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Possible use of waste serpentine from Abdasht chromite mines into the refractory and ceramic industries

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ABSTRACT

There are approximately 20.5 million tons of waste rocks in Abdasht chromite mines which might cause considerable environmental problems in the near future. Serpentine is one of the most important rocks that can be abundantly found in this mine. In this work, the waste serpentine was processed by dry magnetic drum separator. Chemical analysis showed high content of MgO in the non-magnetic fraction (NMF) serpentine that reached to 47.85% after calcining at 1050 °C. The XRD result revealed that antigorite was the main phase of the NMF-serpentine while the major phase of the samples fired at 1050–1650 °C was forsterite. Considerable water absorption after 2 h dwell time at 1650 °C, indicated high refractoriness and high sintering temperature of the waste serpentine from Abdasht mines. These results proved the potential capability of waste serpentine from Abdasht mines as a raw material to be used in high temperature refractory and ceramic products.

1. Introduction

1.1. Olivine and serpentine

Olivine is a magnesium iron–silicate mineral with the formula of $2(Mg^{2+}, Fe^{2+})O \cdot SiO_2$. Its melting temperature depends on the volume fraction of the forsterite ($2MgO \cdot SiO_2$) and fayalite ($2FeO \cdot SiO_2$) phases with the melting temperatures of about 1900 °C and 1200 °C, respectively [1]. Fresh and unweathered olivine is, however, relatively rare because it readily takes up water and alters to serpentine (serpentinization process). Serpentine “polymorph” minerals are chrysotile, lizardite and antigorite [2] with theoretical densities in the range of 2.5–2.6 g/cm^3. It has the theoretical composition of SiO_2 (34.3%), MgO (44.1%), Fe_2O_3 (6%), Al_2O_3 (0.2%) and CaO (0.45%) [3]. Color of serpentine is usually green or grayish green [4]. The presence of aluminum, calcium, and alkaline oxides in serpentine is undesirable because these elements are not removed during the calcining process [5]. On the other hand, presence of chromite ($FeO \cdot Cr_2O_3$) with a high melting point (2160 °C [6]) in serpentine might be advantageous in some cases. For example, in refractories with calcined serpentine (forsterite) as the main raw material, magnesia and chromite (chrome spinel) are added deliberately to improve matrix properties (enhancing the refractoriness, corrosion resistance and high temperature strength) [7]. Presence of chromite reduces degree of wetting and depth of penetration of the forsterite containing refractories by slag (for steel-teeming ladles) [8]. Furthermore, relatively low linear thermal expansion of chromite [9] decreases the serpentine thermal expansion and this may be useful for some applications such as forsterite sands, cordierite ceramics and other kiln furniture.

The major applications for serpentine are flux materials for steel industry, fertilizer production, soil amelioration, extraction of amorphous silicate, carbon sequestration, extraction of pure magnesium compounds [3,10], refractory raw materials [4,5,7,11], ceramic industries raw materials [1,12–14] etc. Some beneficiation methods such as air classification [15,16], dry magnetic separation [5,15], gravitational separation, flotation [5] and calcination [17] may be required for serpentine-olivine ores in order to remove the gangue minerals and enrichment of the MgO content.

It is well known that serpentine should be calcined in order to obtain sintered angular shaped aggregates useful for various applications. The conventional methods for serpentine calcination normally involve firing the serpentine [17], whereby the following chemical reactions take place [17–21]:

dehydration at 600 °C to 780 °C to form a magnesium silicate:

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$$\underset{\text{(serpentine)}}{Mg_3(Si_2O_5)(OH)_4 \rightarrow 3MgO{\cdot}2SiO_2} + \underset{\text{(magnesium silicate)}}{2H_2O}$$

conversion of magnesium silicate into forsterite (Mg_2SiO_4) and free silica (SiO_2) which occurs at approximately 800 °C to 900 °C:

$$2(3MgO{\cdot}2SiO_2) \rightarrow \underset{\text{(forsterite)}}{3Mg_2SiO_4} + \underset{\text{(free silica)}}{2SiO_2}$$

Reaction of forsterite with free silica at 1000–1150 °C:

$$3Mg_2SiO_4 + SiO_2 \rightarrow \underset{\text{(forsterite)}}{2Mg_2SiO_4} + \underset{\text{(enstatite)}}{2MgSiO_3}$$

After firing at 1400 °C, rocks become dense and strong and the color changes from light brown to dark brown or nearly black. Upon further heating, dunites (rocks that contain more than 90% olivine-serpentine) begin to sinter which can be evidenced by decrease in the porosity [21].

1.2. Waste serpentine from Abdasht chromite mines

More than 74 chromite deposits have been discovered in various areas of Iran [22]. The Abdasht chromite mines are located in south of Kerman province (56°46′ 42″ E, 28° 21′ 05″ N) and in the Esphandaghe-Dolatabad zone. There are approximately 20.5 million tons of waste rocks in these mines and it is estimated that the wastes reach to 40 million tons in next five years.

The large quantity of waste rocks from Abdasht chromite mines might cause considerable environmental problems in the near future. Wastes are composed of a series of ultramafic rocks. Serpentine (weathered olivine) is one of the most important rocks which is abundant in this area. There has been no investigation on the use of waste serpentines in Iran.

The waste serpentine from Abdasht mines can be used with low cost but it needs some beneficiations before it becomes useable in various applications. This paper investigates possible use of the waste serpentine from Abdasht chromite mines as a raw material for the refractory and ceramic industries. It offers new economic opportunities and an effective solution to environmental problems.

2. Experimental procedures

Ten as-received samples of the waste serpentine (250 kg) were chemically analyzed (wet chemical analysis). The rocks were crushed with a jaw crusher down to a coarseness of −2.5 mm suitable for dry magnetic separation. Dry magnetic drum separator (Neodymium magnet, Drum rotate speed of 30 rpm, Field intensity of 3500 G) used for Fe^{2+}-silicate (fayalite) and serpentine separation is schematically illustrated in Fig. 1.

Differential scanning calorimetry (DSC, Netzsch, Germany) was used to study thermal behavior of waste serpentine samples (asrecieved) and the NMF serpentines. In order to determine the change in weight loss with calcination temperatures, the NMF serpentines were calcined in batch rotary kiln at a temperature range of 850–1100 °C. DIN 51,063 standard (electrical furnace, Max Temp. 1730 °C) was followed to measure refractoriness of both unfired and calcined NMF serpentine samples at 1050 °C.

Finally, the NMF serpentines were prepared in the form of cube specimens (25 mm) without exerting mechanical pressure to avoid the effect of pressure on sintering process and also to exactly simulate rotary kiln calcining process. Then the cube specimens were fired at 1050 °C, 1150 °C, 1250 °C, 1350 °C, 1450 °C, 1550 °C and 1650 °C in a programmable electrical furnace under air atmosphere using heating and cooling rates of 10 °C min^{-1} and a dwell time of 2 h. X-ray powder diffraction (XRD) patterns of samples acquired by a philips-PW 3710 (40 kV, 30 mA) with Cu Kα Radiation (λ=0.15406 nm) were used to determine the phase changes with increasing the temperature. The bulk density, apparent porosity and water absorption of the samples were measured using the boiling water method (ASTM C20). Shrinkage on firing was evaluated by a caliper and using the $(L_0-L_1)/L_0$ ratio (subscripts 0 and 1 refer to the sample dimensions before and after the sintering).

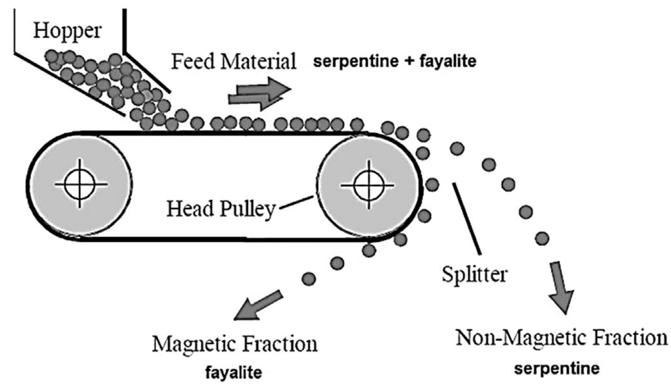

Fig. 1. Schematic illustration of the dry magnetic drum separator for fayalite separating.

3. Results and discussion

3.1. The waste beneficiations

As-received waste serpentines from Abdasht had grayish green appearance, 4.5 mohs' hardness, pH of 8.21 (ASTM D4972) and density of 2.65. Chemical compositions of ten waste serpentine samples and non-magnetic fractions (after drum separating) are presented in Table 1.

According to Table 1, considerable reduction of FeO is evident in the NMF serpentines. As only a negligible change is observed for Cr_2O_3 content during separation process, it can be said that the

Table 1
Chemical composition (wt%) of the waste serpentine and the NMF serpentine samples.

Oxides	MgO	SiO_2	CaO	FeO	Al_2O_3	Cr_2O_3	L.O.I
Waste serpentines							
1	35.43	35.31	0.28	13.29	0.94	3.33	10.78
2	31.21	38.02	0.47	15.07	0.98	3.62	10.01
3	35.03	35.89	0.42	13.78	1.00	3.24	10.11
4	35.78	35.08	0.27	13.17	0.87	3.79	10.45
5	31.24	38.29	0.38	14.11	1.01	3.80	9.79
6	35.80	35.40	0.26	13.38	0.88	3.28	10.48
7	35.77	35.50	0.36	13.01	0.89	3.37	10.61
8	35.81	35.06	0.28	13.29	0.84	3.31	10.79
9	36.40	35.10	0.22	13.03	0.68	3.77	10.37
10	35.14	36.39	0.33	13.32	1.04	3.26	10.04
Average	**34.76**	**36.00**	**0.33**	**13.55**	**0.91**	**3.48**	**10.34**
NMF serpentines							
1	43.49	33.31	0.29	6.91	1.01	3.44	11.39
2	37.12	35.84	0.59	9.78	1.15	3.83	11.52
3	43.26	33.39	0.53	6.94	1.08	3.40	11.27
4	43.33	33.22	0.26	6.32	0.92	3.58	11.94
5	37.11	35.80	0.45	7.79	1.02	3.94	11.95
6	43.66	33.37	0.32	6.91	0.90	3.46	11.22
7	43.91	33.32	0.28	6.92	0.92	3.42	11.05
8	43.23	33.72	0.29	6.16	1.04	3.49	11.90
9	43.52	33.47	0.34	6.90	0.70	3.41	11.55
10	42.49	34.41	0.44	6.96	1.01	3.56	11.00
Average	**42.11**	**33.99**	**0.38**	**7.16**	**0.98**	**3.55**	**11.48**

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