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Refractory concrete based on barium aluminate–barium zirconate cements for steel-making industries

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Abstract

Five refractory cement mixes were prepared from different proportions of barite, zirconia and calcined alumina by sintering at 1500–1550 °C for 3 h. The obtained cements were composed of barium aluminate and barium zirconate minerals in addition to comparable proportions of di-barium silicate.

Cement mix prepared from 70 wt.% barite, 10 wt.% zirconia and 20 wt.% alumina and containing comparable proportions of barium aluminate and barium zirconate minerals ($\approx$38 and $\approx$29 wt.%, respectively) shows a comporomise between good cementing, sintering and refractory properties.

Refractory concretes prepared from 20 wt.% of this cement and 80 wt.% of either bauxite or fused spinel aggregate are composed mainly of mullite, barium aluminate, barium zirconate and α-corundum in case of bauxite aggregate or magnesium aluminate spinel in addition to barium aluminate and barium zirconate in case of fused spinel aggregate. These assemblages of minerals exhibit compact and homogenous microstructure and results in outstanding technological properties that meet the requirements of international standard specifications, i.e., good volume stability (permanent linear change is only 0.62 and 0.28%, respectively) good mechanical properties (680 and 610 kg/cm^2), high spalling resistance (>30 cycles), high refractoriness (>1700 °C) as well as high load bearing capacity (t_a: 1560 and 1590 °C). The combination of these advantages in such refractory concretes makes them suitable for use in severe conditions at high temperature applications especially in steel-making industries.

1. Introduction

The progress of high temperature industrial technology resulted in a substantial advances in monolithic refractories over the last decades. This has led not only to important innovations in castable preparation and application processes but also to significant improvement in product performance, in response to the constantly increasing service conditions imposed mainly by the steel and foundry industries [1,2]. The concretes based on alumina and magnesia are the most widely used high temperature materials. It has been reported that the refractoriness of refractory concretes can be increased substantially, without adversely affecting their compressive strength, when CaO in the cement clinker is partially substituted by MgO [3]. This is due to the formation of magnesium aluminate spinel which results in improved slag resistance and high hot sagging under load. Therefore, they are being used increasingly in steel-making applications such as lining of steel ladles, continuous casting tundishes and degasser snorkels and lancers [4,5]. However, their working temperatures are significantly lower and amount to 1800–1900 °C [6]. Under the service conditions involving temperatures close to 2100 °C, barium aluminate–barium zirconate cement forms the promising materials.

This work aims at the development of barium aluminate–barium zirconate cements. Their applications for the formation of refractory concretes with good technological properties are also considered.

2. Materials and experiment

2.1. Materials

Egyptian barite, calcined alumina and chemically pure zirconia were used in different proportions to prepare five

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Table 1
Chemical composition of the starting materials

	Barite	Al_2O_3	ZrO_2
SiO_2	3.38		
Fe_2O_3	0.53		
Al_2O_3	0.61	99.60	
BaO	62.08		
CaO	0.42		
ZrO_2	–		99.80
SO_3	32.42		

cement mixes designed to contain, after firing, different proportions of barium aluminate (BA)[1] and barium zirconate (BZ) minerals. The chemical analysis of the starting materials is given in Table 1.

2.2. Preparation of cement compositions

The barite, calcined alumina and pure zirconia were properly mixed to give five different cement mixes (shown in Table 2). The required proportions of the starting materials of each mix were dry blended together and then wet finely ground in a fused alumina ball mill for 6 h. After being dried, the prepared mixes were formed into briquettes under pressure of 800 kg/cm^2, dried at 110 °C for 24 h and then fired at temperatures between 1500 and 1550 °C for 3 h by heating and cooling rates of 10 °C min^{-1} to achieve complete sintering.

The resulting sintered products were crushed and then finely ground in a fused alumina ball mill to get a cement powder with Blaine surface area of 3500–4000 cm^2/g.

The cement powders were investigated through their mineralogical compositions using X-ray diffraction technique (XRD) with a Philips PW 1710 diffractometer using Ni filtered Cu Kα radiation operating at 30 mA and 40 kV while the hydrated samples were investigated using both thermal analysis (DTA and TG) with Perkin Elmer 7 analyser and XRD. Cementing properties including; water of consistency (WOC), setting time (ST), cold compressive strength (CCS) and combined water (CW), and sintering parameters including; bulk density (BD) and apparent porosity (AP) were measured using the International Standard Specifications [7].

The optimum cement mix was selected to prepare refractory concretes using either bauxite or fused spinel aggregate. The prepared refractory concretes were investigated through their mineralogical compositions using XRD and scanning electron microscope (SEM), Philips XL30, lined with energy dispersive X-ray unit (EDAX). Standard ceramographic, mounting, grinding and polishing were used and all samples were carbon coated before analysis by SEM. The different technological properties of these concretes such as, permanent linear change, cold compressive strength, thermal shock resistance and load-bearing capacity were tested and correlated with their mineralogical compositions.

3. Results and discussion

3.1. Phase composition of the prepared cements

The different physico-mechanical and chemical properties of the prepared cements are basically a function of their phase compositions. Assuming that the chemical reactions in the fired cement mixes had reached equilibrium, phases developed in the cements could be calculated theoretically [8] using their chemical compositions (Table 2) and based on the following assumptions:

- Fe_2O_3 exists in the cement as B_4AF
- SiO_2 exists as B_2S
- BaO exists as BA
- CaO exists as CA_2
- ZrO_2 exists as BZ
- Remaining alumina exists as corundum

The actual phase compositions of these cements are also determined experimentally by XRD technique (Fig. 1). The experimental results agree qualitatively with theoretical calculations given in Table 2, which means that the solid state reactions in these cements are mostly complete and had almost attained equilibrium under the testing conditions. The results indicate that:

1. From cement mix no. 1 to cement mix no. 5, the amount of BZ phase increases at the expense of BA, i.e., cement

Table 2
Compositions of the cement mixes

Cement mix no.	Mix composition (wt.%)			Chemical analysis (wt.%)						Phase composition (wt.%)					
	Barite	ZrO_2	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	CaO	BaO	ZrO_2	B_4AF	B_2S	BZ	CA_2	BA	A
1	75	2	23	3.37	0.53	31.17	0.42	61.87	2.66	2.88	20.58	5.96	1.95	65.58	3.07
2	72	5	23	3.18	0.50	30.73	0.40	58.60	6.56	2.71	19.40	14.71	1.85	53.88	7.41
3	70	10	20	3.06	0.48	26.53	0.37	56.43	12.98	2.62	18.66	29.12	1.72	38.07	9.46
4	65	15	20	2.80	0.43	26.01	0.34	51.41	19.07	1.54	17.06	42.79	1.51	21.00	16.11
5	70	23	7	3.08	0.48	9.69	0.31	56.53	29.89	2.95	15.41	56.02	1.42	0.39	23.80

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[1] Note: some cement notations are used, e.g., B: BaO, A: Al_2O_3, Z: ZrO_2, F: Fe_2O_3, C: CaO, M: MgO, etc.

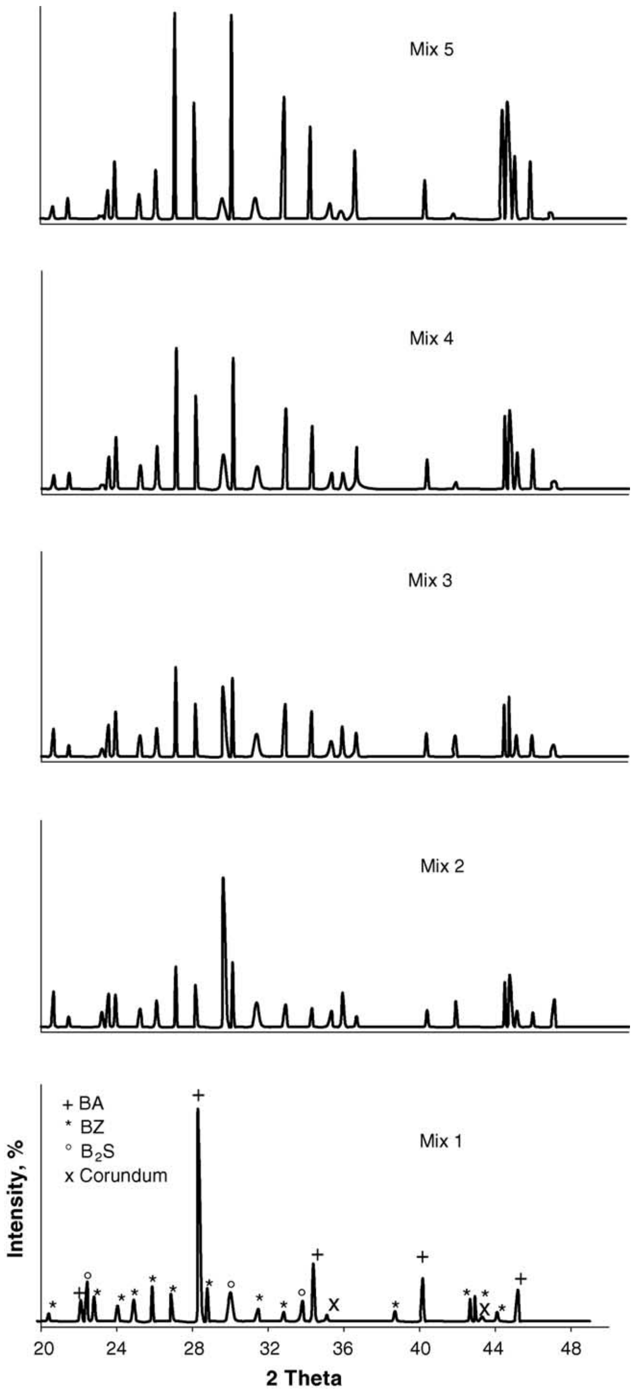

Fig. 1. XRD patterns of the prepared cement mixes.

mix no. 1 was composed mainly of BA (66 wt.%) with little BZ (6 wt.%). Cement mix no. 2 containing lower amount of BA (53 wt.%) and higher amount of BZ (15 wt.%) compared with cement mix no. 1. Cement mix no. 3 was composed of comparable proportions of BA and BZ (38 and 29 wt.%, respectively). Cement mix no. 4 containing higher amount of BZ (43 wt.%) than BA (21 wt.%). In contrast to cement mix no. 1, cement mix no. 5 was composed mainly of BZ (56 wt.%) with very little amount of BA (0.4 wt.%).

2. The amount of free alumina increased from cement mix no. 1 to cement mix no. 5.
3. All cement mixes contain comparable proportions of B_4AF (1–3 wt.%) and also B_2S (15–20 wt.%).

These differences in compositions of the prepared cement mixes result in different cementing, sintering and refractory properties.

3.2. Cementing and sintering properties of the prepared cement mixes

The amount of water added to the cement mix powder to form a cement paste is critical. Much water may lead to high porosity, and hence a deterioration in strength after drying and firing, also, little amount of water may lead to poor consolidation and workability. So, the optimum water/cement ratios were used to form pastes from the prepared cement powders by trial method using Vicat apparatus. The results given in Table 3 indicates that the optimum amount of water required to form cement pastes decreases as the BA content in the cement decreases and BZ content increases, i.e., as we proceed from cement mix no. 1 to cement mix no. 5.

Table 3 also indicates that cement mix no. 1 gives the shortest setting time. The setting becomes slower as we proceed from cement mix no. 1 to cement mix no. 5. Cement mix no. 5 gives the slowest setting among the investigated cement mixes.

Fig. 2 shows a noticeable decrease in the values of cold compressive strength as we proceed from cement mix no. 1 to cement mix no. 5, i.e., cement mix no. 1 > no. 2 > no. 3 > no. 4 > no. 5.

Table 3
Water of consistency and setting time of the cement mixes

Cement mix no.	WOC (%)	Setting time	
		Initial (h:min)	Final (h:min)
1	22	0:40	0:55
2	18	0:55	1:15
3	16	1:05	1:30
4	14	1:20	1:45
5	12	1:45	2:20

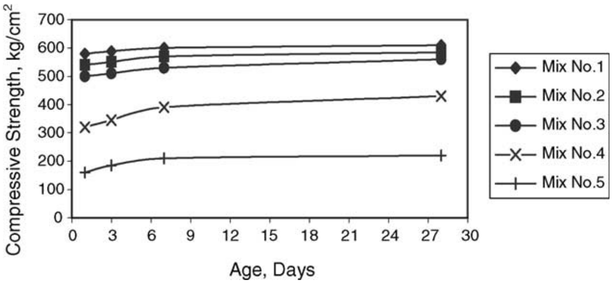

Fig. 2. Compressive strength of the hydrated cement mixes at different curing times.

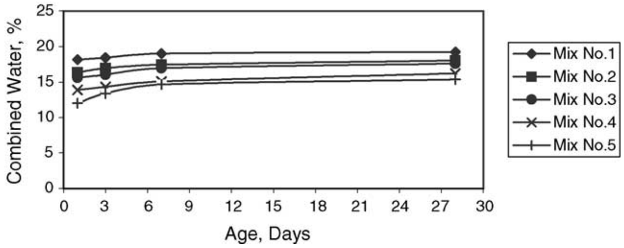

Fig. 3. Combined water of the hydrated cement mixes at different curing times.

The results of the combined water (Fig. 3), as a measure of the hydration behaviour of the cement mixes, go parallel with the mechanical properties shown in Fig. 2.

Fig. 4 shows that the sintering parameters are improved as the BA content in the cement decreases and BZ increases, i.e., as we proceed from cement mix no. 1 to cement mix no. 5 (opposite to mechanical and hydration behaviour).

The above results could be explained on the basis of the mineralogical compositions of the prepared cements shown in Table 2. Cement mix no. 1 composed mainly of BA mineral which is characterized by fast setting and very rapid hardening [6], these properties are reflected on cement mix no. 1. In contrast, cement mix no. 5 composed mainly of BZ, which is known by its slow setting and hardening, these properties are also reflected on cement mix no. 5 [9–12]. Generally, as the amount of BZ in the cement increases at the expense of BA, the cementing properties decrease. However, the cements containing up to 29 wt.% BZ (i.e., cement mixes nos. 1, 2 and 3) maintain good cementing properties, beyond which, i.e., in cement mixes nos. 4 and 5, a great deterioration in cementing properties is observed.

The increase in bulk density and hence decrease in apparent porosity as we proceed from cement mix no. 1 to cement mix no. 5 is due to the increase in the amount of relatively heavier BZ on the expense of the lighter BA [6].

In spite of the lower cementing properties of BZ compared with BA, its presence in the cement is desirable due to its relatively higher refractory properties [6]. So, cement containing the highest amount of BZ and, at the same time, maintaining appropriate mechanical properties is recommended. This is well suited on cement mix no. 3 among the prepared cement mixes. This cement is composed of comparable proportions of BA and BZ and hence it shows a compromise between good cementing and high refractory properties. So, for these technical reasons in addition to an economical reason, as the percent of relatively expensive ZrO_2 in its composition is only 10 wt.%, cement mix no. 3 is selected as the optimum composition among the investigated cement mixes.

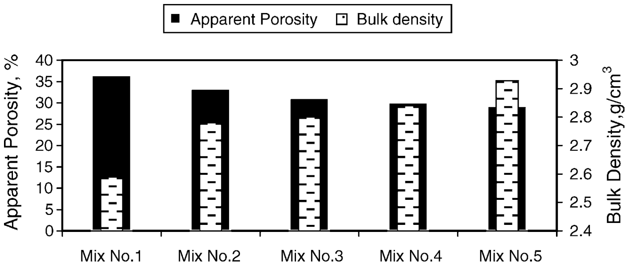

Fig. 4. Sintering parameters of the 7-days hydrated cement mix no. 3.

3.3. Hydration

The hydrated paste of the selected cement mix no. 3 was investigated after 7 days curing in a 100% relative humidity by means of thermal analysis (DTA and TG) as well as XRD technique (Figs. 5–7). The DTA (Fig. 5) shows two endothermic peaks, the first at ≈146 °C corresponding to the dehydration of BAH_2 to BA while the second peak at ≈269 °C corresponding to the dehydration of BZH to BZ [13,14]. These dissociations can be further verified by two stages of weight loss (Fig. 6). The results of thermal analysis have been confirmed by XRD (Fig. 7) which shows the main peaks characterizing the hydration products BAH_2 and BZH. Some of the original peaks of the anhydrous sample are still present after hydration due to the precipitation of the hydrated products on the surface of the hydrated grains preventing further hydration.

3.4. Preparation and characterization of concrete samples

Well-graded bauxite and fused spinel (65 wt.% coarse; 2.36–0.60 mm, 10 wt. % medium: 0.60–0.25 mm and 25 wt.

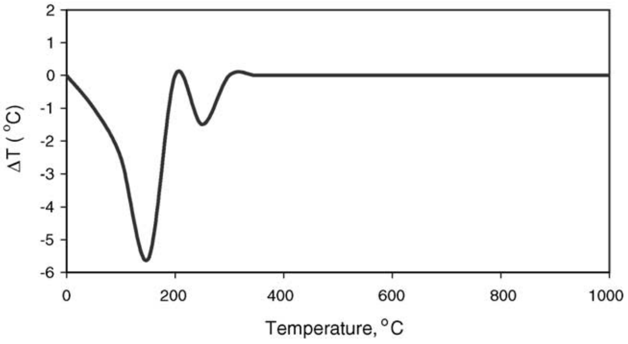

Fig. 5. DTA of the 7-days hydrated cement mix no. 3.

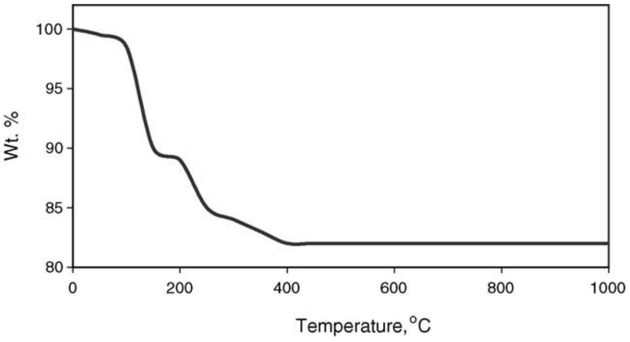

Fig. 6. TG of the 7-days hydrated cement mix no. 3.

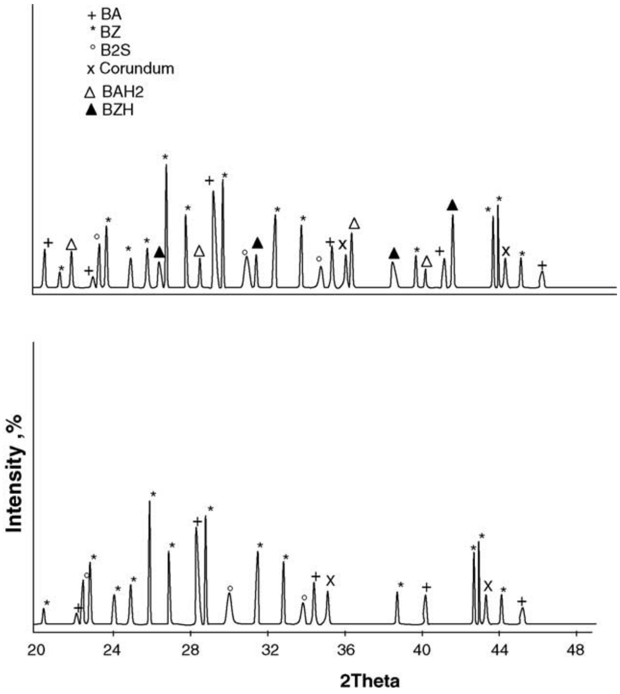

Fig. 7. XRD patterns of the 7-days hydrated cement mix no. 3.

% fine: <0.25 mm) were used as aggregates for the preparation of refractory concretes. In order to determine the optimum cement content, concrete samples were prepared using different amounts of cement (mix no. 3) ranging between 5 and 20 wt.%, in increment of 5 wt.% using the optimum amount of mixing water according to, good ball in hand, test ASTM C860. Fig. 8 indicates that the strength of the refractory concretes increases with the increase in cement proportions up to 20 wt. %, beyond which the increase in strength is less pronounced. Therefore, mixtures of 80 wt.% of either bauxite or fused spinel aggregate and 20 wt.% of cement mix no. 3 (containing comparable proportions of BA and BZ) was considered optimum for the preparation of refractory concretes having appropriate mechanical properties.

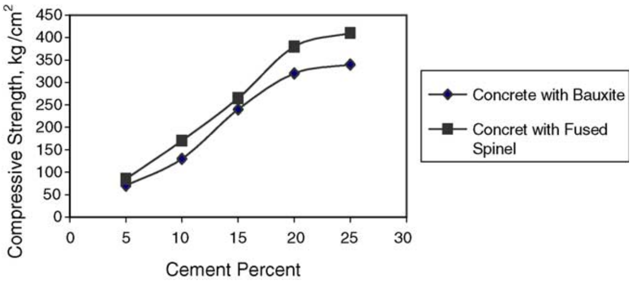

Fig. 8. Effect of cement percent on the compressive strength of refractory concretes made from cement mix no. 3 with bauxite or fused spinel aggregate.

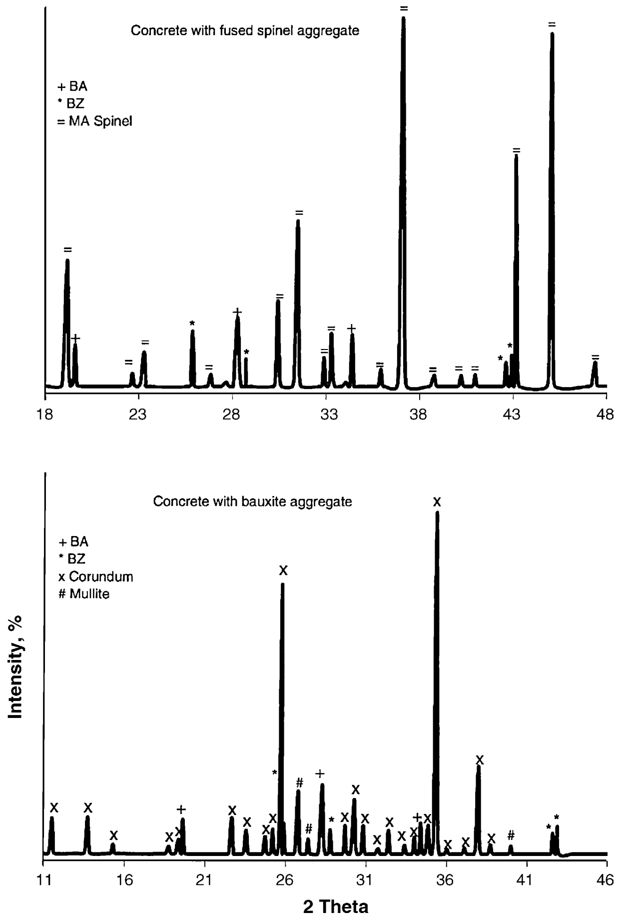

Fig. 9. XRD patterns of refractory concretes made from cement mix no. 3 with bauxite or fused spinel aggregate (after firing at 1500 °C for 3 h).

3.5. Phase composition, microstructure and technological properties of the fired concretes

The phase compositions of the fired concretes (1500 °C for 3 h) were determined by XRD (Fig. 9), and scanning electron microscope (SEM) attached with energy dispersive X-ray unit (EDAX) (Figs. 10 and 11 and Table 4). The obtained results of XRD indicates that the main constituents of concrete sample containing bauxite aggregate are α-corundum, mullite, barium aluminate and barium zirconate phases while that containing fused spinel aggregate composed mainly of magnesium aluminate spinel (MA) mineral in addition to barium aluminate and barium zirconate phases (Fig. 9), no other phases were be detected by XRD.

The photomicrographs shown in Figs. 10 and 11 show a well-compacted microstructure of both concrete samples. Fig. 10a and b shows the microstructure of the concrete sample based on bauxite aggregate, with the characteristic flattened patches of alumina crystals and the elongated rod crystals characteristic of mullite mineral. Small rounded crystals characteristic of BZ and needles characterizing BA

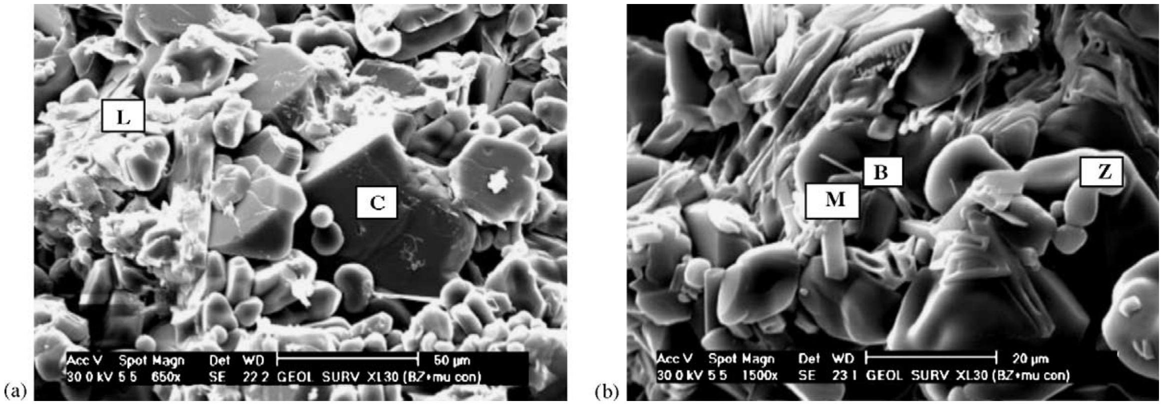

Fig. 10. SEM photomicrograph of refractory concrete made from cement mix no. 3 with bauxite aggregate. C: α-corundum, B: BA, Z; BZ, L: glassy phase.

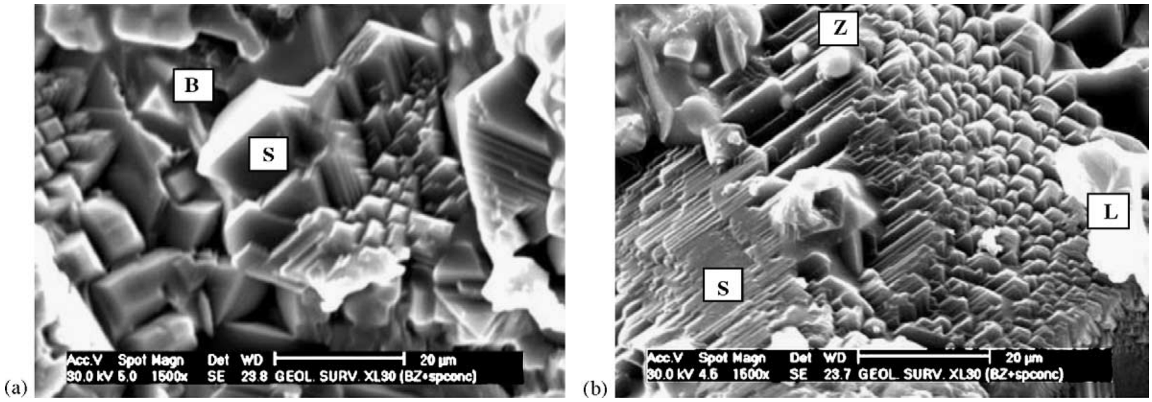

Fig. 11. SEM photomicrograph of refractory concrete made from cement mix no. 3 with fused spinel aggregate. S: MA spinel, B: BA, Z; BZ, L: glassy phase.

could also be observed. Fig. 11a and b shows the microstructure of the concrete sample based on fused spinel aggregate, with an intensive and well arranged array of euhedral magnesium aluminate spinel crystals comprising the barium aluminate and barium zirconate crystals. In both concrete samples, little amount of silicate phases bound all other constituents together. These compositions are observed in Table 4 representing EDAX of the both concrete samples.

The good technological properties of both concrete samples given in Table 5 are correlated not only to compact and homogenous microstructure but also to their phase compositions, i.e., the reactions took place in the investigated fired concrete samples resulting in mineral assemblages of MA spinel (2135 °C), BA (1830 °C), BZ (>2000 °C) in concrete sample containing fused spinel aggregate or α-corundum (2050 °C), mullite (1840 °C) with BA and BZ in concrete samples containing bauxite aggregate. The amount of low-melting phases (B_4AF) in both concrete samples is very low (that could not be detected in Fig. 9 due to their low contents) and did not affect badly their refractory properties. These microstructures lead to a considerable improvement in the mechanical properties,

Table 4
EDAX quantifications of the prepared refractory concrete samples

Element	Concrete with bauxite aggregate (wt.%, ±0.05)	Concrete with fused spinel aggregate (wt.%, ±0.05)
MgO	–	19.51
Al_2O_3	72.89	52.88
SiO_2	8.41	1.28
CaO	1.15	1.79
BaO	12.66	14.06
Fe_2O_3	0.02	0.82
ZrO_2	4.87	9.66

Table 5
Technological properties of the fired concrete samples

	Concrete with bauxite aggregate	Concrete with fused spinel aggregate
P.L.C. (%)	0.62	0.28
TSR (no. of cycles): water quenching	>30	>30
CCS (kg/cm^2)	680	610
Refractoriness (°C)	>1700	>1700
Refractoriness under load (t_a)	1560	1590

refractoriness, spalling resistance as well as load-bearing capacity of such refractory concretes. In additions, the investigated concrete samples showed good volume stability as it suffered a very small linear change which indicates that the solid state reactions in these samples are mostly thermally mature.

4. Conclusion

New types of refractory cements containing barium aluminate and barium zirconate could be prepared using barite, calcined alumina and pure zirconia as starting materials. The cement batch prepared from 70 wt.% barite, 20 wt.% alumina and 10 wt.% zirconia and containing comparable proportions of BA and BZ (38 and 29 wt.%, respectively) shows a comporomise between good cementing, sintering and high refractory properties. Refractory concretes prepared from 20 wt.% of this cement and 80 wt.% of either bauxite or fused spinel aggregate are composed mainly of mullite, barium aluminate, barium zirconate and α-corundum in case of bauxite aggregate or magnesium aluminate spinel in addition to barium aluminate and barium zirconate in case of fused spinel aggregate. These assemblages of minerals exhibit compact and homogenous microstructure which lead to outstanding technological properties that meet the requirements of international standard specifications, i.e., good volume stability, high mechanical properties, good sintering, high refractoriness, high spalling resistance as well as high load-bearing capacity. The combination of these advantages in these refractory concretes enables their use at high temperature applications, especially in steel-making industries.

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