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Refractory aspects of Egyptian alum-waste material

N.M. Khalil

Ceramic Department, National Research Centre, EL-Tahrir Str., Dokki, Cairo, Egypt

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Abstract

The material studied was Egyptian alum-waste, which consists mainly of SiO_2 and Al_2O_3. Mixes were made with appropriate additions of magnesia to bind SiO_2 as forsterite ($2MgO{\cdot}SiO_2$) and Al_2O_3 as spinel ($MgO{\cdot}Al_2O_3$), in an attempt to asses their suitability as a refractory forsterite material. The formation of spinel in these materials helped in the improvement of the quality of the prepared forsterite bodies. The phase reactions that may occur during the firing at 1550 °C of the prepared mixes, which belong to the five component system $CaO–MgO–SiO_2–R_2O_3$ were investigated. The mineral composition of the resulting forsterite bodies were determined theoretically by calculations from their thermal equilibrium data and experimentally by means of X-ray analysis and scanning electron microscopy. The technological properties of the resulting refractory bodies were determined and correlated with their mineral composition. Such properties were found to compare favourably with those of the parallel imported types.

Keywords: Refractory properties; Egyptian alum-waste

1. Introduction

In Egypt, the industrial production of alum (aluminium sulphate) is carried out through treating calcined kaolin with sulphuric acid. However several tons (about 200 tons/day) of by-product material are wasted and accumulated, which causes many environmental pollutions in addition to occupying a large place in the factory. So, it was scientifically planned to overcome this problem through consuming this material in a suitable industry. Since this waste material contains considerable proportions of SiO_2 and Al_2O_3, attempts have been made to prepare forsterite-type refractory material, through mixing it with magnesia to bind SiO_2 as forsterite ($2MgO{\cdot}SiO_2$) and Al_2O_3 as spinel ($MgO{\cdot}Al_2O_3$).

Forsterite refractories are noted for their comparatively excellent load bearing capacity in the basic field as a result of the strong bond developed within the crystals of forsterite. The raw materials for commercial production of forsterite refractories are magnesium silicate materials. The addition of magnesia to these materials is necessary to maintain the composition of forsterite mineral. Sometimes the forsterite grog is combined with 10–15% Al_2O_3 to produce the fertified forsterite bricks. The addition of Al_2O_3 helps to stabilize the forsterite grains by reacting with excess MgO to form MA spinel. Fortunately, the investigated alum-waste material contains ~12% Al_2O_3 which helps in the improvement of the quality of the end product through the formation of MA spinel within the produced bodies.

Many investigations have been carried out to use some industrial wastes for the production of forsterite refractories [1–7] through addition of magnesia to these materials, in order to bring the M/S[1] molecular ratio of the mixes to >2 after firing, which is necessary for the formation of forsterite material.

The re-use of such industrial wastes involves economy of deficient raw materials and fuel and permits improvement of ecological situation at metallurgical and refractory works.

The present work was carried out to determine the constitutions of the investigated alum-waste, in an attempt to evaluate its suitability for making high temperature forsterite-type refractory materials.

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[1] Some notations are used in this investigation: M: MgO; S: SiO_2; A: Al_2O_3; C: CaO; F: Fe_2O_3; T: TiO_2.

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2. Materials and methods of investigations

2.1. Materials

The materials used in this investigation are described in the following sections.

2.1.1. Alum-waste

Alum-waste was supplied in the form of slurry. This slurry was allowed to dry at 110°C for 24 h. The dried samples were crushed in a jaw crusher and then ground in a porcelain ball mill to pass completely through 40 μm sieve.

2.1.2. Calcined magnesite

Calcined magnesite was used as a source of MgO. The chemical constitution of the starting materials was determined applying standard methods [8]. The results given in Table 1 show that the alum-waste contains considerable proportions of SiO_2 and Al_2O_3. The CaO content is very low (0.72%), which is of particular importance when its suitability for making basic forsterite refractories is assessed. Calcined magnesite composed mainly of MgO.

The mineralogical composition of such materials was determined by means of X-ray diffraction method using a Philips X-ray diffraction equipment model PW/1710 with a Ni filter, Cu target ($\lambda = 1.542$ Å). The results shown in Fig. 1 reveal that the alum-waste crystalline phases composed mainly of aluminum sulphate hydrate ($Al_2(SO_4)_3 \cdot 18H_2O$) and quartz, while calcined magnesite is mainly periclase mineral (MgO).

2.2. Preparation of refractory bodies

To obtain a high grade forsterite-type refractories, the co-clinker method was adopted [9]. This method involves the production of forsterite clinkers by dead burning the mixtures of the finely ground materials to a temperature of 1550°C, to give a homogeneous microstructure. Afterwards, the produced clinkers are crushed, ground, sized and then formed into bricks and fired at 1550°C. When forsterite bricks are manufactured by this method, a more homogeneous phase composition can be achieved and high physicomechanical indexes are attained.

Table 1
Chemical analysis of the starting materials

Component (wt.%)	Alum-waste material	Calcined magnesite
SiO_2	56.17	2.99
Al_2O_3	12.52	0.24
Fe_2O_3	0.54	0.48
TiO_2	2.62	–
CaO	0.72	2.16
MgO	0.20	94.07
SO_3	5.70	–
L.O.I	21.50	–

Accordingly, six batches were formed from a finely milled blend of alum-waste and calcined magnesite Table 2. The batches were formed at 80 MPa to yield green bricks. The formed bricks, after being dried at 110°C were fired at temperatures ranging between 1350–1550°C in an oxidizing atmosphere to produce forsterite clinker. The selected forsterite clinkers (mixes 5 and 6) were then crushed, ground and sieved. An attempt was made to obtain the highest compact mixes through proper mix gradings. The results indicated that a mix composition consisting of 70 wt.% coarse fraction (3.34–0.125 mm) and 30 wt.% of fine fraction (−0.125 mm) gave the best packing results. Forsterite briquettes (1 inch diameter × 1 inch height) were shaped by the semi-dry pressing technique, where the dry mixes were moistened with ~6% sulphite lye solution as a temporary bond, and then pressed under pressure of 80 MPa. The formed briquettes which were easy to be handled, were left to dry at 110°C, and then fired at 1550°C for 3 h. The produced forsterite briquettes were hard, with sharp edges and corners, and no cracks could be visually detected.

2.3. Mineral composition of the fired mixes

The mineral composition of the fired mixes was determined theoretically by calculations from the data of their chemical compositions. The calculations proceeded in accordance with the equilibrium phase combinations in the system $CaO–MgO–Fe_2O_3–Al_2O_3–SiO_2$ [10]. The chemical composition, together with their calculated mineral composition, is given in Table 3. The mineral composition of these fired bodies was also determined experimentally by means of X-ray diffraction method (Fig. 2).

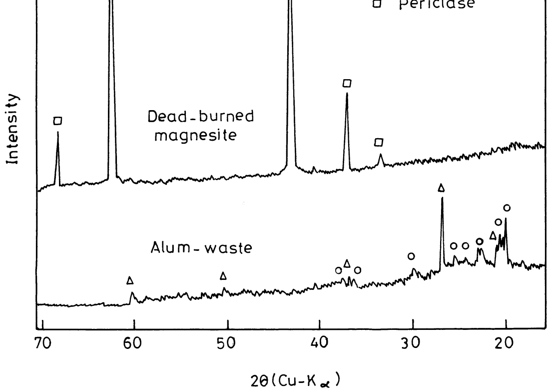


Fig. 1. X-ray diffraction patterns of the starting materials.

Table 2
Sintering parameters of the prepared mixes

	Composition (wt.%)		Bulk density (g/cm^3)					Apparent porosity (%)				
Mix no.	Alum-waste material	Magnesite	1350°C	1400°C	1450°C	1500 °C	1550 °C	1350°C	1400°C	1450°C	1500 °C	1550 °C
1	90	10	Fused	–	–	–	–	–	–	–	–	–
2	80	20	2.50	Fused	–	–	–	6.28	–	–	–	–
3	70	30	2.48	2.54	Fused	–	–	12.33	7.21	–	–	–
4	60	40	2.46	2.50	2.54	Fused	–	18.65	18.07	9.00	–	–
5	50	50	2.44	2.48	2.52	2.57	2.59	20.81	19.60	18.14	17.80	16.77
6	45	55	2.47	2.53	2.58	2.60	2.62	19.62	18.93	17.69	16.92	16.68

Table 3
Thermal equilibrium data on the composition of the fired mixes

	Composition (wt.%)		Chemical Composition (%)							Calculated phase composition (%)							
Mix no.	Alum-waste material	Magnesite	S	F	A	T	C	M	M/S ratio	CMS	M2S	MS	MF	MA	MT	M	S
1	90	10	67.36	0.71	14.94	3.13	1.14	12.70	0.28	3.18	–	10.71	0.88	20.83	4.64	–	59.73
2	80	20	58.23	068	12.87	2.68	1.28	24.26	0.63	3.57	–	42.00	0.80	17.92	4.02	–	31.65
3	70	30	49.71	0.65	10.92	2.57	1.42	35.05	1.06	3.96	–	71.15	0.80	15.20	3.39	–	5.47
4	60	40	41.88	0.61	9.13	1.52	1.56	45.30	1.62	4.34	45.11	34.79	0.76	12.71	2.29	–	–
5	50	50	34.31	0.59	7.40	1.31	1.67	54.72	2.39	4.65	75.89	–	0.74	10.20	2.25	6.35	–
6	45	55	30.69	0.58	6.57	1.34	1.72	59.08	2.89	4.80	67.28	–	0.72	9.14	2.02	16.00	–

2.4. Composition and properties of the selected forsterite bodies

The mineral composition of the selected forsterite bodies was determined using X-ray powder diffraction technique (Fig. 3). On the other hand, microstructure of these bodies was investigated using scanning electron microscope (Jeol JSM-T20) after being coated with gold using S150A, Sputter Coater. The obtained photomicrographs are shown in Fig. 4. The technological properties of the selected forsterite bodies, in terms of densification parameters, volume stability, thermal shock resistance, refractoriness and load bearing capacity, (Table 4), were determined, adopting the BSS testing procedures [11] and correlated in the light of their composition and microstructure.

Thermal shock resistance was carried out using air quenching method in which the samples were heated to 1000°C and subsequently cooled in air. The test was repeated until the destruction of the samples.

The cone fusion test, originated by Segar, was used for the determination of the refractoriness of the prepared batches. This test depends on comparing the bending characteristics of the test samples with those of a series of standard pyromometric cones, all fired together under uniform conditions. The temperature was raised until the tip of the cones was bent over level with the base. The refractoriness values of the test materials were reported in terms of the standard pyrometric cones.

3. Results and discussion

For the production of forsterite-type refractories from a mixture of alum-waste material and calcined magnesite, it is essential that the M/S molecular ratio should be within 2, the necessary range for the formation of M_2S, after firing; otherwise the low melting clinoenstatite mineral MS (1543°C) will be formed which affects badly the refractory properties of the fired bodies. However, through the addition of the required amount of MgO, MS mineral would disappear and M_2S is formed [12].

Accordingly mixes 1, 2, 3 and 4 were fused at a temperature range 1350°–1500°C (Table 2). This is due to defficiency of MgO which leads to the formation of the low melting MS in these mixes. It was found that with increasing the amount of MgO in the fired mixes, the M/S molecular ratio increased with the result that the low melting MS progressively decreased with corresponding increase of the M_2S content (Table 3). However, mixes 5 and 6 resist high temperatures (> 1550°C). This is due to fact that the M/S ratio in these mixes lies within the limits necessary for the formation of M_2S, after firing.

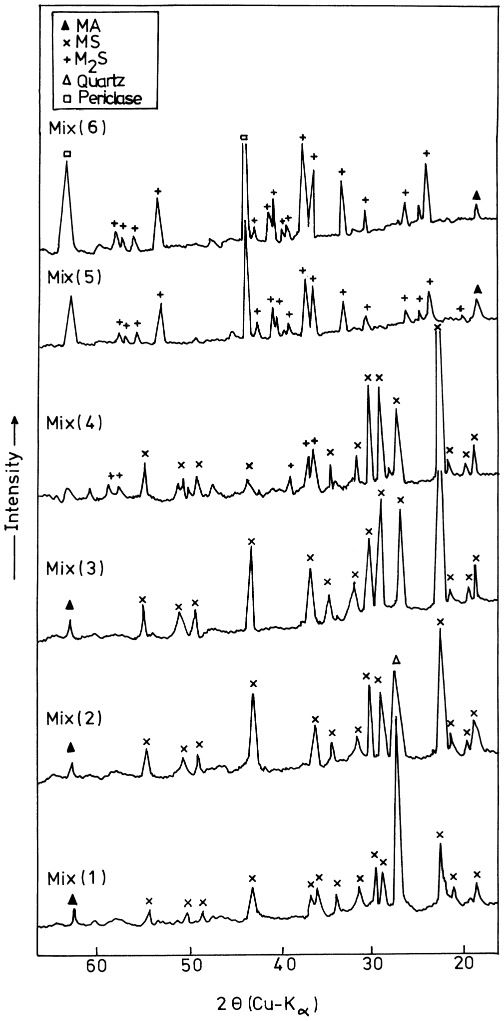


Fig. 2. X-ray diffraction patterns of the clinkered mixes.

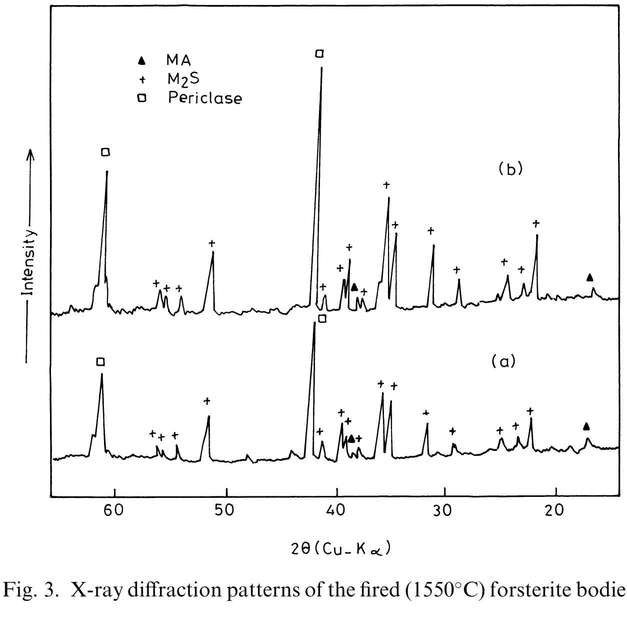


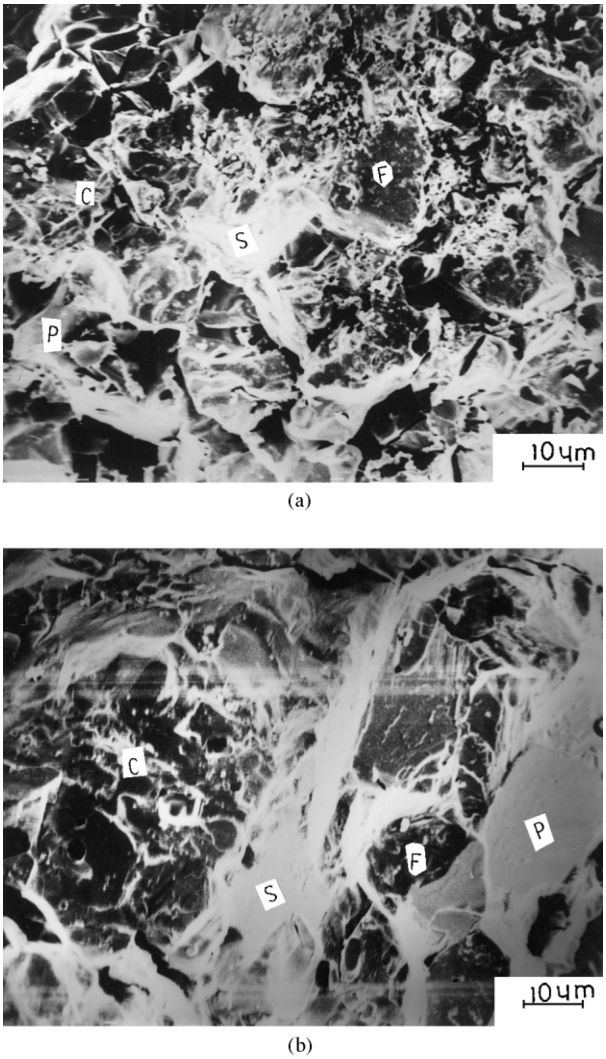
Fig. 3. X-ray diffraction patterns of the fired (1550°C) forsterite bodies.

The phase calculations given in Table 3, indicate that in all the prepared mixes, the C/S molecular ratio was less than 1. So, the mineral assemblages that exist in equilibrium, in the presence of free MgO in the system CaO–MgO–SiO_2–R_2O_3 are CMS, M_2S, MF, MA and MT. However in mixes 1, 2, 3 and 4, there was insufficient MgO to satisfy all C and S as CMS and M_2S, all F as MF, all A as MA and all T as MT. Therefore, the low melting MS mineral would be formed. The amount of the formed MS was found to decrease with the increased addition of MgO, where the amount of M_2S increased. In mixes 5 and 6 there was sufficient MgO to satisfy all C as CMS, all F as MF, all A as MA, all T as MT, and the remaining S combined to form M_2S. Therefore the MS phase disappeared and the excess magnesia was present as periclase.

The X-ray diffraction results of the prepared clinkered batches, given in Fig. 2 supported the above findings and indicated that mixes 1, 2 and 3 composed of MS mineral in addition to quartz and MA spinel. By increasing the magnesite content up to 40 wt.% (mix 4), a noticeable decrease in the amount of MS is observed, while no quartz could be detected. The new formed M_2S mineral could also be detected in addition to MA spinel. Mixes 5 and 6 are composed mainly of M_2S and periclase minerals in addition to MA spinel. It was also found that the mineral composition found out by calculations agrees qualitatively with those determined by means of X-ray analysis. This indicates that all reactions are thermally mature at the corresponding clinkering temperatures. Table 2 indicates also that the bulk density of the fired batches decreases as the magnesite content increases, reaches its minimum value with mix 5. Also, each batch shows a gradualy increase in bulk density as the firing temperature increases. Mix 6 gives a relatively higher density compared with that of mix 5 at different firing temperatures. The apparent porosity goes in the opposite direction, i.e. increased as the wt.% of magnesite increased reaching its maximum value with mix 5 and decreased by further increasing of the magnesite content (mix 6). The continuous decrease in bulk density corresponded by continuous increase in apparent porosity is attributed to the continuous formation of the new mineral MS in mixes 1, 2, 3 and 4 in addition to M_2S in mix 4. The formation of these minerals is usually accompanied by some volume increase which may lead to weakening of the sample structure. The improvement of the sintering parameters (high density and low porosity) of the samples with raising firing temperature up to 1550°C revealed that the sintering had gone to a great extent after firing at this temperature. This indicated the complete interaction between the different components of the test mixes and the enhancement of densification and grain growth are the main processes to take place on firing up to 1550°C. The relatively higher densification parameters of the latter two mixes (5 and 6) are due to their relatively higher content of periclase mineral.

Based on the above mentioned evaluations, mixes 5 and 6, containing 50 and 55 wt.% magnesite, were selected for preparing forsterite refractory bodies. Forsterite briquettes were prepared from the graded forsterite clinkers, after firing at 1550°C for 3 h. The X-ray results of such briquettes (Fig. 3), indicated that they consist mainly of M_2S (melting point: 1890°C), MA (2135°C) and M (2800°C). Mix 6 showed a relatively higher content of periclase mineral compared with mix 5, as indicated from the intensities of its corresponding peaks.

SEM photomicrographs (Fig. 4), showed forsterite grains (dark grey) distributed throughout the sections, periclase grains (grey) containing very fine spinel particles (light). Open and closed pores (dark) are also observed. All these constituents are bounded together by interstitial CMS mineral. The fine forsterite particles form a vitrified groundmass which bonds together the particles of large sizes. The character and continuity of this groundmass and its degree of adherence to the larger particles have very important effects upon the properties of the fired refractory bodies. The spinel phase is distributed uniformly through the forsterite structures to protect them against chemical attack and to avoid any mechanical weakness, i.e. more homogeneous phase composition has been achieved and high physico-mechanical properties could be attained.



(a)

(b)

Fig. 4. SEM photomicrograph of the fired (1550°C) forsterite-bodies: (a)made from mix (5), ×500; (b)made from mix (6), ×500. F: forsterite; P: periclase; S:MA spinel; C: CMS.

Such selected forsterite-type refractory bodies would be advantageous for their good physico-mechanical and refractory properties (Table 4). The results indicate that these briquettes show higher refractoriness as they consist mainly of high melting point minerals, except CMS (1498°C). The formation of this mineral in basic refractories is highly objected to, as it has a low melting point and being highly mobile when molten. Such mineral exists in a very low amount ($<5\%$) and did not badly affect the refractory properties of the end product, but may assist sintering process. The relatively higher content of the recrystalized periclase mineral in mix 6, explains the improvements achieved in its sintering parameters and load bearing capacity. This improving effect can be attributed to the enhanced mineralization and crystallization of periclase mineral which leads in its turn to strong MgO–MgO bonding [13–15].

The forsterite bodies showed good volume stability (−0.1 to −0.4%) when reheated at 1550°C for 2 h, in addition to suitable sintering parameters. This indicates the great access given for complete interaction between different components as well as the enhancement of sintering and densification.

Table 4
Technological properties of the prepared forsterite-type bodies [16]

Property	Mix 5	Mix 6	Commercial type
Bulk density (g/cm^3)	2.60	2.64	2.50–2.70
Apparent porosity (%)	20.22	19.80	18–25
Cold crushing strength (MPa)	32	41	23
Permanent linear change (%) (2 h at 1550°C)	−0.27	−0.21	−0.20–−0.40
RTE coefficient	9.6×10^{-6}	10×10^{-6}	9.5×10^{-6}
Thermal shock resistance in air (no. of cycles)	+30	+30	+30
Refractoriness, Sk.Co.No. (°C)	33–34 (1740–1760)	>34 (>1760)	>32 (>1730)
Refractoriness under load, 0.2 MPa:			
•Beginning of subsidence (°C)	1510	1540	1500–1520
•5% Subsidence (°C)	1600	1650	1600

Magnesium silicates in general have relatively high reversible thermal expansion coefficient (RTE). However, the presence of considerable amount of MA spinel with relatively lower RTE (7.6×10^{-6} at 25–850°C) reduces to some extent the reversible thermal expansion coefficient of the prepared forsterite bodies. Accordingly, such forsterite bodies showed good thermal shock resistance (more than 30 cycles). Also, the presence of MA spinel around the surface of forsterite grains, which is characterized by its good thermomechanical properties, protects the forsterite grains and periclase against chemical attack. Accordingly, such forsterite bodies could be used advantgeously in lining the checker work of the glass melting furnaces and also in the lining of the upper transition zones of the rotary cement kilns and the roofs of the electric-arc furnaces [16–18].

The results of the technological properties of the prepared forsterite bodies, given in (Table 4), compare favourably with those of the parallel commercially produced types [16].

4. Conclusion

In the light of the above mentioned considerations, the investigated alum-waste material is recommended as a valuable supply of materials suitable for the manufacture of forsterite-type refractories. Such type of refractories could be prepared from batches consisting of 45–50 wt.% of alum-waste material and 55–50 wt.% calcined magnesite after firing at 1550°C. The obtained forsterite bodies show high sintering parameters (high density and low porosity) and good refractory properties. The presence of considerable amount of MA spinel is desirable as it helps in the improvement of the refractory properties of the prepared forsterite-type bodies. Such improved bodies could be used advantgeously in lining the upper transition zones of rotary cement kilns and regenerators of the steel furnaces.

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