Chemical Processing of Egyptian Magnesite Rocks for Refractory Purposes

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ABSTRACT. Chemical processing of two dolomitic magnesite rocks by scrubbing with dilute hydrochloric acid has delivered magnesia concentrates of good quality, containing very low levels of calcium oxide. The recovered magnesia samples were used for the preparation of magnesia and magnesia-chrome refractory bricks of acceptable properties.

The Egyptian magnesite rocks contain variable amounts of dolomite as impurity and, therefore, they are not suitable for production of good-quality basic refractories. At the present time, all basic refractory industries in Egypt mainly depend on imported magnesia. Magnesia containing free CaO has a great tendency to slake with a large increase in volume causing the mass to disintegrate. Such slaking might occur during transport and storage of the calcined materials or during the preparation of magnesia bricks.

The complete dead-burning of lime present in magnesite ores was not found to be satisfactory. The traditional solution of this problem is the formation of hydration-resistant compounds through addition of certain stabilizer materials which are capable to bring the C/S mole ratio in the fired magnesite bodies to less than 2 (Girgis and Gad 1970). This prevailing ratio could also be obtained by elimination of a certain percentage of the lime impurity in the magnesite rocks either by mechanical or chemical processing.

The present work deals with chemical processing of some Egyptian dolomitic magnesite rocks to obtain good-quality magnesia concentrate containing low level of CaO, and suitable for the preparation of magnesia and magnesia-chrome refractory products.

Materials and Methods

The two magnesite rocks under investigation were presented from Gebel Maiyet, Barramiya, and from Ambaout, Mersa Alam (Fig. 1). They are found in the form of veins of varying thickness along joint plains in serpentine rocks. Serpentine and dolomite are often found associated with the magnesite rocks. Their origin has been cited to be metamorphic, formed by the action of
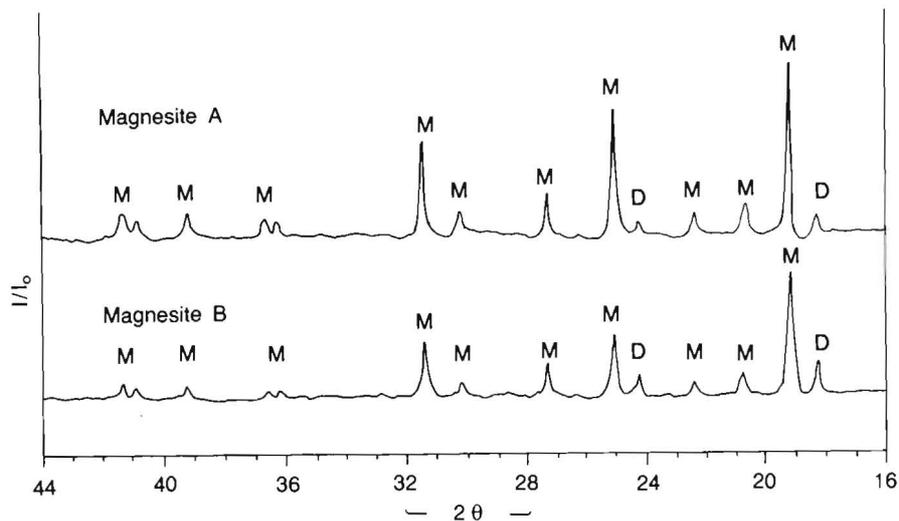

Fig. 1. Locations of the investigated Egyptian magnesite rocks

hydrothermal carbonate solution in rocks rich in magnesium silicates (Hume 1934 and Attia 1948). The chemical constitutions of these magnesite rocks were determined by applying the standard methods, and their mineral compositions were identified through a combination of differential thermal analysis and X-ray diffraction method.

Both samples were ground to -1 mm and calcined at 1000°C and were then processed by scrubbing with amounts of dilute hydrochloric acid equivalent to the calcium content in the magnesite ores at a solid:liquid ratio of 1:4 in a porcelain ball mill run at 30 rpm for 15 min. The samples were then filtered, washed, dried and analysed. The magnesia concentrates were subjected to some physico-chemical tests and were used as a starting material for the preparation of magnesia and chrome-bearing magnesia refractory bricks.

Two different batches were prepared from the magnesia concentrates. The first batch of magnesia was mixed with 3 weight % of ilmenite ore as a densification agent. The second batch of magnesia was mixed with 20 weight % of finely ground (−0.1 mm) chromite ore for producing magnesia-chrome bricks. Sample briquettes of 25 mm diameter and about 25 mm height were semi-dry moulded under a pressure of 800 kg/cm^2. The moulded samples were dried in air for 24 hr, dried in an oven at 100°C for another 24 hr, and were fired at 1550°C in a tunnel kiln. The resulting clinkers were subjected to several tests including: chemical analysis, specific gravity determination, hydration tendency measurements, and X-ray diffraction in order to identify their quality.

Magnesia and chrome-bearing magnesia bricks should have regular texture, all particles being less than 3.34 mm diameter and are graded so as to fill the interstices without significant voids. The produced clinkers were crushed, ground, and classified into two grain sizes -3.34 + 0.125 and -0.125 mm. Optimum grain size combinations were found through a series of packing density determinations. The results revealed that a mix composition of 70 weight % of coarse fraction and 30 weight % of fine fraction gave the best packing results. The grain size distribution of the selected compact mix was determined by means of mechanical sieve analysis. Anyhow, the following gradings were used for the preparation of the bricks:

| −3.34 + 0.5 mm	−0.5 + 0.125 mm	−0.125 mm
60 weight %	10 weight %	30 weight %

Sample briquettes of 50 mm diameter and about 50 mm height were semi-dry moulded under a pressure of 800 kg/cm^2, carefully dried and fired at 1550°C in a tunnel kiln. The physical and refractory properties of the fired bricks were determined by the British Standard Testing (1967) procedure. The mineralogical constitution of the fired bricks were determined by means of X-ray diffraction analysis.

Results and Discussion

The chemical constitutions of the raw and calcined magnesite rocks are presented together with that of the Barramiya chromite ore in Table 1. The results indicated that the magnesite rock of Mersa Alam contains much higher calcium oxide as compared to that of Barramiya. Figure 2 shows the X-ray diffraction patterns of the two magnesite rocks which indicate that magnesite is the major constituent mineral in both samples whereas dolomite is present in relatively higher amount in the magnesite rock of Mersa Alam. Differential thermal analysis of the two magnesite rocks was carried out at a heating rate of 10°/min up to 1000°C. The plots (Fig. 3) show a deep endothermic peak "a" at 650°C due to the decomposition

Table 1. Chemical constitution of the raw materials

Component %	Barramiya magnesite (A)		Mersa alam magnesite (B)		Barramiya chromite ore
	Raw	Calcined	Raw	Calcined	
SiO_2	0.70	1.40	1.21	2.39	6.31
Fe_2O_3	0.11	0.22	0.32	0.53	18.36
Al_2O_3	0.64	1.39	0.77	0.52	15.10
CaO	4.47	8.61	8.30	16.35	0.82
MgO	44.67	88.35	40.16	79.23	17.11
Cr_2O_3	—	—	—	—	39.78
L.O.I.	49.38		49.26		2.26
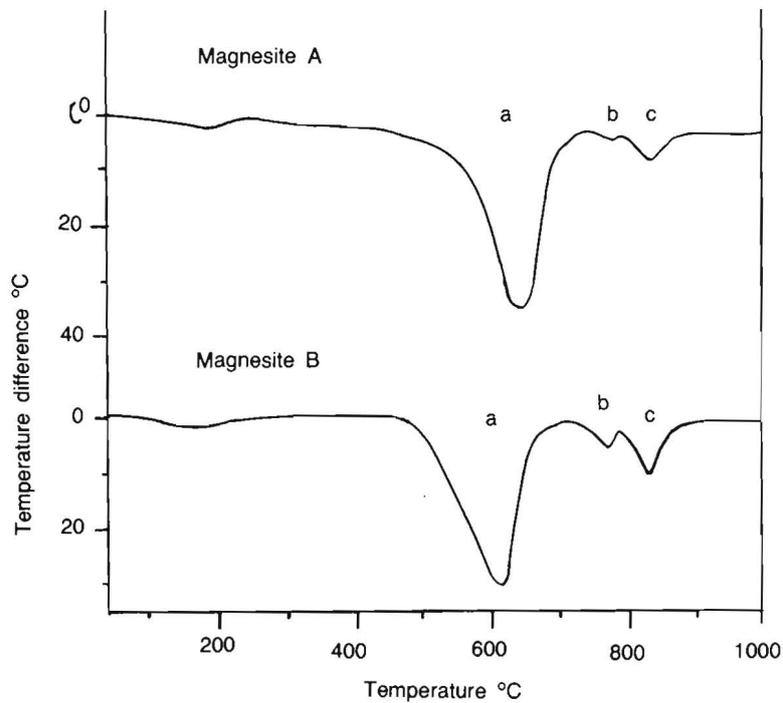
Fig. 2. X-ray diffraction patterns of the raw magnesite (Co Kα Radiation).
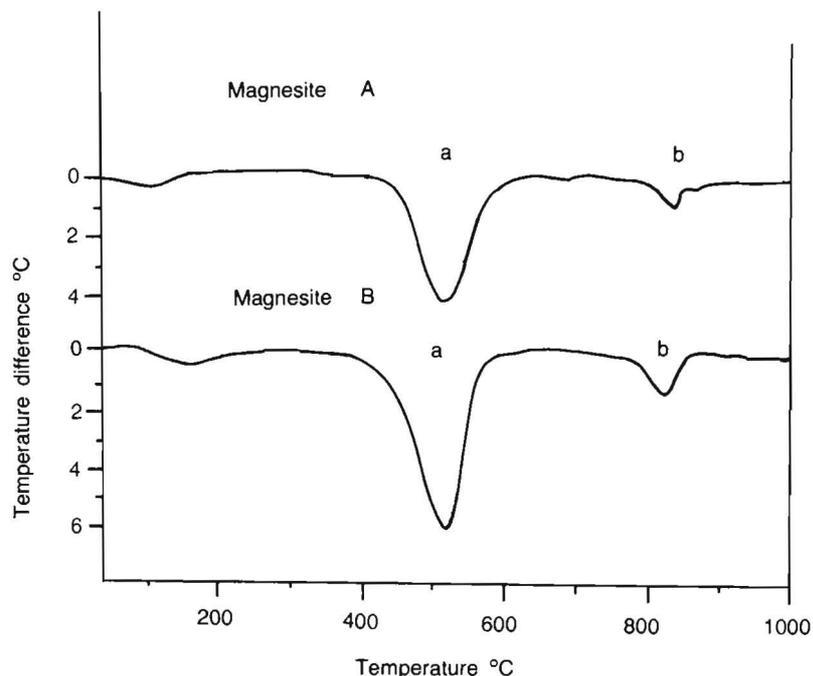M = Magnesite mineral
D = Dolomite

Fig. 3. Differential thermal analysis curves of the raw magnesites

of magnesite. The double endothermic peaks "b" and "c" at 810° and 860°C respectively are characteristic of the decomposition of dolomite. Thus, the D.T.A. plots support the results of the X-ray diffraction that the dolomite content is much higher in the Mersa Alam magnesite rock. The D.T.A. plots for the two calcined samples after hydration are shown in Figure 4. The endothermic peak "a" at 510°C is due to the dehydration of $Ca(OH)_2$. The endothermic peak "b" at 810 is due to the decomposition of a $CaCO_3$ compound. These results confirm the presence of free lime in both samples which was hydrated and partly converted to $CaCO_3$ during storage of the calcined samples. The presence of free CaO in both samples is also confirmed by thermal equilibrium data on the composition of the calcined magnesite rocks as shown in Table 2.

Beneficiation of such type of magnesite rocks by flotation technique may be economically unpromising. The finely disseminated dolomite impurity requires grinding of the magnesite ores to extremely fine particle size (−0.1 mm) in order to
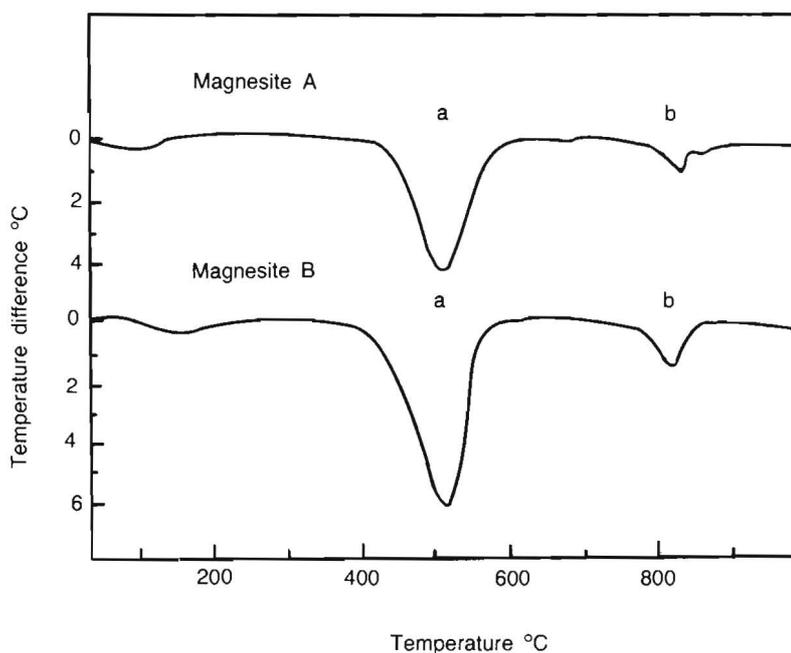
Fig. 4. Differential thermal analysis curves of calcined magnesites

Table 2. Thermal equilibrium data on the composition of the fired magnesite raw materials

Phase	C/S mole ratio	C_3S	C_4AFS	C_3A	Free CaO	MgO
Barramiya rock	1:6.6	5.32	0.56	3.32	2.43	88.35
Mersa alam rock	1:7.3	9.06	1.93	2.97	6.92	79.13

achieve a high degree of liberation. Fine grinding of the hard magnesite rocks seems to be costly because of high energy consumption.

Scrubbing of the calcined magnesite rocks with dilute hydrochloric acid selectively leached out the lime impurity, delivering high grade magnesia concentrates. Table 3 presents the chemical composition of the two processed

Table 3. Chemical analysis of the magnesia concentrates

Component %	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
Barramiya rock	1.26	0.40	1.41	0.52	96.20
Mersa alam rock	1.93	0.72	1.64	0.77	94.70

magnesia concentrates which seem to be very close to each other. The levels of calcium oxide in the two concentrates are in the range of 0.52 - 0.77% CaO.

To adapt these magnesia concentrates for refractory purposes, they should be fired at very high temperatures to render them dead-burned and suitable for brick-making without undue difficulties of hydration and shrinkage. The specific gravity of the dead-burned magnesia should not be less than 3.50. Hydration tendency should be at minimum ($< 2\%$ L.O.I.). These conditions may be achieved by increased bulk density and decreased apparent porosity to ensure that a lower surface area of the refractory body is exposed to the atmosphere.

It was found difficult to sinter the magnesia concentrates to a high density on firing at 1550°C. Therefore, sintering aids such as TiO_2 or Fe_2O_3 should be added in order to enhance sintering. In the present work, 3 weight % of the cheap domestic ilmenite ore (42% TiO_2 and 39% Fe_2O_3) was added as a densification agent which proved to be effective for achieving good sintering performance (Table 4). Densification of magnesia in the presence of ilmenite is a result of intensive recrystallization of periclase. High sintering effect is achieved in the presence of cations with higher valency than Mg^{2+} (such as Fe^{3+}, Ti^{4+}, or Zr^{4+}) (Bron and Bicharina 1960).

Table 4. Characteristics of dead-burned magnesia concentrates

Sample	SiO_2	Fe_2O_3	Al_2O_3 + TiO_2	CaO	MgO	Specific gravity	Hydration tendency
Free magnesia concentrate	1.40	0.58	1.53	0.65	95.72	3.45	2.90
Magnesia concentrate + 3 weight % ilmenite	1.42	1.02	2.43	0.62	94.40	3.50	1.30

The refractory-grade dead-burned magnesia produced from natural magnesite rocks should contain MgO in the range of 88 - 94%. The presence of about 5%

Fe_2O_3 and 3 - 3.5% SiO_2 is not usually objectionable, but they nevertheless reduce the refractoriness of the end-product. The most harmful impurity in dead-burned magnesia is CaO, and an amount less than 2.5% is practically acceptable. Only a small amount of liquid CMS is formed at low levels of CaO ($<$2.5%) and consequently does not deteriorate the refractory properties of the end-product (Wecht 1960). The chemical constitution of some commercial-grade dead-burned magnesia derived from natural magnesite rocks is given in Table (5) (Chesters 1957). It is clear that the characteristics of the prepared dead-burned magnesia concentrates meet the specifications of the refractory-grade magnesia, and may be considered as a suitable starting material for the production of magnesia and magnesia-chrome refractory products.

Table 5. Chemical constitution of some selected dead-burned magnesite (Chesters 1957)

Component %	Austria Radenhein	Greece Euboea	Russia	Manchuria	India	Egypt (present work)
SiO_2	2.1	2.6	4.7	2.8	5.4	1.42
Al_2O_3	2.4	0.4	1.1	2.3	0.4	2.43
Fe_2O_3	3.9	0.5	2.7	1.9	0.7	1.02
CaO	2.3	2.0	5.7	1.8	2.6	0.62
MgO	89.0	95.3	85.2	90.8	90.8	94.40

Alternatively, addition of 20 weight % of chrome ore to the magnesia concentrates resulted in volume-stable magnesia-chrome clinker when being fired at 1550°C. For manufacturing magnesia-chrome mixes, low CaO/SiO_2 mole ratio ($<$ 1) should be present in order to prevent the formation of the low-melting chromia and calcia compounds which deteriorate the quality of the end product (Staut 1972). Firing of the sample at high temperatures converts the components into highly stable refractory spinels and bounds the silica into forsterite M_2S and monticellite CMS.

The MgO content of magnesia raw material is not in itself the major characteristic controlling the properties and performance of the refractory product. The type, quantity, and relative proportions of the chemical impurities present in the magnesia have a fundamental effect on its properties. The technical properties of the prepared refractory bricks directly depend on the amount and nature of the phases present. The mineral composition of the two types of refractory bricks was calculated from the data of the chemical analysis (Table 6) and is in agreement with the results of the X-ray diffraction patterns (Fig. 5). The calculations proceeded in

Table 6. Thermal equilibrium data on the composition of the prepared magnesia- and magnesia-chrome bricks

Type of refractory bricks	Chemical constitution, weight %						CaO/SiO$_2$ mole ratio	Calculated Mineralogical Composition, weight %					
	SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	Cr$_2$O$_3$	CaO	MgO		CMS	M$_2$S	MF	MA	MK	M
Magnesia Bricks	1.42	1.02	2.43	–	0.62	94.40	0.466	1.72	1.76	[1.28	3.38]	–	91.75
Magnesia-chrome bricks	2.13	3.74	3.07	7.65	0.70	82.58	0.352	1.95	3.22	[4.67	4.27	9.66]	76.10

S = SiO$_2$, C = CaO, F = Fe$_2$O$_3$, A = Al$_2$O$_3$, K = Cr$_2$O$_3$, M = MgO
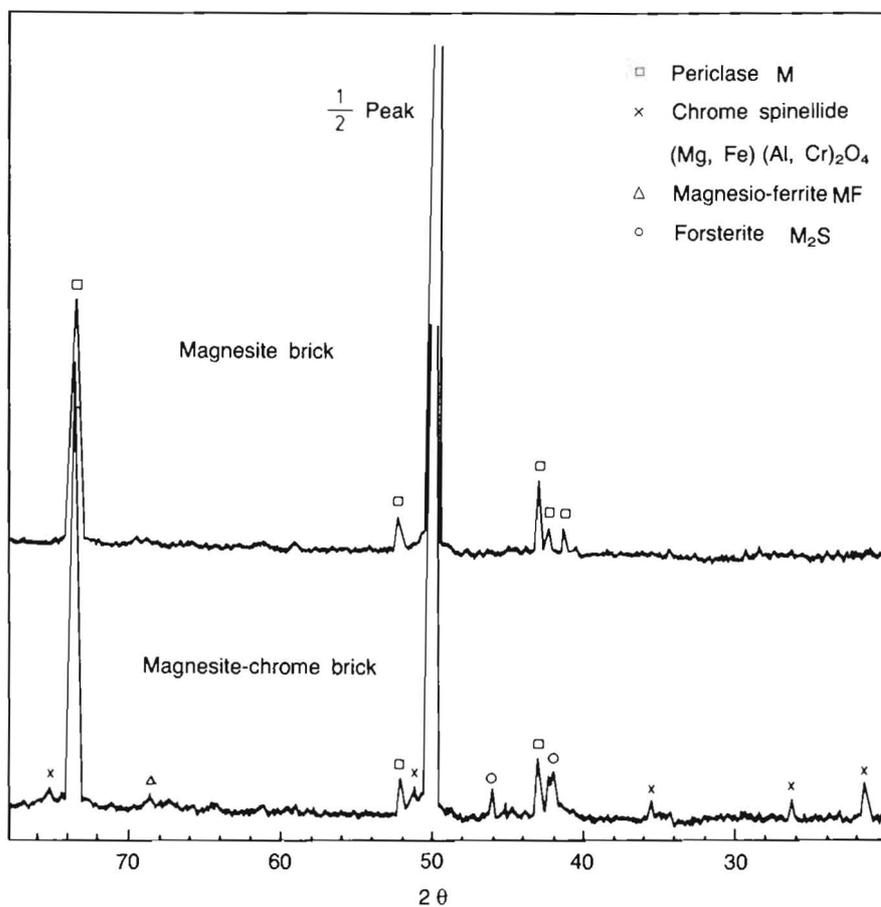Phase enclosed in brackets denote single solid solution.

Fig. 5. X-ray diffraction patterns of the magnesite and magnesite-chrome bricks.
(Co Kα Radiation)

accordance with the equilibrium phase combinations in the system "CaO-MgO-SiO$_2$-Fe$_2$O$_3$-Al$_2$O$_3$-Cr$_2$O$_3$" (White 1962). The data presented in Table 6 revealed that the C/S mole ratio in the investigated bricks is less than one. The phases that exist in equilibrium at this ratio are monticellite CMS 1498°C, forsterite M$_2$S 1900°C, and a solid solution of the secondary spinels, magnesia spinels MA 2135°C, magnesioferrite MF 1750°C, and picrochromite MK 2000°C, in addition to the prevailing periclase mineral M 2800°C. The variation in the proportions of

these minerals depends on the nature of the used dead-burned magnesite and the chrome/magnesia ratio in the bricks.

Data on the physical and technical properties of the prepared magnesia and magnesia-chrome bricks are presented in Table 7. The good sintering parameters of the well-graded bricks, fired at 1550°C, reflected a complete interaction between the different components in the batches, as well as the enhancement of sintering and densification. The determined properties of the investigated magnesia and magnesia-chrome refractory bricks are comparable with those of the commercially produced types (Table 7).

Table 7. Physical and technical properties of the prepared magnesia- and magnesia-chrome bricks

Properties	Magnesia bricks		Magnesia-chrome bricks	
	Present work	Chesters 1973	Present work	Chesters 1973
Bulk density, g/cm³	2.75	2.79	2.82	2.96 - 3.06
Specific gravity	3.50	—	4.15	—
Apparent porosity %	19.32	20.0	20.80	15 - 19
Hydration resistance %	1.30	—	0.70	—
Absorption %	7.02	—	7.43	—
Cold crushing strength, kg/cm²	380	380	320	282 - 423
Permanent linear change % 2 hours at 1550°C	− 0.21	− 0.1	− 0.16	0.0 - 0.4

Noteworthy, the working conditions of 800 kg/cm² for moulding pressure and 1550°C for the firing temperature of the magnesia clinkers, outlined in the present work, simulate the currently operating conditions available in the Egyptian refractories industry. Nevertheless, still better refractory properties of the magnesia and chrome-bearing magnesia bricks might be achieved when much higher moulding pressures and firing temperatures become available. On commercial scale, rotary kilns should be used for the production of magnesia clinkers.

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تـركيز خـامات المغنسيت المصرية لاستخـدامهـا في صنـاعـة الحراريات القاعدية

لمعي جندي جرجس و سليم فهمي اسطفان

المركز القومي للبحوث ـ الدقي ـ القاهرة ـ مصر

تحتوي خامات المغنسيت المصرية على نسب متفاوتـة من شوائب الـدولوميت، وعنـد حرق هذه الخامات فإن أكسيد الكـالسيوم المحـرر يتعرض لعمليـات الإماهـة بمضي الـوقت ويتسبب ذلك في تصـدع وتفتيت الأجسام الحـرارية . لـذلك فهي لا تصلح بصورتها الطبيعية لصناعة الحراريات القاعدية ذات الكفاءة العالية .

ومن خلال هذه الدراسة فقد أمكن تركيز خامات المغنسيت وتخليصها من أكسيد الكالسيوم وذلك بمعالجتها ـ بعد طحنها وكلسنتها ـ في طاحونة الكور الصيني بكميات من حـامض الهـدروكلوريـك المخفف تكـافىء مـا تحتـويـه تلك الخـامـات من فلز الكـالسيوم . وقـد أمكن الحصول علـى ركازات عـالية الجـودة لا تتعدى نسبـة وجـود أكسيد الكالسيوم فيها ٠ , ٥ ـ ٧ , ٠ ٪ .

استخدمت ركازات المغنيسيا في تحضير حراريات المغنسيت بعـد أن أضيف إليها ٣٪ وزنـاً من خام الألمنيت وتم حرقها عند ١٥٥٠م° . كما استخدمت الـركازات في تحضـير حـراريـات المغنسيت ـ كـروم بعـد أن أضيف إليهـا ٢٠٪ وزنـاً من خـام الكروميت وتم حرقها عند ١٥٥٠م° . وقد درست الخواص الكيميـائية والفيـزيـائية والحرارية لنـوعي الطوب الحـراري اللذين تم تحضيرهمـا، وقـد أكـدت النتـائـج جودة هـذين النوعين من الطوب الحـراري وأنهما يطابقان المواصفـات العاليـة لمثيلهمـا من الطوب الحراري المصنع من خامات المغنسيت المستوردة .