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# Studies on densification, mechanical, microstructural and structure–properties relationship of refractory aggregates prepared from Indian magnesite by changing lime–silica ratio

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**Abstract**

The present work intends to study the development of refractory aggregates from Indian magnesite by modifying the lime–silica ratio. The raw magnesite has been evaluated in terms of chemical analysis, DTA-TG, IR Spectroscopy, XRD analysis. The material has been sintered at temperatures ranging from 1550 °C to 1700 °C along with modification of the lime–silica ratio. The sintered material has been characterized in terms of bulk density, apparent porosity, true density, relative density, cold modulus of rupture, hot modulus of rupture, thermal shock resistance, structural properties by XRD in terms of phase identification and evaluation of crystal structure parameters of corresponding phases by Rietveld analysis. The microstructures developed at different temperatures have been analyzed by FESEM study and compositional analysis of the developed phases has been carried out by EDAX study.


*Keywords:* A. Sintering; B. Microstructure-final; D. MgO; E. Refractories

## 1. Introduction

Magnesite is a well known raw material widely used for making magnesia refractories. The importance of basic oxide based refractories has increased considerably over the years due to the rapid expansion and changes in technology used in the iron and steel industry. The primary attributes which make magnesia an attractive choice are its high melting point (2800 °C) and excellent resistance to attack by iron oxides, alkalis and high lime content of flakes formed at the working temperature of steel melting furnaces [1]. Moreover, it does not suffer from issues of hydration like dolomite and lime while also being non-toxic. Today, magnesia for refractory production is obtained from three basic sources [2] (a) natural magnesite, (b) extraction from sea water, and (c) extraction from inland brine.

Magnesia refractories in India are manufactured mainly from naturally occurring magnesite. Though India has vast resources of natural magnesite, the Indian refractory industries are mostly dependent on imported magnesia. This is mainly due to the fact that Indian magnesite is rich in impurities like $SiO_2$ and $Fe_2O_3$ which degrade refractory properties at elevated temperatures.

In recent times, improvements in the performance of refractories have been made by using raw materials of high purity. However, cost becomes a limiting factor in the manufacture of high purity refractory. An alternative method to improve the refractory properties is to carefully design the phase assemblage or microstructure e.g., distribution of low melting phases which influences the thermal, thermo-mechanical, physico-chemical, mineralogical properties at high temperatures [3,4]. One of the most important and critical parameters in magnesia refractory is

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$CaO/SiO_2$ ratio [5] which significantly affects the formation of low melting phases.

In this background, an attempt has been made to study the effect of changing the $CaO/SiO_2$ ratio of lean grade Indian magnesite on its sintering characteristics, mechanical and thermo-mechanical properties and microstructural developments.

## 2. Experimental

Natural Indian magnesite of Salem district in Tamilnadu (supplied by erstwhile Burn Standard Co. Ltd., presently SAIL Refractory Co. Ltd., India) was selected for the present study. The $CaCO_3$ of S.D. Fine Chemical Limited, India was selected for changing the $CaO/SiO_2$ ratio of the batches. The chemical analysis was done by standard wet chemical procedure. 0.25 g of the sample was taken into a platinum crucible and the sample was thoroughly mixed with borax sodium carbonate fusion mixture and melted at around 900 °C for 1 h. After melting, the mass was cooled down and digested with nitric acid to obtain a solution. $Fe_2O_3$ and $TiO_2$ were measured by the colorimetric method. MgO, $Al_2O_3$ and CaO were determined by the complexometric method using EDTA solution. $Na_2O$ and $K_2O$ were measured by flame photometry using hydrofluoric acid and perchloric acid digested magnesite solution. $SiO_2$ was measured by the gravimetric method.

The magnesite, as received, was subjected to differential thermal analysis and thermogravimetric analysis which was carried out in Netzsch simultaneous thermal analyzer STA 449C. Samples in this study were ground to −200 mesh. The rate of heating was 5 °C/min upto 1000 °C and α-alumina was used as the reference material. The sample was also analyzed in terms of infrared analysis. A small amount of sample (0.2 g) was thoroughly mixed with ground KBr in an agate mortar and a disc (2.5 mm dia) was prepared in vacuum maintained at a pressing pressure of 33 kg/cm$^2$. The IR spectrograms of these discs were taken by Hitachi spectrophotometer (270-90). The structural characterization of the sintered aggregates in terms of phase identification and evaluation of crystal structure parameters like lattice parameters, unit cell volume etc was performed by X-ray diffraction technique. The XRD patterns of the samples were recorded in X'pert Pro MPD diffractometer (PANalytical) by X'Celerator operating at 40 kV and 30 mA, using Ni-filtered CuKα radiation. The XRD data were recorded with step size of 0.05° ($2\theta$), step time of 75 s, from 10° to 90°. The magnesite ores were crushed in a jaw crusher and hammered to pass through 100 mesh sieve. These powders were mixed with $CaCO_3$ in such a proportion so that the batch contained $CaO:SiO_2$ in 1:1 M ratio. Table 2 shows the batch composition and the sample code used in the experiment. Both the batches were milled separately in an attritor mill for 1 h with isopropyl alcohol as media. The slurry thus obtained was dried in a laboratory oven at 50 ± 2 °C for 24 h and passed through 100 mesh sieve. These powdered samples of both the batches were mixed with 5% (w/v) of polyvinyl alcohol (PVA) solution used as binder. Thereafter, these mixes were granulated by sieving and uni-axially pressed at 140 MPa pressure to produce pellets having 2.5 cm diameter and 1 cm height for densification studies and rectangular bars of 80 mm × 8 mm × 8 mm for thermo-mechanical and mechanical studies. Few rectangular bars were cold iso-statically pressed at 140 MPa for thermal shock studies. These green samples were dried at 110 ± 5 °C for 24 h and sintered in the temperature range of 1550–1700 °C with 2 h soaking at the peak temperature for evaluation of different properties. Sintered samples were characterized in terms of bulk density, apparent porosity, true density, relative density (% densification). The bulk density and apparent porosity were measured by water displacement method using Archimedes' principle. True density was measured with powdered samples in a pycnometer bottle. From these two values, percentage densification of the sintered samples was measured. The linear shrinkage of the sintered samples was measured using digital slide callipers. Crystalline phases of the sintered samples were identified from XRD patterns. The cold modulus of rupture (flexural strength at room temperature) of the sintered rectangular bars was measured by three point bending method using an Instron-1185 universal testing machine. The span of the bars was 40 mm and the cross head speed was 0.5 mm min$^{-1}$. The hot modulus of rupture (high temperature flexural strength) was measured at 1300 °C by an instrument supplied by Stedfast International Company Limited, India. The test was done under three point loading on a span of 45 mm during testing. The rate of temperature rise was maintained at 5 °C/min and samples were allowed a soaking period of 30 min at test temperature. The load then applied at a rate of 0.5 mm min$^{-1}$. Thermal shock resistance of the sintered samples was measured using the following test method. The sintered rectangular bars were heated upto 1200 °C with a soaking period of 30 min initially. Then they were exposed to normal room temperature air (without any draught in the surroundings) for 10 min and again put into furnace for 10 min. These complete one cycle. These samples are put upto ten cycles. The samples of second, fourth, sixth, eighth and tenth cycle were examined by measuring the retained flexural strength through three point bending method using an Instron-1185 universal testing machine. The span was maintained at 40 mm and the cross head speed was 0.5 mm min$^{-1}$. Microstructure evaluation of the sintered samples was done by scanning electron microscopy (Make Zeiss, Germany) on the polished surface after thermal etching. Elemental analysis was done by EDX technique using sintered polished samples.

## 3. Results and discussions

### 3.1. Raw material properties

The chemical analysis (Table 1) of raw magnesite shows that it contains impurities like 4.8 wt% $SiO_2$, 2.79 wt% CaO, 0.34 wt% $Al_2O_3$ and 0.48 wt% $Fe_2O_3$, on loss free basis. XRD pattern of raw magnesite shows the presence of rhombohedral Magnesite ($MgCO_3$) (ICSD code 40119) as the major phase & hexagonal Quartz ($SiO_2$) (ICSD code 18172) as the minor phase. The X-ray diffraction pattern is shown in Fig. 1 and indexed accordingly. Natural magnesite contains different