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Effect of waste serpentine on the properties of basic insulating refractories

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ABSTRACT

Basic insulating refractories were fabricated by the pressing route using dead-burned magnesia, pure calcined alumina, expanded perlite, and calcined waste serpentine as starting raw materials in four compositions from F1 to F4. Periclase and forsterite were major phases in F1 and F2 compositions, while spinel was also detected in the XRD patterns of F3 and F4 samples. Quantitative phase analysis showed that F4 sample sintered at 1450 °C has the highest forsterite content among all other samples. On the other hand, it has lower thermal conductivity compared to F1 to F3, and even lower than aluminosilicate IFBs with the same bulk density. It is concluded that forsterite is a highly insulating material, compared to periclase, corundum, periclase-spinel, aluminosilicates, such as mullite, etc.

1. Introduction

Insulating firebricks (IFB) were developed in the 1930s. The development of insulating refractories was followed by insulating castable and fiber refractories. Alumina-silicate insulating refractories are susceptible to basic environments. For this reason, basic insulating refractories, which are more resistant to alkaline conditions, are used extensively in basic environments [1]. Basic insulating refractories can be composed of cordierite, forsterite, chromite, magnesium aluminate spinel, and periclase or a mixture of them [2]. Magnesia (MgO), therefore, is one of the main components of all basic insulating refractories.

Although the importance of the basic insulating refractories is well recognized, there is a paucity of literature on the basic porous refractories. E. D. Miller et al. [2] invented basic refractory insulating shapes with various compositions from dead-burned magnesia (DBM), olivine, chromite, calcined alpha alumina, ball clay, and expanded perlite raw materials. Lightweight forsterite bricks were manufactured using combustible additives and formed by the semi-dry powder pressing, as reported by Tsigler et al. [3]. Kurilova et al. produced forsterite tuyeres and considered their wettability through molten metal and refractoriness as a possible replacement for the fused periclase [4]. Lightweight insulation materials were prepared by extrusion of raw forsterite tailings, caustic magnesia, and fused magnesia as the main raw materials, and rice hull powder was also used as a pore-forming agent [5]. Tsigler et al. [6] successfully employed lightweight forsterite refractories in the lining of kiln cars. Ding et al. produced a porous composite insulating material from forsterite and sodium carbonate media via a novel route [7]. Porous forsterite, spinel and periclase-spinel materials were invented in several patents [8–15]. W. Yan et al. produced porous MgO-Al_2O_3 refractory aggregates using an in-situ decomposition pore-forming technique [16]. In another study, they manufactured porous spinel ceramics from magnesite and $Al(OH)_3$ [17]. Deng et al. [18] used inexpensive foam-gelcasting to produce porous magnesium aluminate spinel. Porous magnesium aluminate spinel ceramic supports were fabricated by reactive sintering from low-cost bauxite and magnesite by Wanga et al. [19]. Porous magnesium spinel with directional pores was also fabricated by unidirectional solidification [20]. Sadek et al. [21] used a waste source of waste silica fume to prepare porous forsterite.

As mentioned in our earlier work [22], there are several million tons of waste serpentine in Abdasht chromite mines. In order to recycle waste serpentine, beneficiation process was conducted based on dry magnetic separation via drum separator. The non-magnetic fraction of the drum processing has high MgO content, so it can reach 47.85% after calcination at 1050 °C [22]. Forsterite, cordierite and cordierite-mullite ceramics were synthesized successfully using the beneficiated waste serpentine in our earlier works [22,23]. With the aim of finding a novel application of waste serpentine, we incorporated the calcined waste serpentine of Abdasht chromite mines into basic insulating refractories.

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Table 1
Chemical compositions (wt%) of the raw materials (Loss free).

Raw materials	NedMag DBM	Calcined alumina	Forsterite	Expanded Perlite
MgO	97.93	–	47.85	0.40
SiO_2	0.2	0.02	37.98	74.12
Al_2O_3	0.12	99.7	1.15	13.19
Fe_2O_3	0.52	0.03	7.96	1.34
CaO	0.74	0.03	0.42	1.34
Cr_2O_3	–	–	3.92	–
$Na_2O + K_2O$	–	0.15	–	9.51

2. Experimental procedures

2.1. Materials

High-grade dead-burned magnesium oxide (DBM, < 75 μm, NedMag), calcined alpha alumina (< 45 μm, CT 19, Almatis Co.), expanded perlite (Sepahan perlite, Isfahan, Iran) along with forsterite (Calcined waste serpentine at 1550 °C from our earlier work [22], < 75 μm) were used as raw materials, whose chemical compositions were determined with XRF method, as listed in Table 1. Polyvinyl alcohol (PVA) aqueous solution was also used as a binder. No combustible additive was used as a pore-forming agent. Table 2 shows technical data for Sepahan expanded perlite.

2.2. Methods

According to the recipes listed in Table 3, four groups of powder's mixtures were initially chosen for further investigation. Tumbling type mixer was used to minimize breakdown of the fragile perlite particles. For the least agglomeration of the mixture, the expanded perlite was mixed initially with 8 wt% of the binder aqueous solution for one minute. Other raw materials were then added to the wet perlite and mixed for more than 3 min. The mixture of powders was weighed and compacted to various molds according to different, standard tests by the low-pressure hydraulic pressing machine. With such a forming machine, a predetermined amount was calculated resulting in the green density of about 1130 kg/m^3, and it was charged to each mold, and then, the charge was compacted by the press to obtain the desired thickness. Thereafter, the specimens were dried naturally in a slightly warm environment for 24 h. An electrical furnace under air atmosphere was used for firing specimens at temperatures of 1250, 1350, and 1450 °C with holding time of an hour.

Phase analyses of ground powders prepared from sintered samples were performed using an X-ray diffractometer (philips-PW 3710) using Cu Kα (λ = 0.15406 nm) radiation at 40 kV and 30 mA. The wt% fraction of different phases (i.e., periclase, forsterite, MA spinel, cordierite) in the sintered samples was calculated on the basis of Rietveld refinement method. In this method, peak profile fitting was calculated based on the following equation [24]:

Table 2
Technical data for Sepahan expanded perlite.

Loose bulk density	59 (kg/m^3)
Hardness	5.5–7 (Mohs)
Melting point	1190 (°C)
Softening point	1093 (°C)
Thermal conductivity at 500 °C	0.05 (W/m K)
Particle size	0.5–3 (mm)

Table 3
Mixing recipes (wt%).

Raw materials	Formulation 1 (F1)	Formulation 2 (F2)	Formulation 3 (F3)	Formulation 4 (F4)
NedMag DBM	83	63	63	43
Calcined alumina	0	0	20	20
Forsterite	0	20	0	20
Expanded perlite	17	17	17	17

$$G_{ik} = \gamma \frac{C_0^{1/2}}{H_k \pi}[1 + c_0 X_{ik}^2]^{-1} + (1 - \gamma)\frac{c_1^{1/2}}{H_k \pi^{1/2}} \exp[-C_1 x_{ik}^2] \quad (1)$$

where G_{ik} is pseudo-Voigt function, $C_0 = 2$, $C_1 = 4 \ln 2$, H_k is the full width at half maximum (FWHM) of the K^{th} brag reflection, γ is shape parameter, and $X_{ik} = (2\theta_i - 2\theta_k)/H_k$.

ASTM C134 was applied to evaluate bulk density and dimensional measurements of the insulating specimens. Shrinkage on firing was measured using $(L_0\text{-}L_1)/L_0$ ratio (subscripts 0 and 1 refer to the sample dimensions before and after the sintering). ASTM C20 was also used to determine the apparent porosity. The cold crushing strength of the sintered samples at 1450 °C was measured using ASTM C133.

ASTM C210 (heating schedule of group 28, 1510 °C as the highest temperature) was used to measure permanent reheat change of the samples fired at 1450 °C. The thermal conductivity of the sintered samples at 1450 °C was measured up to 1000 °C using ASTM C182. Finally, the porous structures of the specimens sintered at 1450 °C were investigated by a scanning electron microscope (VEGA/TESCAN).

3. Results and discussion

3.1. Starting materials

Insulating refractory shapes and bricks naturally shrink during firing and require sizing step. However, in the semi-dry press technique, fired bricks are not subjected to the sizing process. Although the cost of production can be reduced regardless of sizing process, the firing shrinkage should be minimized to obtain the desired dimensions. The starting materials, therefore, must be pre-heated above 1510 °C, except for expanded perlite, due to prevention of shrinkage and undesirable phase changes of the samples in both thermal treatment up to 1450 °C (final sintering temperature) and during reheating test up to 1510 °C (final reheating temperature according to group 28 of insulating refractories). Therefore, NedMag DBM and calcined alpha alumina sintered at the temperature of around 1800 and 1600 °C, respectively, are the qualified starting materials. Furthermore, they are of high purity that prevents undesirable phases due to the impurities.

We showed that beneficiated waste serpentine derived from Abdasht chromite mines has 89.6 wt% of forsterite after firing process at 1550 °C. Moreover, it has the apparent porosity of 30.94% at this sintering temperature [22]. Therefore, thermal stability up to 1550 °C, considerable porosity level, and high MgO content (see Table 1) constitute the qualified characteristics of a semi-porous forsterite raw material for use in the composition of basic insulating refractories according to group 28.

Expanded perlite softens and melts at temperatures below 1200 °C (see Table 2); however, compositions of F1 to F4 are designed to take advantage of this fact. It is predicted that the perlite remains within the resulting structure through its combination with, or absorption into, more refractory constituents of the batch, i.e., the magnesia. The size of the expanded perlite particles is not significant, as reported in another