Estimation and addition of MgO dose for upgrading the refractory characteristics of magnesite ore mining wastes/by-products

E. Pagona¹, K. Kalaitzidou¹, E. Tzamos^{2, 3, 4}, K. Simeonidis^{4, 5}, A. Zouboulis², M. Mitrakas¹

¹Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece ²Department of Chemistry, School of Sciences, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

³ R&D Department, North Aegean Slops SA, 54627 Thessaloniki, Greece

⁴EcoResources PC, 54627 Thessaloniki, Greece

⁵ Department of Physics, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece

Corresponding author: mmitraka@auth.gr, Tel: +30 2310 996248

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Abstract

The optimum dose of MgO, in mining wastes/by-products of magnesite mine "Grecian Magnesite SA" (Chalkidiki, N. Greece), containing mainly serpentine ores, was calculated in order to maximize the formation of desirable olivine (forsterite) after thermal treatment at 1300° C, aiming to upgrade their refractory properties and find alternative uses under circular economy concept. For this purpose, five representative samples from the existing stocked piles of mining wastes were collected and their mineralogical phases were evaluated. The optimum doses of MgO addition (wt.%), calculated with a mass balance procedure, according to the expected mineralogical transformation reactions, ranged from 9.3-16 wt.%. Then, the effect of caustic calcined magnesia (MgO) addition of 5, 10, 15 wt.% to the mining wastes W12 and W13 was investigated, based on the fact that their optimum MgO doses are 9.4 wt.% and 15.6 wt.%, respectively. The main parameters, influencing refractoriness, i.e., firing shrinkage, water absorption, apparent porosity and bulk density, were determined. Mineralogical characterization was performed by X-Ray Diffraction (XRD) measurements. The addition of MgO increased the percentage of desirable olivine and eliminated the percentage of undesirable pyroxenes (enstatite) after thermal treatment (1300° C), improving refractory properties. The MgO addition also induced the formation of magnesioferrite and periclase (important refractory material). Firing shrinkage showed a decreasing trend, whereas water absorption and apparent porosity presented a small increase and bulk density a small decrease. These results indicate MgO as a suitable additive for upgrading the refractory properties of magnesite mining wastes, mainly by increasing forsterite formation and decreasing firing shrinkage.

Introduction

In the magnesite mine of "Grecian Magnesite SA" company at Gerakini (Chalkidiki, N. Greece) the total amount of mining wastes/by-products, generated due to the application of magnesite ore enrichment processes, is currently estimated to more than 35×10^6 tons. These mining by-products are consisting mainly of dunite and ultramafic rocks, stock-pilled in the mining area, without currently presenting any further utilization options. Dunites minerals are usually partially or completely transformed to serpentinites, which result from the modification of primary minerals (i.e., olivine and/or pyroxenes) towards the secondary minerals of serpentine group (e.g. lizardite, antigorite) [1-3]. Also, the ultramafic minerals from the same area, have not been subjected only to the serpentinization procedure, but they have also undergone to carbonization, silification and clay alteration [4].

Due to the mentioned serpentinization process, the volume of ultramafic rocks increases, because of large water quantities absorption. This fact leads to the decrease of their density, resulting finally to the deterioration of technologically desired physicochemical properties and eliminating their further use as refractory materials. This degradation procedure constitutes an important negative outcome, since it limits the possible economic and commercial exploitation of serpentinized rocks. The investigation of geochemical and thermodynamic parameters that influence the process of serpentinization, along with the development and application of an appropriate thermal treatment process with/or without the presence of specific additives could lead to the conversion of these mining wastes to refractory products, such as firebricks or magnesium-olivine refractory metallurgical masses. In addition, this approach is expected to favor new economic opportunities and an effective solution for potential environmental (e.g. disposal) problems, especially for the magnesite producing companies.

The scope of this research is the estimation of necessary MgO addition for improving the refractory properties of ultramafic rocks, which are hosting the magnesite ore deposits, by using the existing stocked piles of magnesite mining inert wastes. Also, how the MgO addition is affecting the main refractory parameters of selected samples, regarding the possibility to find new (alternative) uses for them after the application of a common thermal treatment process. The main characteristics that make magnesia (MgO) an attractive choice for refractories, are its high melting point (2800°C) and excellent resistance to attack by iron oxides and alkalis [5]. For this purpose, caustic calcined MgO added in 5, 10, 15 wt.% in the representative mining waste samples W12 and W13 and the fired samples at 1300° C evaluated accordingly, intending to develop an appropriate method for the conversion of these mining wastes into a potential commercial product with added value.

Experimental procedures

Qualitative and quantitative characterization of five samples (W12-W16) from stock-piled magnesite mining inertwastes performed in this study. The chemical composition of these samples was determined by Flame Atomic Absorption Spectroscopy (FAAS) and the mineral characterization of them was performed by X-Ray Diffraction (XRD); supplementary information received by Thermo-Gravimetric and Differential Thermal Analysis (TG-DTA). The Lossof-Ignition (LOI) test applied also to estimate the presence of volatile substances (hydroxyls, hydrates, carbonyls) in these mineral samples, which also subjected to thermal treatment, heated up to three different temperatures, i.e. 650°, 850° and 1300° C, by a programmable control electric furnace (type SNOL 6.7/1300 LSC01).

The samples W12 and W13 were further selected for the study of MgO addition, because they represent the minimum and maximum dose of MgO, respectively, for total forsterite formation. These samples blended/mixed with the MgO addition of 5, 10, 15 wt.% and subsequently, homogenized with the help of a laboratory ball mill. The total weight of each blend was 5 g. Therefore, the quantity of additives (for the respective ratios 5, 10 and 15 wt.%) was 0.25, 0.5 and 0.75 g respectively, and the rest of the blend was the examined mining waste sample. MgO which was added, is caustic calcined magnesia (CCM) with: 84,5 wt.% MgO, 0.2 wt% FeO, 0.5 wt% Al₂O₃, 1.85 wt.% CaO, 0.65 wt% Na₂O, 7.9 wt.% SiO₂ and LOI 4.2%. The ground/homogenized samples were pressed into cylindrical pellets of 2 cm diameter, and heated with a programmable control electric furnace (type SNOL 6.7/1300 LSC01) up to 1300° C. The temperature was increased with a heating rate 10° C/min and remained at the desired value for 2 h; afterwards, the samples were cooled to room temperature. Following the thermal treatment process, and in order to evaluate the refractory behavior of produced specimens, the following parameters measured: Apparent Porosity (AP(%), Bulk Density (BD) and Water Absorption (WA(%), by applying the boiling water method (ASTM C20), whereas the Firing shrinkage (FS(%) parameter measured by a calibrated calibrated the diameter and using the $(D_0-D_1)/D_0$ ratio, where the subscripts 0 and 1 refer to the sample dimensions before and after the application of thermal process. Finally, the thermally treated pellets were sufficiently pulverized for the subsequent mineralogical characterization. The structural and mineralogical characterization of fired samples was performed with the X-Ray Diffraction (XRD), using a Brücker D8 Advance diffractometer (powder XRD); the respective data collected at 2θ from 5° to 70°, scan time 0.2 s and increment of 0.02. The filament X-ray tube of Cu with a wavelength 1.5418 Å and the detector LYNXEYE (1 D mode) were used. The qualitative and quantitative analysis of XRD patterns performed with the JADE XRD data analysis software.

Results and discussion

The results from the applied characterization methods reveal the mineral and chemical composition of examined samples, as well as their degree of serpentinization. The chemical composition of these samples (Table 1) shows the following range of constituents' percentages: SiO₂ 40.5-45.3 wt%, MgO 40.8-42.9 wt%, FeO 7.1–7.4 wt%, Al₂O₃ 0.4-1.4 wt%, CaO 0.35-1.6 wt%, Na₂O 0.30-0.40 wt%; smaller content of the components K₂O, MnO₂, NiO, Cr₂O₃ also detected. In the TG-DTA curves an exothermic peak was observed, due to the formation of forsterite, at temperatures around 850° C [6, 7] which is higher for the sample W12 compared to W13 (Figure 1).

Sample	W12	W13	W14	W15	W16
			%		
MgO	42.9	40.8	41.5	42.2	41.8
FeO	7.3	7.2	7.1	7.2	7.4
Al ₂ O ₃	0.50	1.4	0.65	0.70	0.40
CaO	0.35	1.6	0.71	0.85	0.35
Na ₂ O	0.30	0.30	0.35	0.40	0.30
SiO ₂	41.5	44.5	45.3	44.1	40.5
LOI	6.7	4.1	3.8	4.1	8.8
			mg/kg		
K ₂ O	650	730	80	720	920
MnO ₂	1460	1510	1560	1490	1410
NiO	3110	2870	2880	2930	2990
Cr ₂ O ₃	450	850	790	835	320

Table 1. Chemical composition of major and minor oxides content (%) in the examined mineral waste samples.



Fig1. TG-DTA curves of samples W12 and W13.

The XRD patterns of these samples show the presence of various serpentine minerals, such as antigorite and lizardite [1]. Depending on the obtained results, the samples can be further divided in two sub-categories: (1) samples W12-W15, consisting mainly from olivine, serpentine and enstatite, and (2) sample W16, consisting mostly from olivine and serpentine. These samples (W12-W16) selected for further thermal treatment, applying three different temperatures, i.e., 650°, 850° and 1300° C, and the mineralogical and structural transformation of the so treated fired products re-evaluated by applying XRD measurements for these three different temperatures. It was demonstrated that for the temperature range 650-680° C serpentine is almost totally decomposed and at the temperature around 850° C it has been totally recrystallized towards the olivine and pyroxenes phases. At even higher temperature treatment (1300° C), it seems that there is a re-crystallization process, favoring the deformation of olivine and the further configuration of pyroxenes, due to the excess of Si presence (Table 2) [8]. Also, the increase of treatment temperature seems to favor the formation of an amorphous phase, which is not desired for the production of refractory materials.

Sample (Temperature, °C)	Olivine	Pyroxenes	Serpentine
W12 (25)	65.1	8.4	26.4
W12 (650)	79.0	13.1	7.9
W12 (850)	80.9	19.1	
W12 (1300)	66.0	34.0	
W13 (25)	52.9	19.6	27.5
W13 (650)	64.8	26.8	8.3
W13 (850)	76.3	23.7	
W13 (1300)	55.0	45.0	
W14 (25)	56.3	25.6	18.1
W14 (650)	66.6	29.3	4.1
W14 (850)	65.4	34.6	
W14 (1300)	50.5	49.5	
W15 (25)	64.6	20.5	14.9
W15 (650)	73.8	24.0	2.2
W15 (850)	76.2	23.8	
W15 (1300)	60.9	39.1	
W16 (25)	49.1		50.9
W16 (650)	58.1		41.9
W16 (850)	100.0		
W16 (1300)	61.8	32.2	

 Table 2. Mineralogical content (wt.%) for the thermally untreated (25° C) and treated at various temperatures mineral waste samples.

Based on the initial concentrations of MgO, FeO and SiO₂ in samples W12-W16 and the mass balance equations, it was made possible to calculate the necessary quantity of MgO (moles)/100 g for each sample. Afterwards, the wt.% dose of MgO additive was calculated, in order to quantify the theoretical addition of MgO for the optimization of olivine formation [9], according to the respective chemical/mineralogical equations. The calculations rely on the fact that, MgO react with SiO₂ and forms forsterite, in ratio 2:1 (Equation 1).

 $2MgO + SiO_2 \rightarrow Mg_2SiO_4$ (forsterite) (1)

From the results of Table 3, it can be clearly shown that in all cases, samples are deficient in MgO. The ideal molar ratio of ([MgO]+[FeO])/[SiO₂] is two, while the results show that the values are lower than the ideal ratio, because the qualified chemical composition of these samples don't reflect the presence of 100 wt.% olivine, which is related with the ideal ratio Theoretically the calculated MgO dose could lead to the optimum crystallization performance in these conditions for the improvement of the refractory properties of the treated material, for the optimized olivine formation, in the starting material at 1300° C. The theoretical addition of wt% MgO for the optimization of olivine formation, ranges between 9.3-16 wt.%. Regarding the wt.% necessary dose of MgO, the samples W12 (deficient dose 9.3 wt.%) and W13 (deficient dose 15.6 wt.%) were selected for the production of pellets with 5, 10 and 15 wt.% MgO supplementary addition.

Table 3. Calculation of MgO dose for optimization of olivine formation

Sample	MgO	SiO ₂	FeO	Optimum MgO dose	Optimum MgO dose
		mol/100 g			wt.%
W12	1.141	0.741	0.109	0.232	9.4
W13	1.056	0.773	0.104	0.386	15.6
W14	1.070	0.785	0.104	0.397	16.0
W15	1.092	0.766	0.103	0.337	13.6
W16	1.137	0.740	0.113	0.230	9.3

The Firing Shrinkage (FS(%) levels (Figure 2) showed a decreasing trend for both selected mineral waste samples. For the samples W12 and W13 the FS(%) of the initial samples from 4.9% and 4.8% decreased down to 1.9% and 2.3%, respectively, with the addition of 15 wt.% MgO. The addition of MgO can maximize the formation of forsterite for the examined firing temperature of 1300° C [Table 2], resulting to the improvement of refractory properties of fired products, enhancing in that way the FS(%) levels and keeping them in $\leq 2.5\%$ values. The shrinkage during the firing process constitutes an important factor for the production of refractories, as a firing shrinkage more than 5% degrades the material, either due to the formation of cracking, or because of large parts' detachment from the product, thereby affecting the mechanical strength (e.g., of bricks). Therefore, the relatively high values of firing shrinkage for the final products, is an important problem that should be carefully addressed during the preparation and use of refractory materials [10].



Fig2. Firing shrinkage of samples W12 and W13 vs. the wt.% presence of MgO.

The WA(%) and AP(%) values with the addition of MgO increased from 9 to 12.8% and from 21 to 28%, respectively for the sample W12, and from 6.3 to 10.8% and from 16 to 25% for the sample W13 (Figure 3). These values are considered as slightly higher, than the permissible limits to produce MgO commercially applicable refractory products, as the AP(%) values range usually between 18-21% for the bricks containing 90% MgO, and between 17-20% for the respective bricks with 98% MgO [11].



Fig 3. WA(%) and AP(%) values of samples W12 and W13 vs. the wt.% presence of MgO addition.

Bulk Density (BD) values showed a decreasing trend with the increase of MgO addition, e.g. for the sample W12 this parameter decreased from 2.49 g/cm³ of the initial sample to 2.23 g/cm³ by 15 wt.% MgO addition and for the sample W13 from 2.57 g/cm³ to 2.37 g/cm³, respectively (Figure 4).The decrease of BD values agrees with the small increase of AP(%), following the addition of MgO, since the BD measurements present generally a reverse relation with the AP(%) measurements. The BD levels in this case are lower, than the BD levels of common magnesium refractories ranging from 2.8-2.95 g/cm³) [11]. The higher AP(%) levels when combined with the lower BD values indicate that the fired products are not sufficiently sintered (and homogenized) in this high temperature (1300° C) by applying the specific percentage of additives. This fact agrees also with the low FS(%) levels, because sintering is often associated with volume reduction (shrinkage increase), which can affect WA, AP, BD, as well as the dimensional and geometrical precision.



Fig 4. Bulk density measurements of samples W12 and W13 vs. the wt.% presence of MgO.

The XRD patterns of examined samples with the addition of MgO reveal the following (Table 3 and Figure 5):

- ✓ The initial samples (i.e., without the MgO addition) consist mainly of olivine (forsterite) and pyroxenes (enstatite).
- ✓ The addition of MgO has induced the formation of magnesioferrite and periclase. The percentage of magnesioferrite is rather stable at around ~7-9% (Figure 5).

✓ The percentage of unwanted pyroxenes (mainly enstatite) decreased with the increasing addition of MgO, while the percentage of desirable forsterite increased. The increase of MgO quantity maximizes the formation of olivine after the application of thermal treatment at 1300°C. This was considered a positive result, due to the overall better refractory properties of olivine, compared with the presence of pyroxenes. The products with the highest percentage of olivine and the lowest percentage of pyroxenes have shown better refractory properties after the application of thermal treatment at temperature 1300° C, i.e., present lower firing shrinkage values.



Fig. 5. XRD patterns of samples W12 and W13 with 5, 10 and 15 wt.% of MgO addition, after the application of thermal treatment at 1300° C.

 Table 4. The mineralogical content (wt.%) of examined mineral waste samples with the addition of MgO after firing at 1300° C.

Sample (MgO wt.%)	Olivine (Forsterite)	Pyroxenes (Enstatite)	Magnesioferrite	Periclase
W12	66.5±4.6	33.5±2.4		
W12 (5%)	84.2±5.6	7.7±0.9	8.1±0.6	
W12 (10%)	90.3±6.4		8.6±0.6	1.1
W12 (15%)	85.2±5.7		8.2±0.6	6.6±0.6
W13	56.2±3.9	43.8±2.7		
W13 (5%)	74.8 ± 4.9	15.8 ± 1.4	$9.4{\pm}0.7$	
W13(10%)	86.2±5.8		7.1±0.6	
W13(15%)	90.2±6.2		7.7±0.6	2.1±0.4

Conclusions

The thermal treatment in combination with the addition of MgO, as was applied to the mining wastes from stocked piles of magnesite enrichment ores processes can modify them, favoring the production of potentially useful refractory products, and improving the circular economy in the mining field. The important FS(%) parameter decreased in combination with the increase of desirable forsterite percentage and the decrease of unwanted enstatite in the fired products. The physical properties of AP(%) and BD are a little higher and lower, respectively, than the relevant technical requirement levels for the common magnesium refractory products. The higher AP(%) values combined with the lower BD values indicate that the fired products are not sintered enough by applying this temperature at the specific percentages of examined additives, which in turn can reduce the enstatite and increase the forsterite percentage, respectively, a very important factor for the refractory properties of fired products.

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