ELSEVIER

Ceramics International 27 (2001) 865–873

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Aluminous cements containing magnesium aluminate spinel from Egyptian dolomite

Nagy M.A. Khalil*, S.A.S. El-Hemaly, Lamey G. Girgis

Ceramic Department, National Research Centre, El-Tahrir Str., Dokki 12622, Cairo, Egypt

Received 4 September 2000; received in revised form 13 December 2000; accepted 13 March 2001

Abstract

Three mixes of calcium aluminate cements containing MA spinel were prepared using appropriate mixtures of Egyptian dolomite (MgO, 20.16% and CaO, 31.32%) with active alumina (99.50% A)[1]. The cement mixes were prepared at 1600°C using the sintering method. The products were finely ground and their chemical and mineralogical compositions were investigated using the appropriate techniques. Also, their physicomechanical and refractory properties had been determined. The results indicated that their mineralogical compositions were refractory MA spinel, in addition to CA and/or CA_2 phases depending on the composition of the starting materials. The prepared cements exhibited a compromise between considerable strength and higher refractoriness. When 10% of such cements were added to refractory grade magnesia aggregate, in the presence of 0.1% Li_2CO_3 as a strength modifier, refractory castable bodies with improved hot-strength and thermal shock resistance had been achieved.

Keywords: Cement; Magnesium aluminate spinel; Egyptian dolomite

1. Introduction

It has been reported that the refractoriness of the high alumina cements can be increased substantially, without adversely affecting their compressive strength, when CaO in the cement clinker is partially substituted by MgO. This is due to the formation of MA spinel (2135°C) in the end product [1]. This type of aluminous cement which contains from 6 to 13% MgO is known as spinel-type cement. Such types of cement could be fabricated either by grinding a mixture of pre-prepared high alumina cement (> 70% alumina) and prefabricated MA spinel, or the use of appropriate mixtures of raw dolomite (source of CaO and MgO) and active alumina as primary materials, where MA spinel (20–50%) in addition to the calcium aluminate hydraulic phases (CA and CA_2) are formed during the sintering process. The spinel mineral, whether artificially added or formed in situ during sintering, is hydraulically inert and does not behave as a binder, but it permits the utilization of refractory castables with a suitable aggregate (tabular alumina, spinel or dead burnt magnesite) up to 1800°C [2]. The presence of spinel mineral in these types of cements results in improved slag resistance and high hot sagging under load [3]. Therefore, they are being used increasingly in steel-making applications, such as lining of steel ladles, continuous casting tundishes and degasser snorkels and lancers [4]. The object of the present work is the development of aluminous cements containing MA spinel from Egyptian dolomite rock. Their application for the formation of castable bodies with high hot strength is also considered.

2. Experimental

2.1. Synthesis of pure phases

The main pure phases constituting the spinel-type cement, according to the relevant phase diagram [5] are CA,CA_2 and MA. Synthesis of these phases from pure reagents ($CaCO_3$, Al_2O_3 and $MgCO_3$) were carried out and the products were investigated for their physicomechanical properties. In order to optimize the proportions of phases that constitute such spinel-type cements, a series of mixtures of the synthesized CA and/or CA_2 with MA spinel, was prepared. The measured 7-days compressive strength in a 100% relative humidity and

---

* Corresponding author. Fax: +202-337-0931.
E-mail address: nagv20@yahoo.com (N.M.A. Khalil).

[1] The following cement notations are used: C, CaO; M, MgO; S, SiO_2; F, Fe_2O_3; A, Al_2O_3; H, H_2O.

0272-8842/01/$20.00
PII: S0272-8842(01)00042-6

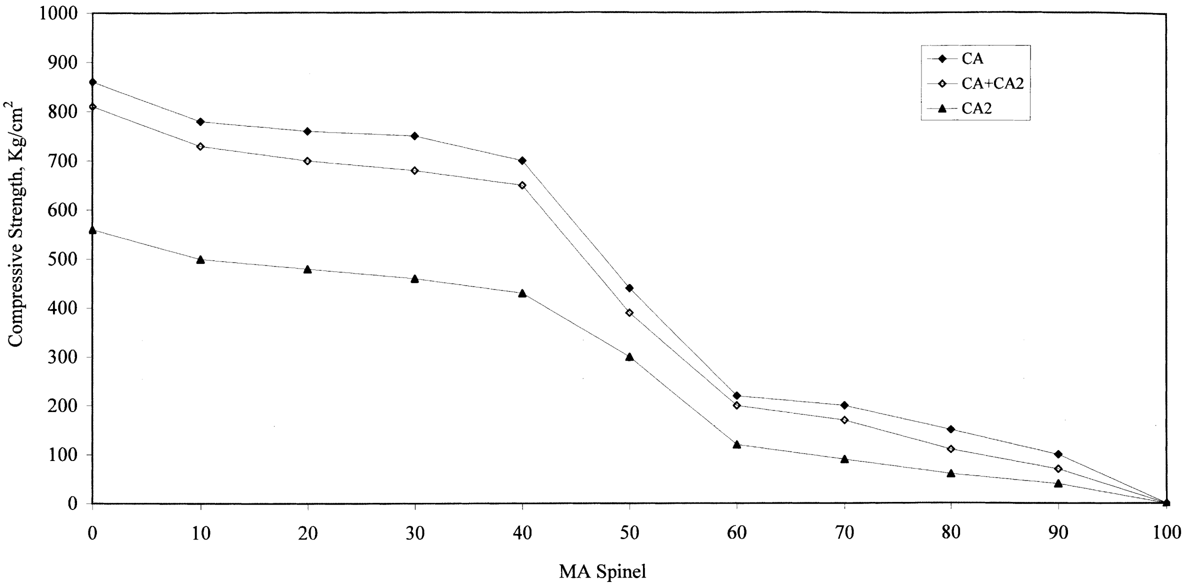

Fig. 1. Effect of additon of MA spinel on the compressive strength of synthesized CA and/or CA_2.

refractoriness of each mix, were employed as a useful means for the sake of comparison. The results given in Fig. 1, indicate that the compressive strength of these mixes decreases, parallel to the increase of the added inert MA. On the other hand, it was found that the refractoriness of such mixes is increased. However, the presence of up to 40 wt.% MA spinel showed a compromise between considerable compressive strength and high refractoriness. Such results were taken into consideration during the preparation of the spinel-type cements.

2.2. Starting materials

Highly pure local raw dolomite (source of CaO and MgO) and calcined alumina (source of Al_2O_3) were employed for the preparation of aluminous cements containing MA spinel. The refractory aggregate used for the preparation of the castable bodies is dead burnt magnesia. The chemical constitution of these starting materials are given in Table 1.

Table 1
Chemical composition of the starting materials

Oxides	Raw dolomite	Calcined alumina
SiO_2	0.51	0.02
Fe_2O_3	0.27	0.02
Al_2O_3	0.54	99.50
CaO	31.32	–
MgO	20.16	–
L.O.I	46.82	0.11

2.3. Preparation of cement compositions

The raw dolomite and calcined alumina raw mixes were properly proportioned to yield approximately 40 wt.% MA spinel in the prepared cements. Three cement batches of different mineral compositions were prepared adopting the sintering technique. The first mix yields CA as a major phase, the second one consists of a mixture of CA and CA_2, while the third one gives CA_2 as a main constituent (Table 2). The required proportions of the starting materials of each mix were dry blended together, then wet finely ground in a fused alumina ball mill. After being dried, the prepared mixes were formed into briquettes under pressure of 800 kg/cm^2, dried at 110°C and then fired at temperatures ranging between 1550 and 1600°C, with a soaking time of 5 h, until complete sintering was achieved. The resulting sintered products were crushed, then finely ground in a fused alumina ball mill to get a cement powder of a suitable

Table 2
Phase equilibrium data on the composition of the prepared cements

Cement no.	Composition of the cement mixes (wt.%)		Chemical composition of the cement mixes (wt.%)					Calculated phase composition of the cement mixes (wt.%)				
	Dolomite	Calcined alumina	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	C_2AS	C_2F	CA	CA_2	MA
1	50	50	0.32	0.17	67.35	19.59	12.53	1.45	0.29	52.53	1.25	44.44
2	45	55	0.29	0.15	69.89	18.04	11.54	1.32	0.26	36.03	21.40	40.9
3	40	60	0.24	0.14	74.85	15.10	9.66	1.12	0.22	4.87	59.53	34.25

fineness. The Blaine surface area of the produced cements was maintained in the range of 3500–4000 cm^2/g.

3. Results and discussion

3.1. Phase composition of the prepared cements

The different physicomechanical and chemical properties of the prepared cements are basically a function of the various phases comprising these cements. Accordingly, by assuming that the chemical reactions in the fired cement mixes had attained equilibrium, the different phases developed in these cements could be determined theoretically [6] by calculations from their determined chemical analysis data (Table 2).

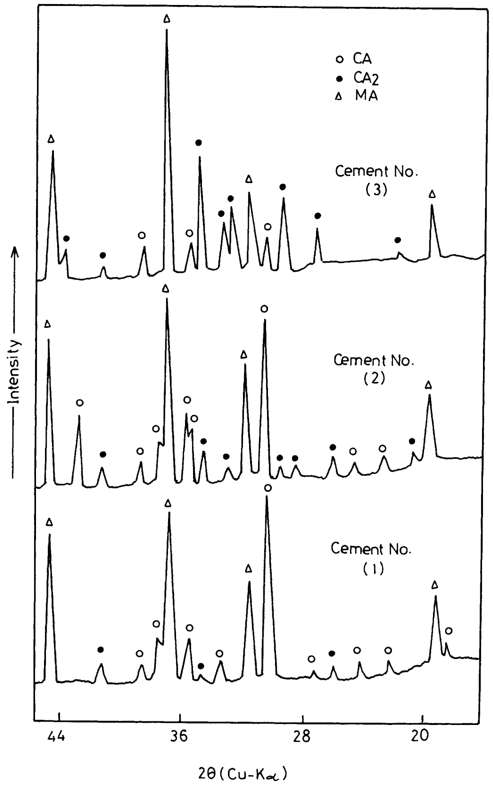

Fig. 2. X-ray diffraction patterns of the prepared cement mixes.

In the process of calculations, the following assumptions had been considered:

- Fe_2O_3 exists in the cements as C_2F.
- SiO_2 exists as C_2AS.
- Remaining CaO exists as CA and/or CA_2.
- MgO exists as MA spinel.

The actual phase composition of these cements is also determined experimentally by the XRD technique. The results shown in Fig. 2 indicate that the most important phases in these cements are CA and/or CA_2, in addition to MA spinel. Other minor phases,C_2AS and C_2F, present in small quantities ($< 2\%$), could not be detected by XRD analysis. It has also been found that the phase composition of the prepared spinel-type cements determined theoretically by calculations agree qualitatively with those found experimentally by XRD analysis. This means that the solid state reactions in these cements are mostly complete and had almost attained equilibrium, after being fired at the selected firing temperature of 1550–1600°C.

3.2. Characterization of the prepared cements

The physicomechanical properties of the investigated cements usually vary as a function of their overall compositions. Such properties were measured for each cement powder or paste, adopting the appropriate standard methods [7]. The experimental data of their specific gravity, refractoriness, water of consistency and setting time are given in Table 3. The compressive strength and rate of hydration were measured on hand formed cubic test samples using 0.23–0.25 water/cement ratio. These tests were measured after curing in a 100% relative humidity for 1, 3, 7 and 28 days. The results are shown in Figs. 3 and 4.

The results given in Table 3 indicate that the investigated cements showed a very high fusion point, above cone 34 (>1760°C). This is due to their higher content of MA spinel (2135°C), in addition to different proportions of CA (1600°C) and/or CA_2 (1750°C) phases. The presence of small amounts ($<2\%$) of the low melting point compounds C_2AS (1590°C) and C_2F (1435°C) did not badly affect the refractoriness of these cements but may assist their sintering properties.

Table 3
Characteristics of the prepared cements

Cement no.	Composition of cement mixes (wt%)		Sp.gr (g/cm)^3	Refractoriness (°C) (Segar cone)	Surface area (cm^2/g)	W/C ratio	Setting time (min)	
	Dolomite	Calcined alumina					Initial	Final
1	50	50	3.15	> 1760 (cone 34)	3800	0.25	175	190
2	45	55	3.08	> 1760 (cone 34)	3890	0.24	196	217
3	40	60	3.02	> 1760 (cone 34)	3900	0.23	249	299

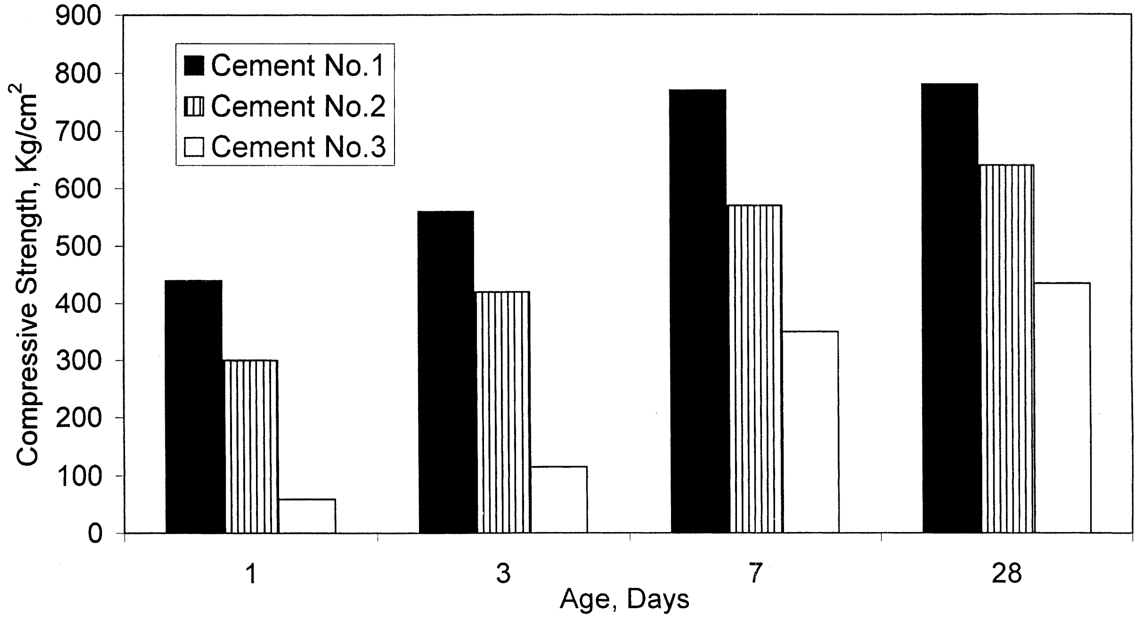

Fig. 3. Compressive strength of the prepared cements as a function of curing time.

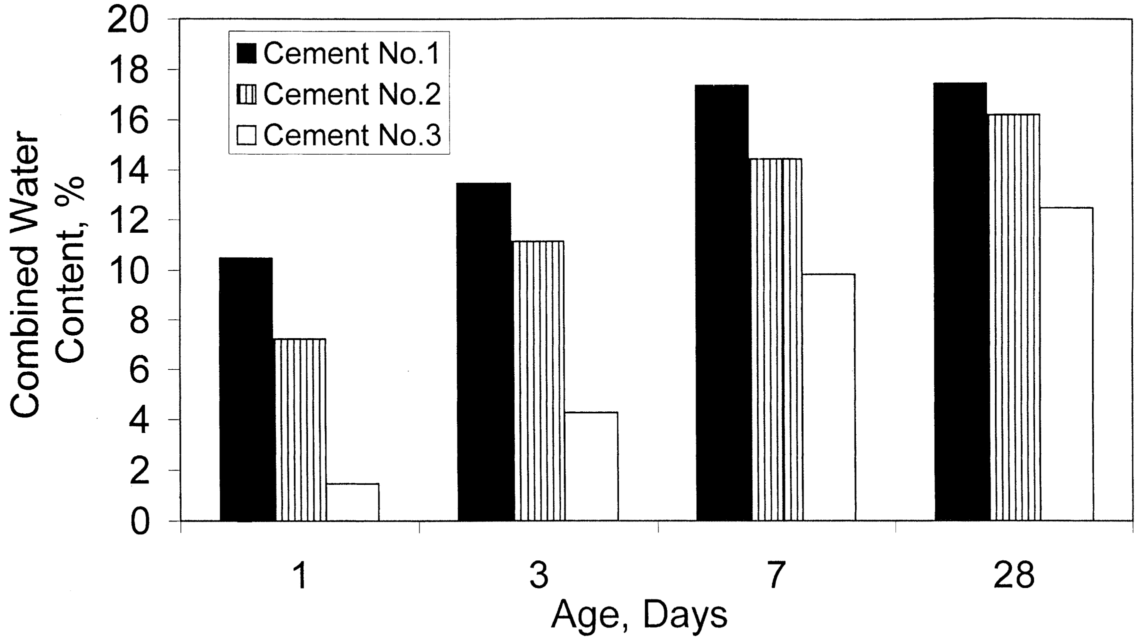

Fig. 4. Combined water content of the prepared cements as a function of curing time.

The measured specific gravity of the tested cements showed values ranging between 3.02 and 3.15, depending on the contribution of their contents of the following phases CA (2.98), CA_2 (2.91) and MA (3.60). The prepared cement pastes exhibit slow setting time as they contain high proportions of the hydraulically inert MA spinel. On the other hand the presence of CA phase accelerates the setting time whereas CA_2 retards it. Accordingly, the order of shortening of the setting time proceeds from cement No. 3 to cement No. 1. The strength development and increase in the rate of hydration of these cements with curing time (Figs. 3 and 4), are due to the continuous hydration of the hydraulically active cement phases CA and CA_2 that hydrate differently [8,9]. Such behavior depends on the type and proportion of each phase. Therefore, cement No. 1 has the highest binding characteristics after curing due to its higher content of CA phase. In any case, the three cements possess considerable strength development, despite their higher content of the hydraulically inert MA phase.

3.3. Hydration products of cement pastes

The hydrated phases of the cement pastes after 7 days curing in a 100% relative humidity were investigated by means of DTA (Fig. 5) and XRD (Fig. 6). The DTA curves showed endothermic peaks between 70 and 300°C which are characteristic of the hydration of CAH_{10}, the main hydration product of CA and CA_2 phases [10]. Another endothermic peak was also detected between 750 and 780°C which is due to the decomposition of the stable carbonated phase formed during the partial carbonation of CAH_{10} phase during curing and drying. The DTA results have been confirmed by XRD analysis, that shows the main peaks characterizing CAH_{10}. However, some peaks characterizing the original anhydrous phases CA, CA_2 and MA are still present after hydration and have been detected by XRD. This is due to the precipitation of the formed hydrated products on the surfaces of the anhydrous grains, preventing their further hydration.

3.4. Factors affecting mechanical properties of the prepared cements

Some factors which help in the improvement of the strength of the prepared cements have been studied, such as surface area of the cement powder (fineness) and the use of some additives.

3.4.1. Surface area

The cement powder No. 1, as an example, had been ground to various degrees of surface area between 2500 and 4000 cm^2/g as determined by the Blaine air-permeability method. The strength of the hardened pastes made of this cement, after curing in a 100% relative humidity for different periods up to 28 days, was determined. The results shown in Fig. 7, indicate that the strength of the hardened pastes made of this cement increases significantly with the increase of surface area at different curing periods, up to 3500 cm^2/g, beyond which the rate of strength increase was less pronounced. Accordingly, the optimum surface area of such a type of cement required for obtaining considerable strength should not be less than 3500 cm^2/g.

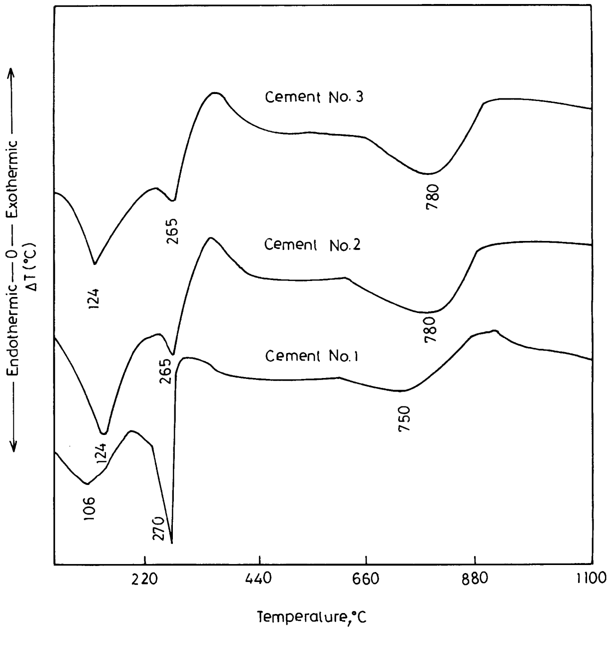

Fig. 5. DTA curves on the hydrated cement mixes.

3.4.2. Additives

In refractory castable production, small quantities of various additives are frequently used to modify the hydration behavior of the used cement binder. Preliminary tests had been carried out to improve the hydration characteristics of the investigated spinel-type cements, using different doses of various lithium salts. The results shown in Fig. 8, indicate that the use of 0.1 wt.% Li_2CO_3 additive was the most effective one, and proved to be useful for the improvement of the strength of the tested cement No 1, at all curing periods up to 28 days. Such an improvement was due to the strong hydration of the original cement phases (CA and CA_2) in the presence of such a cement strength modifier. This

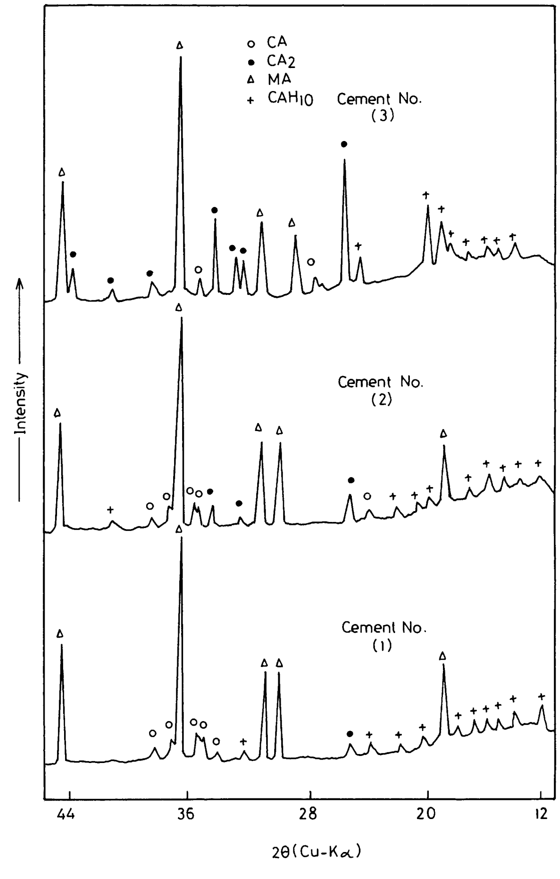

Fig. 6. X-ray diffraction patterns of the 7-days hydrated cement mixes.

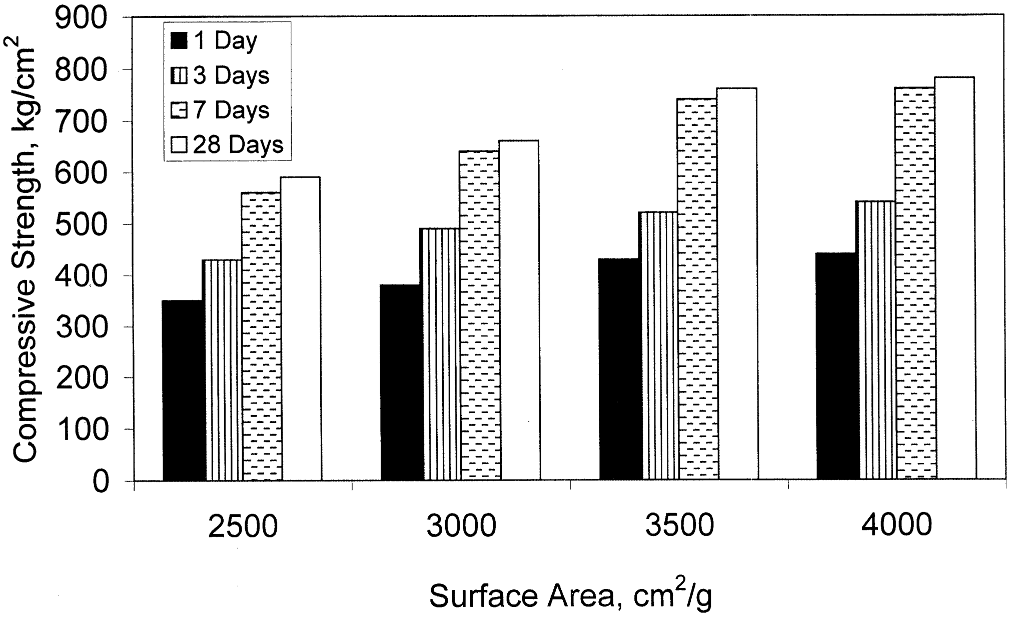

Fig. 7. Effect of surface area on the strenth development of pastes made from cement no. 1.

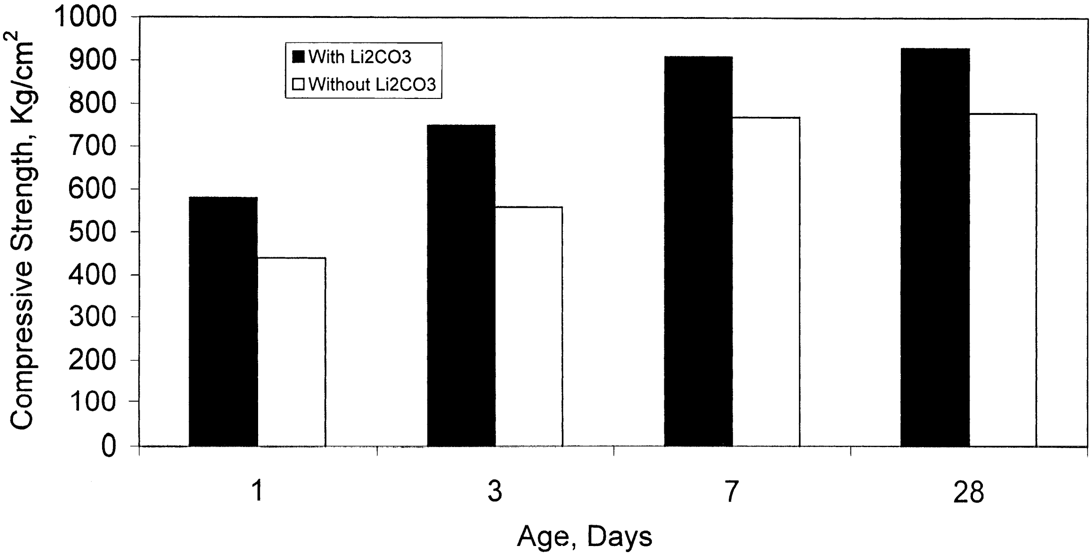

Fig. 8. Effect of 0.1 wt.% Li_2CO_3 on the compressive strength of cement no. 1 at different curing time.

in turn, leads to a bigger tendency to form a lime-rich product (C_2AH_8) which shows higher and more rapid hardening than that of the usually formed (CAH_{10}) [11].

The effect of the previous factors was also tried with the other two cements (Nos. 2 and 3), and the results obtained, in general, agree well with those of cement No. 1.

3.5. Preparation and characterization of castable bodies

The use of neat cement only is not recommended as a structural material. Therefore, the use of angular and volume stable aggregate is very important in castable preparation, in order to reduce the shrinkage arising during firing. In the present work, well-graded dead burnt magnesia is used as an aggregate for the preparation of refractory castables. The experimental results showed that the grain batch composed of 60% coarse aggregate (2.80–0.15 mm) and 40% fine aggregate (−0.15 mm) was optimum for achieving maximum dense packing. To achieve optimum conditions for castable preparation, some additional factors were also investigated e.g. water/solid ratio and amount of cement in the castable composition. Accordingly, the test method (good-ball in hand ASTM C860) is used for the determination of castable water content and consistency. The obtained results indicated that the water demanded for pastes having the required workability, range between 10 and 14%, depending on the amount of cement used.

In order to determine the optimum cement percentage, castable bodies were prepared with cement No.1, as an example. The amount of the added cement in the batches, ranging between 5 and 20 wt.%, in increments of 5 wt.%. The results given in Fig. 9 indicted that the strength of the castable bodies increases with the increase of cement proportions up to 20 wt.%. The castable bodies containing 10 wt.% cement in the presence of 0.1 wt.% Li_2CO_3 as a strength modifier, achieved about 95% of the strength developed for samples containing 20 wt.% cement without Li_2CO_3 additives. Therefore, a mixture of 90 wt.% well graded magnesia and 10 wt.% cement in the presence of 0.1 wt.% Li_2CO_3 as a strength modifier, was considered optimum for the preparation of castable bodies having considerable strength.

3.6. *Effect of heat on the strength of the prepared castable bodies*

The refractory castables are usually exposed to heat during service conditions. Therefore, the changes in the strength development of the castable samples, prepared with cement No. 1, at different firing temperatures up to 1550°C, was determined and evaluated. The experimental results shown in Fig. 10, indicate that the 7-days strength of the castable samples after curing at 20°C are determined by the binding properties of the cement used i.e. the hydration product of cement phases CA and CA_2. The variation in strength values was found to vary according to the change in the type and amount of the hydraulic phases, i.e. cement No. 1 > cement No. 2 > cement No. 3. During the drying process at 110°C, the slight improvement observed in their strength was due to the removal of the mechanical water in the castable bodies which results in the close contact of the grains of the castables to each other. In the temperature range up to 1200°C, such properties are influenced by the dehydration of CAH_{10} and the decomposition of the stable carbonated phases resulting from the carbonation of $CAH_{10.}$ Consequently, the castable bodies showed a marked decrease in their strength. On further firing up to 1550°C, the castable bodies showed pronounced improvement in their strength. This is due to the fact that all the ceramic reactions in the fired castable bodies are accomplished and the strength development is controlled by the properties of the various phases formed at these temperature ranges. Accordingly, the castable bodies, after firing up to 1550°C, developed the highest values of compressive strength.

3.7. *Phase composition, microstructure and technological properties of the fired castables*

The phase composition of the castable bodies fired at 1550°C, was determined theoretically by calculations from the data of their chemical compositions. The calculations were proceeded in accordance with the equilibrium phase combinations in the system "CaO–MgO–SiO_2–R_2O_3" [12]. The results are given in Table 4. The actual phase composition of such castable bodies was also determined experimentally by means of the XRD analysis

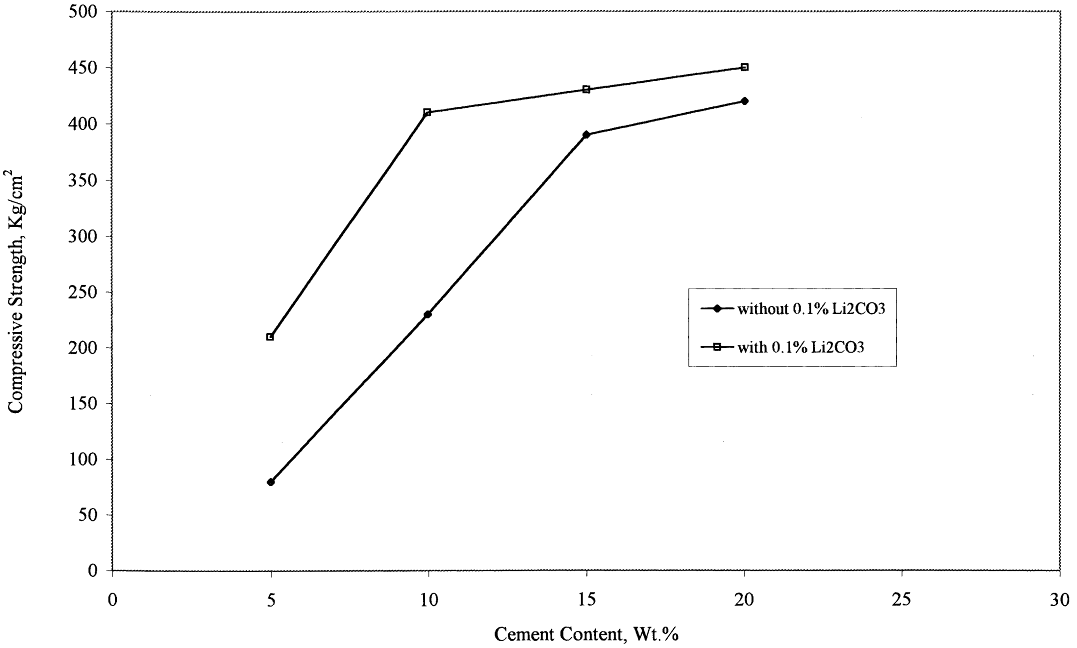

Fig. 9. The compressive strength of castable bodies as a function of the amount of cement no. 1.

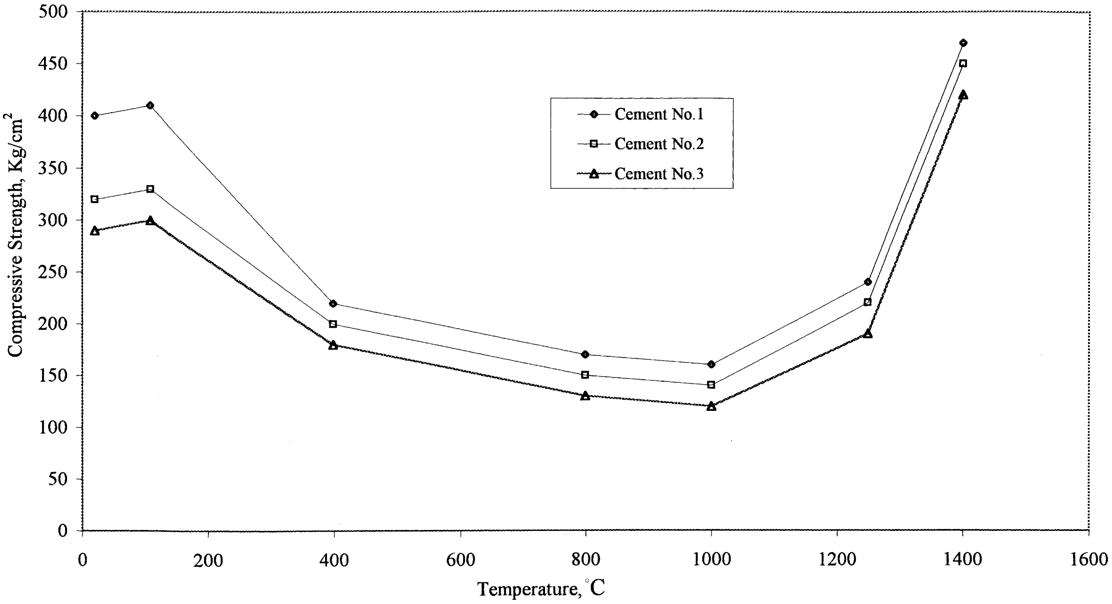

Fig. 10. Effect of heat on the 7-days compressive strength of the castable samples made with the prepared cements.

Table 4
Phase equilibrium data on the phase composition of the fired castable bodies

Castable no.	Chemical composition of the fired castable bodies (wt.%)					C/S mole ratio	Calculated phase composition of the fired castable bodies (wt.%)				
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO		C_2S	C_3MS_2	MF	MA	M
1	1.95	2.04	8.19	3.04	84.63	1.67	1.92	3.50	2.55	11.40	80.47
2	1.95	2.04	8.19	2.90	84.46	1.59	1.03	4.32	2.55	11.77	80.14
3	1.95	2.04	8.19	2.75	84.15	1.51	0.67	4.59	2.55	12.45	79.57

technique, Fig. 11. The obtained results indicate that the periclase mineral and [MA + MF] spinel phases are the main constituents of these castable bodies. The other phases C_2S and C_3MS_2 could not be detected by XRD, due to their presence in very small amounts. However, the determined phases of the fired castable bodies are mostly similar. So it is decided to study the microstructure and the technological properties of the castable body prepared with cement No. 1, as an example.

The microstructure of such castable body was studied using a scanning electron microscope (SEM) of the type Jeol Jsm-T20. The obtained photomicrograph, Fig. 12, shows periclase (light grey: P) and MA spinel crystals (white: S) of different sizes and shapes. Secondary MA spinel (white spots: SS) are present inside the periclase grains and at its boundaries. The periclase and MA spinel crystals are bounded with little silicate minerals (C_3MS_2 and C_2S: L).

The technological properties of the fired castable body prepared with cement No. 1, given in Table 5, were determined, adopting the British Standard Testing procedure [13]. The variation in properties was found to vary according, not only to change in phase composition, but also to microstructure of such a sample.

The reactions took place in the investigated fired castable body, and resulted in the mineral assemblages of the high melting periclase (2800°C) and solid solution of MF ($>$1750°C) and MA (2135°C) which represent the major constituent phases. The amount of the low melting phase C_3MS_2 (1570°C) was very small ($<$ 5%) in this sample and did not badly affect their refractoriness. During firing of this castable body, a part of the secondary MA phase goes into the intergranular spaces between the periclase grains and is situated at their boundaries, with the result that the MA spinel grains are cemented together around these grains. This microstructure brings about a considerable improvement in their spalling resistance, slag resistance as well as their load bearing capacity. Another part of the formed MA spinel is incorporated into solid solution with periclase grains, helping in their sintering and grain growth. In addition, the investigated castable body showed good

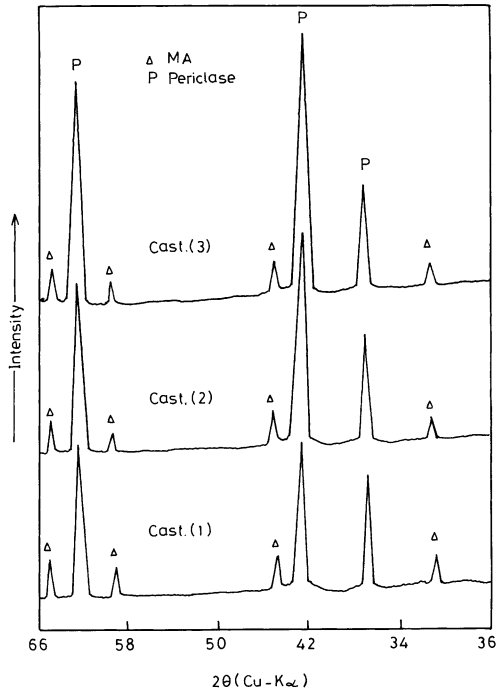

Fig. 11. XRD patterns of the fired castables made from cement mixes nos. 1–3 with magnesite aggregate.

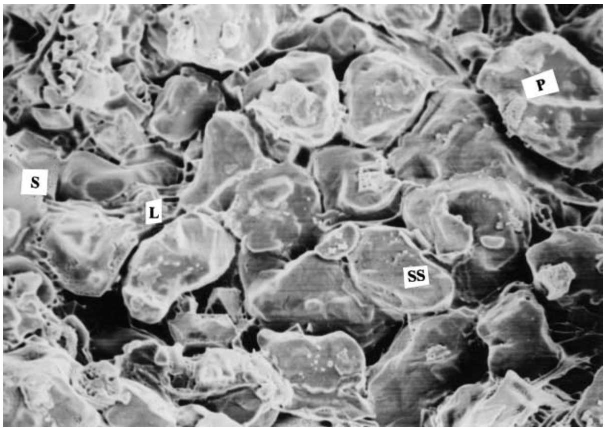

Fig. 12. SEM photomicrograph of castable sample made from cement no. 1 and magnesia aggregate (×1000).

Table 5
The technological properties of the castable body made with cement no. 1

Properties	
Bulk density, g/cm^3	2.86
Apparent porosity, %	19.63
Compressive strength, kg/cm^2	470
Permanent linear change, % (2 h at 1600°C)	−0.15
Thermal shock resistance, no. of cycles (1000°C/water)	+20
Refractoriness, Segar cone no. (°C)	> Cone 34 (>1760°C)
Refractoriness under load (2 kg/cm^2)	
Beginning of subsidence	1580°C
Amount of subsidence at 1650°C	1.5%

volume stability, as it suffered very small linear shrinkage of −0.15%, which indicates that the solid state reactions in this sample are mostly thermally mature.

4. Conclusion

High quality castable compositions could be prepared from a mixture of 90 wt.% well graded magnesia aggregate, 10 wt.% of aluminous cements containing MA spinel, in the presence of 0.1 wt.% Li_2CO_3 as a strength modifier. Such castable compositions are easily cast into desired shapes without prefiring. They are characterized with higher strength and lower shrinkage in the cured, dried and fired states. They are capable of withstanding high temperatures, with a better hot-load strength and excellent thermal shock resistance. The combination of these properties makes them useful in a wide variety of high temperature applications, especially as precast monolithic shapes for steel plant ladles and electric furnaces.

References

[1] M. Muntean, O. Sancu, Refractory aluminous cements, Mater. Constr. 4 (2) (1974) 62–69.
[2] M. Jung, Properties and uses of refractory cements developed in GDR, Silikatte Technick 27 (7) (1976) 224–226.
[3] M. Jung, Comparison of the properties and possible applications of high temperature alumina cements containing spinel and cements containing barium aluminate, Bull. Soc. Fr. Ceram. 107 (1975) 29–38.
[4] J. Mori, W. Watanabe, M. Yoshimura, Y. Oguchi, T. Kawakami, Material design of monolithic refractories for steel ladle, Bull. Am. Ceram. Soc. 69 (7) (1990) 1172–1176.
[5] G.A. Rankin, H.E. Merwin, CaO–MgO–Al_2O_3, Z. Anorg. Allg. Chem. 96 (1916) 309.
[6] A.C.C. Tseung, T.G. Carruthers, Refractory concrete based on pure calcium aluminate cement, Trans. Br. Ceram. Soc. 62(4) (1963).
[7] DIN-Normen fur Keramische Roh- und Werkstoffe des Deutschen Instituts fur Normung e.v, Stand, 1989.
[8] K.M. Parker, J.H. Sharp, Refractory calcium aluminate cements, Trans. Br. Ceram. Soc. 81 (2) (1982) 35–42;
B.M. Mohamed, J.H. Sharp. Kinetics and mechanism of formation of calcium aluminates. Solid State Chemistry, Bratislava, 6-12 Juli 1996.
[9] B.M. Mohamed, J.H. Sharp. Kinetics and mechanism of formation of calcium aluminates, Solid State Chemistry, Bratislava, 6–12 Juli 1996.
[10] V.S. Ramachandran, Applications of Differential Thermal Analysis in Cement Chemistry, Chemical Publishing Company, New York, 1969.
[11] J.D. Cox, J.H. Sharp. The use of admixtures with calcium aluminate cements In: Proceedings of the Conchem International Conference, Karlsruhe, Germany, 22–24 November 1994, pp. 381–85.
[12] J. White, High Temperature Oxides, Endn. Alper, M.A., Academic Press, New York, 1970, p. 77.
[13] British Standard Methods for Testing Refractory Materials, B.S. No. 1902, 1967.