the volume with re – firing of specimen. Finally it may be concluded that Cr_2O_3 will be a very good additive for making positive PLC dolomite brick. Its CCS is slightly lower than nano Iron Oxide containing brick, further intensive studies is required to improve the CCS of the positive composition.

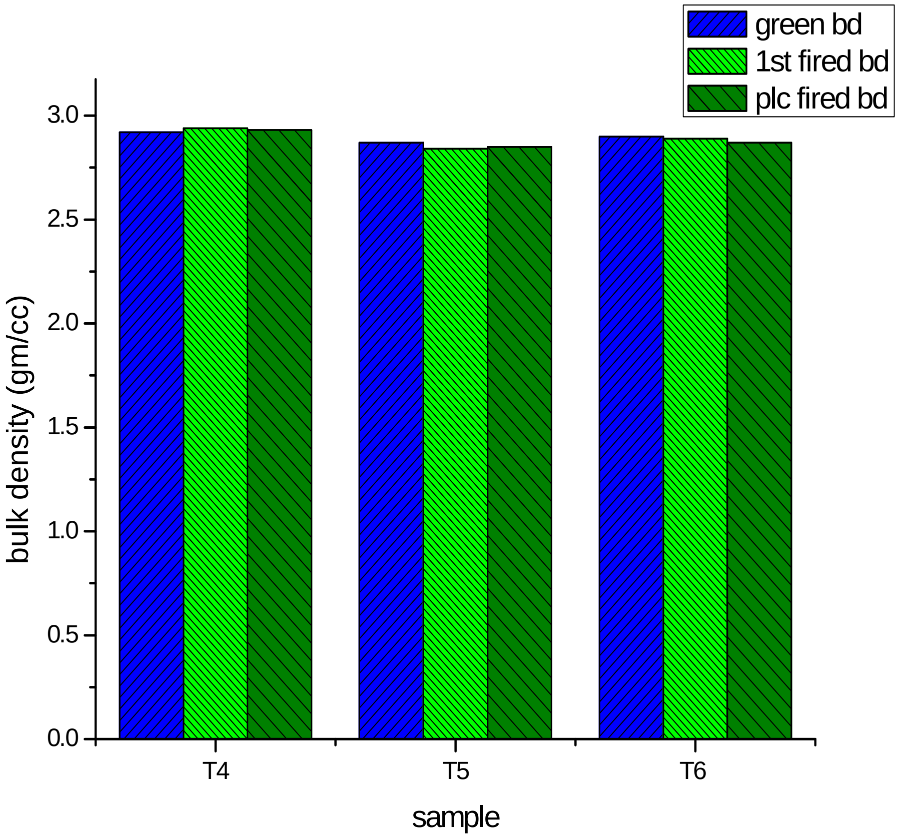


Fig .26 BD of Specimen T4, T5, T6

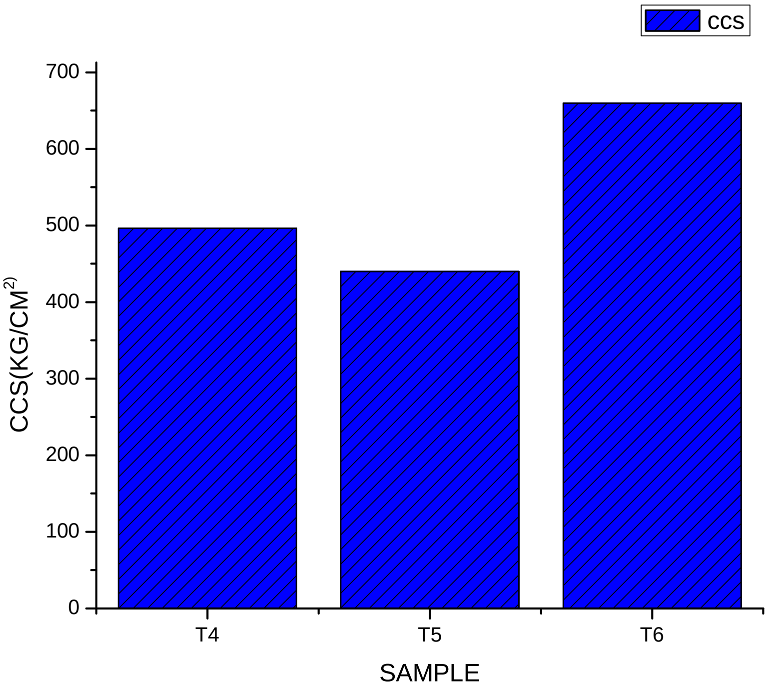


Fig. 27 CCS OF Specimen T4, T5, T6

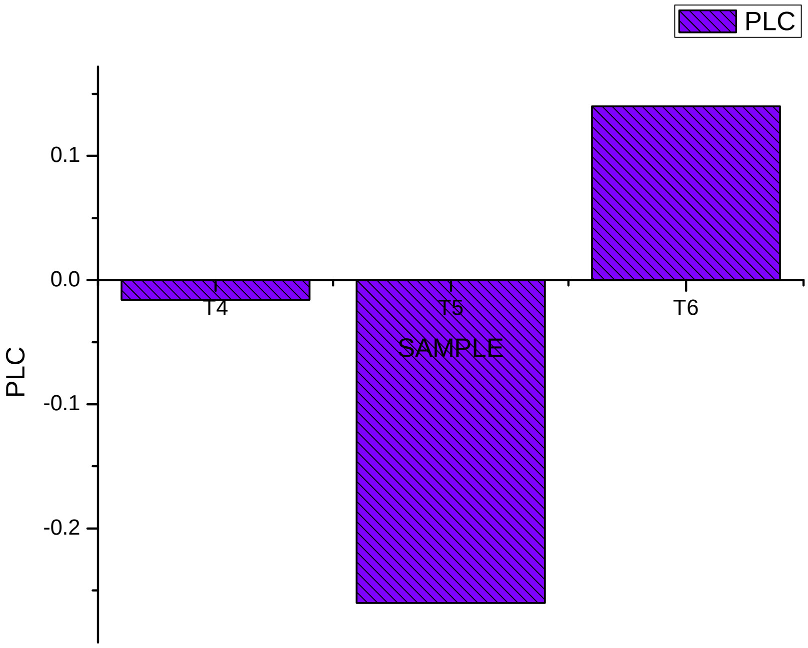


Fig. 28 PLC of specimen T4, T5, T6

TABLE: 10 Green BD,BD after 1STfiring and BD after 2ndfiring, CCS after PLC firing and PLC of six different samples

Sample No.	Dimensional BD (gm/cc)			CCS (kg/cm^2)	PLC acc. to height
	Green	1st fired	PLC fired		
T1	2.9	2.92	2.95	795	-0.23
T2	2.90	2.89	2.92	810	-0.34
T3	2.87	2.91	2.93	925	-0.19
T4	2.92	2.94	2.93	497	-0.016
T5	2.87	2.84	2.85	440	-0.26
T6	2.90	2.89	2.87	660	0.14

Table 10 shows that the green BD of all the specimen are almost similar which can be compared in the figure. The BD of allspecimenshowever decreases after firing to a little extent. The decrease in the BD upon firing may be due to evaporation of binder used for making the sample.BD also decreases due to poor firing (less sintering). According to the graph plotted (Fig.29) it can be said that the samples containing iron oxide and mill scale (T1, T2,T3) have higher CCS. Whereas the samples containing chrome (T4, T5, T6) has lower CCS than the iron oxide content samples. The specimen T4 contains zirconia and chrome, thus it has average CCS.

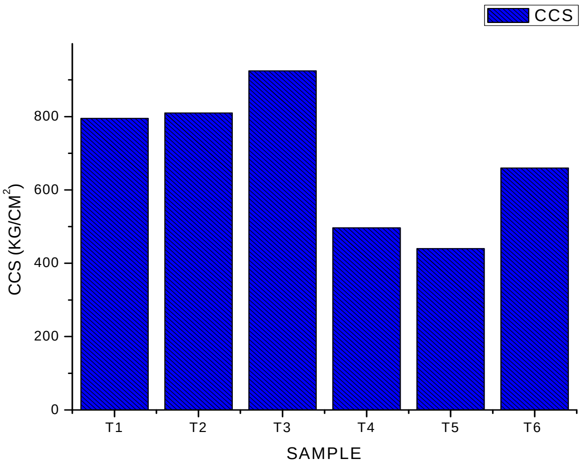


Fig .29 CCS of all the specimen

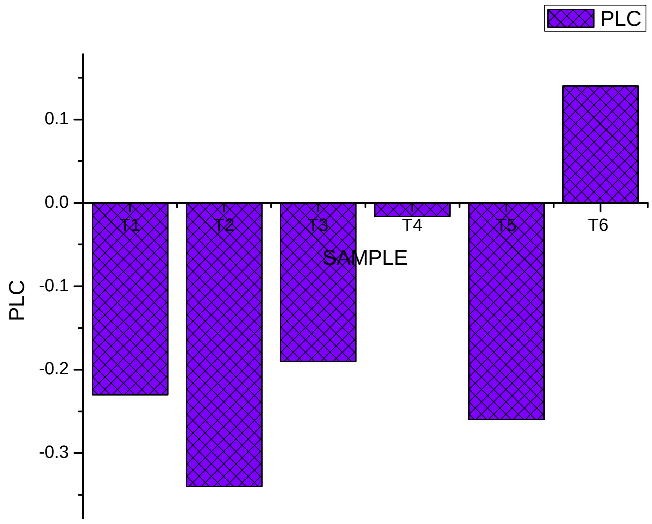


Fig .30 PLC of all the specimen

WEIGHT LOSS

The following table 11and Fig. 31 shows the weight loss during 1st firing and PLC firing. The weight loss during 1st firing is due to the evaporation of binder from the sample. During the PLC firing the dust raw material loses its grip from the outer surface and begins to come out in dust form, thus weight loss occurs.

Table 11:Weight loss of the specimen

Sample No.	Weight loss acc. to 1st firing	Weight loss acc. to PLC firing
T1	2.36	0.00
T2	2.33	0.00
T3	2.35	-0.03
T4	2.3	0.03
T5	2.37	0.03
T6	2.15	0.013

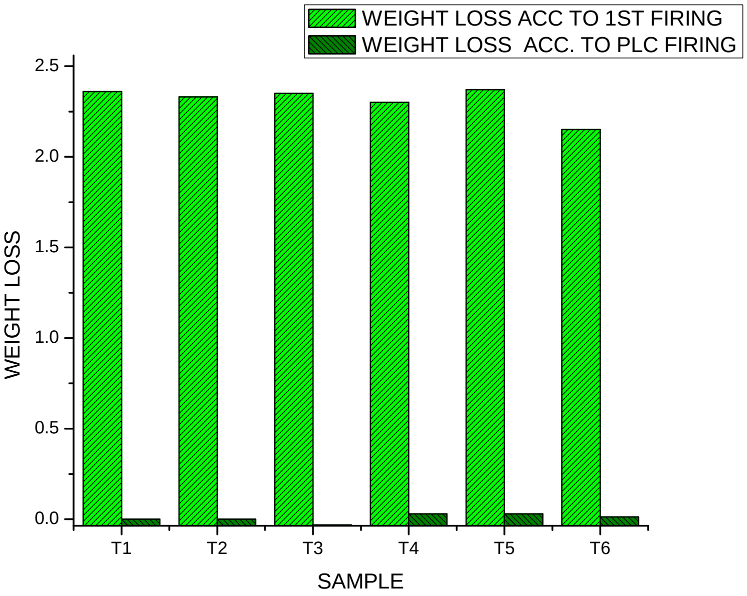


Fig .31Weight loss of different specimen

CONCLUSION

The major findings are:

- ✓ Able to achieve positive PLC (0.14%) by the addition of green chrome in the composition.
- ✓ CCS values of Trial Bricks T2, T3 containing iron oxide were excellent about 800 kg/cm^2.
- ✓ Uniform distribution of nano-iron oxide accelerate the formation of CaZrO3.

Finally, according to the work done, it can be concluded that by using chrome oxide we can achieve positive PLC, and thus it was successful.

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