

# Magnesia-Zirconia Refractory Materials with Aluminate Phases

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The work concerns magnesia-calcium zirconate and magnesia-calcium zirconate-spinel refractory materials intended for use in cement industry. At the material design stage, the economic aspects, wear mechanism of materials and their thermomechanical properties were taken into account. The magnesia materials were composed of coarse-grained  $\text{CaZrO}_3$  grains and fine-grained  $\text{MgAl}_2\text{O}_4$  in the amount up to 4 vol.-%. Proper selection of  $\text{CaZrO}_3$  and  $\text{MgAl}_2\text{O}_4$  contents allowed to obtain a material with very good and controlled corrosion resistance. The corrosion test of tested materials was conducted at 1450 °C, the materials were in contact with the hot kiln meal for cement clinker production. Consciously, designed intelligent materials “defended themselves” against corrosive effects during operation by properly microstructure development. A protective layer developed to prevent further corrosion of the material.

## Introduction

Introducing new technical and technological solutions in the cement industry significantly change the working conditions of the refractory lining of heating devices and cement rotary kilns [1, 2]. Example can be the use of alternative fuels, particularly scrap tires, industrial and household waste, biomass, solvent and liquid waste etc. instead of traditional fuels, which is especially observed in recent years. The alternative fuels utilization as scrap tires started at the beginning of the 1950s in Germany [3–5].

On the one hand, the use of alternative fuels is beneficial because it reduces production costs and allows obtaining higher energy efficiency, thus increasing the efficiency of the cement plant and simultaneously environmental aspects can be achieved. In the cement industry, a wide range of alternative fuels can be used. Due to long residence times at higher temperatures, cement clinker can incorporate many metal ions into its structure [6, 7]. The use of alternative fuels has a great impact on refractory materials. The destructive effect of refractory lining is

a compilation of mechanical, thermal and chemical interactions. Moreover, on the one hand, they are intended to be a structural element with suitable thermomechanical properties and, on the other hand, durable and corrosion resistant materials that have a major impact on the economics and service life of the cement kiln.

The main cause of wear of the refractory lining is the interaction of firing material, liquid phase, intermediated components, alkalis and other aggressive corrosive factors introducing with alternative fuels. Typically, their effects occur simultaneously, which results in an intensification of wear processes especially in the high-temperature zone of cement rotary kiln [8, 9].

Taking into account the above aspects, the work has attempted to design, obtain and test from the corrosion resistance point of view refractory materials. It is therefore important to introduce innovative solutions such as new types of rotary kiln refractory lining for cement clinker production that will improve the cement manufacturing process and will reduce production costs while

taking into account ecological (withdrawing the materials containing chromium) and economic (extending the refractory lining life) aspects. In the studies presented in this paper, the above and also following consideration was taken into account:

- chemical composition and phase composition of cement clinker and raw meal,
- conditions of cement clinker production and cement rotary kiln operating conditions,
- corrosive effects,
- ability to form a stable protective coating,
- currently manufactured and used refractory materials for the cement rotary kiln.

## Experimental procedure

Presented investigations were focused on the corrosion resistance improvement of magnesia materials by addition of  $\text{CaZrO}_3$  and spinel,  $\text{MgAl}_2\text{O}_4$ . The tested materials were magnesia-calcium zirconate (MCZ) and the magnesia-calcium zirconate-spinel (MCZSp) refractories. The materials were manufactured with magnesia clinker, pre-synthesized calcium zirconate and spinel at a temperature of 1580 °C. Spinel has a chemical composition similar to stoichiometric one ( $\text{MgO}$ : 28,2 mass-%;  $\text{Al}_2\text{O}_3$ : 71,8 mass-%). Magnesia clinker was characterized by  $\text{MgO}$  content above 98,5 mass-%.  $\text{CaZrO}_3$  in coarse-grained

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**Tab. 1** The chemical composition of the hot kiln meal after the stage-IV cyclone of cement kiln preheater

Components	Hot Kiln Meal after Stage-IV Cyclone of Cement Kiln Preheater	
	[mass-%]	
CaO	66,53	Main components
SiO <sub>2</sub>	13,40	
Al <sub>2</sub> O <sub>3</sub>	4,32	
Fe <sub>2</sub> O <sub>3</sub>	2,09	
K <sub>2</sub> O	4,40	Volatile components
SO <sub>3</sub>	3,82	
Na <sub>2</sub> O	0,41	
Cl	2,90	
MgO	1,01	Others
TiO <sub>2</sub>	0,43	
PbO	0,16	
SrO	0,14	
ZnO	0,10	
P <sub>2</sub> O <sub>5</sub>	0,09	
F	0,08	
Br	0,05	
MnO	0,04	
Cr <sub>2</sub> O <sub>3</sub>	0,02	
Others	0,01	

form and MgAl<sub>2</sub>O<sub>4</sub> in fine-grained form were introduced in an amount up to 4 vol.-%. The corrosion resistance of the materials was carried out with coating test at a maximum temperature of the sintered cement material (1450 °C). Hot kiln meal after the stage-IV cyclone of cement kiln preheater was used as corrosive agent. The hot kiln meal came from the cement plant where firing was carried out using alternative fuels. Tab. 1 shows the chemical composition of the hot kiln meal. The major oxide components were CaO,

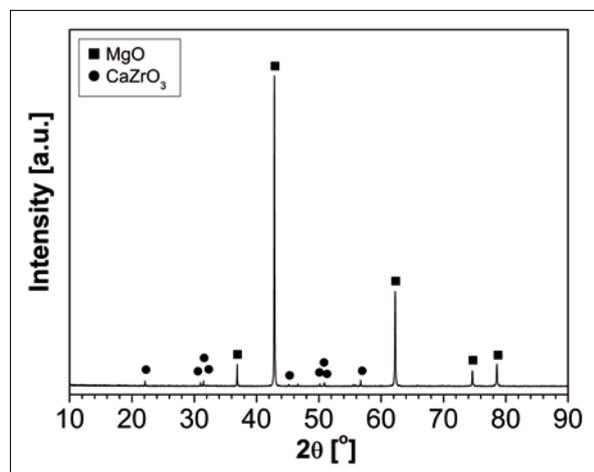
SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, which constituted 86,34 mass-%. The hot kiln meal was rich in volatile components as sulfur, chlorine, potassium and sodium oxides. The hot kiln meal consisted of β-C<sub>2</sub>S, CaCO<sub>3</sub>, SiO<sub>2</sub>, C<sub>12</sub>A<sub>7</sub>, KCl, CaSO<sub>4</sub> and CaO (C: CaO, S: SiO<sub>2</sub>, A: Al<sub>2</sub>O<sub>3</sub>). Samples of the pressed hot kiln meal were applied to refractory samples and then fired at 1450 °C with 24-h soaking time. After firing, the obtained materials were cut along the diameter and characterized. Crystalline phases were detected using X-ray powder

diffraction measurements. X-ray analyses were performed using Panalytical Empyrean diffractometer using CuK<sub>α</sub> radiation. All measurements were carried out with a 0,008° step size at 10–90° scanning range. Results analysis was carried out using the HighScore software and ICDD (International Centre for Diffraction Data) identification cards.

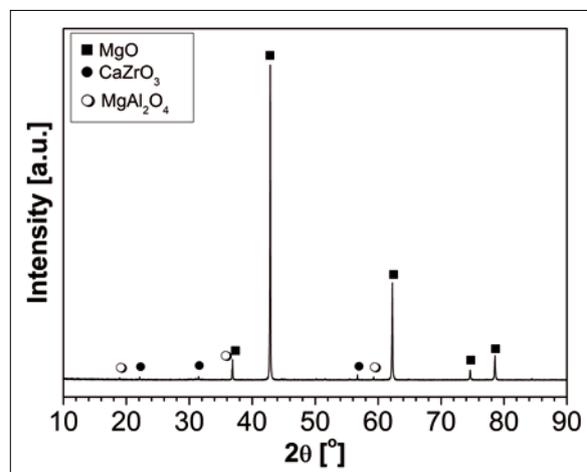
Apparent density and open porosity were measured by conventional liquid displacement method using Archimedes' principle. Additionally, pore size distribution was measured using mercury porosimetry (Pore-Master 60, Quantachrome Instruments). Microstructure was analysed using the Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDX, FEI Nova Nano SEM 200) coupled with EDAX Genesis analyser. The images were obtained using polished surfaces.

**Results**

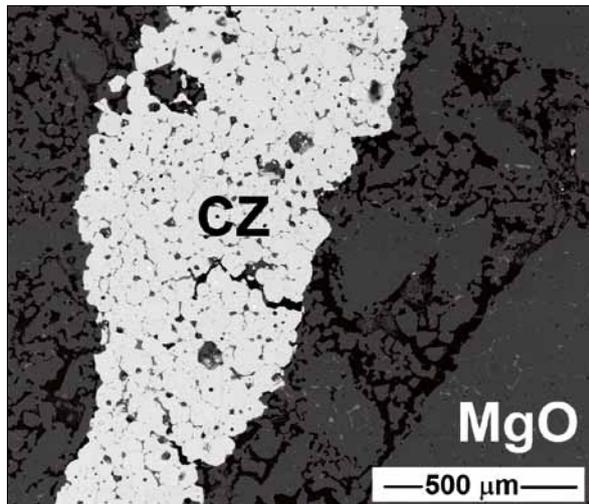
The phase composition of the tested materials was controlled using XRD. The results are presented in Figs. 1–2. The analysis showed that MCZ material consisted of two crystalline components: MgO and CaZrO<sub>3</sub>. The phase composition of the second material (MCZSp) consisted of three phases: MgO, CaZrO<sub>3</sub>, and MgAl<sub>2</sub>O<sub>4</sub>. Moreover, in both analysed materials the starting phase composition was similar to the composition finally formed after firing at 1580 °C. The microstructure of the materials is shown in Figs. 3–4. The microstructure of MCZ material showed CaZrO<sub>3</sub> aggregates (CZ) surrounded by periclase groundmass. The material was characterised by an open



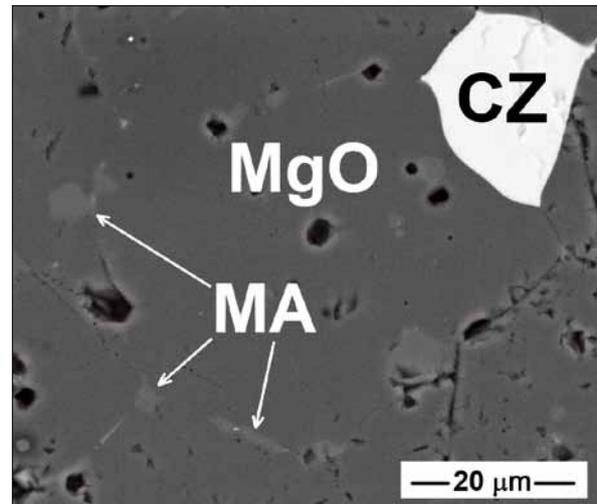
**Fig. 1** XRD pattern of the MgO–CaZrO<sub>3</sub> material



**Fig. 2** XRD pattern of the MgO–CaZrO<sub>3</sub>–MgAl<sub>2</sub>O<sub>4</sub> material



**Fig. 3** SEM micrograph of the MgO–CaZrO<sub>3</sub> material (CZ: CaZrO<sub>3</sub>)



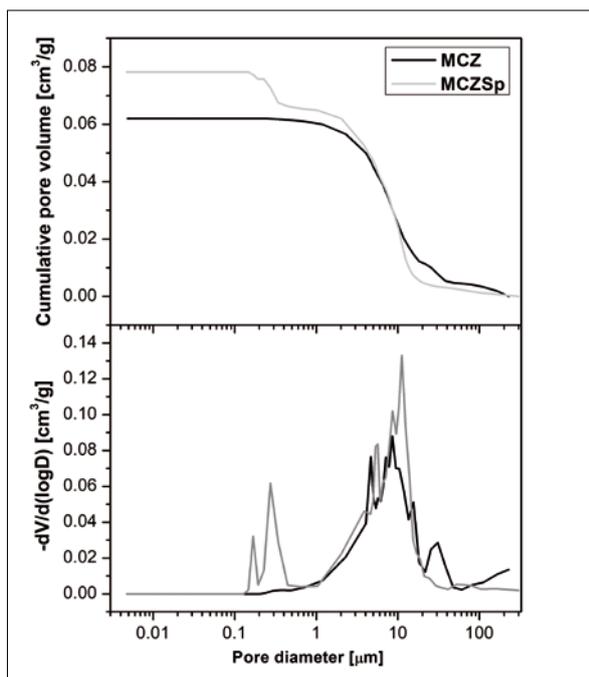
**Fig. 4** SEM micrograph of the MgO–CaZrO<sub>3</sub>–MgAl<sub>2</sub>O<sub>4</sub> material (CZ: CaZrO<sub>3</sub>; MA: MgAl<sub>2</sub>O<sub>4</sub>)

porosity of about 17,1 %. The similar microstructure was obtained for MCZSp material. The SEM image in higher magnification of the MCZSp material is shown in Fig. 4. Fine-grained MgAl<sub>2</sub>O<sub>4</sub> grains were located between MgO and CaZrO<sub>3</sub> grains at grain boundaries and triple points. MgAl<sub>2</sub>O<sub>4</sub> grains reached the maximum size of about 10 μm and were uniformly distributed. The MCZSp material was characterized by lower open porosity than the MCZ material, i.e. about 15,7 %.

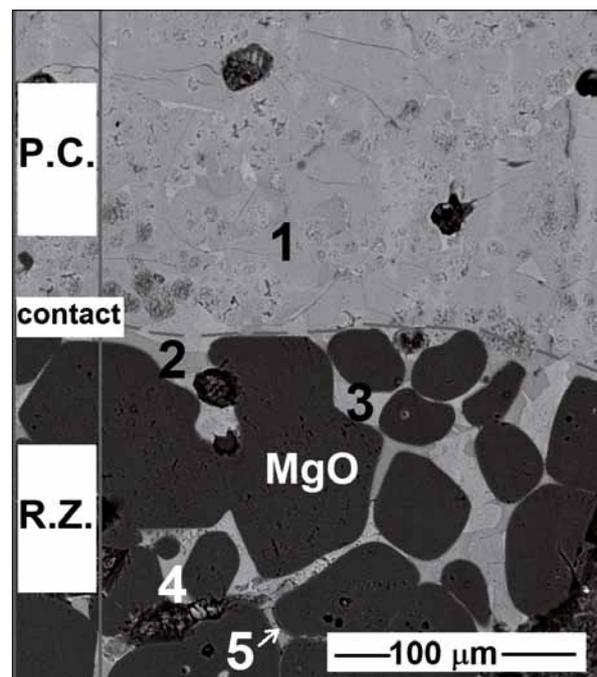
Changes in volume and pores diameter of the MCZ and MCZSp materials were analysed using mercury porosimetry (Fig. 5). The results indicate that the materials exhibited a multimodal pore size distribution. Both materials were characterized by a high amount of pores between 1–20 μm. In MCZ material a population of about 30 μm in diameter was observed. This population of pores was not observed for the second material, but there were smaller pores in the range 0,1–1 μm.

After contact corrosion, a protective cement clinker coating developed on both tested materials. This coating was easy to remove from the MCZ material. Fig. 6 shows the SEM microstructure of MCZSp material after corrosion. The EDS analysis is presented in Tab. 2.

In the upper part of the micrograph, the protective cement clinker coating – P.C. (light gray area) with the specified alite grain – point 1 is showed. The zone in the refractory material in the contact area con-



**Fig. 5** Cumulative pore volume changes and pore size distributions (pore frequency curve)



**Fig. 6** SEM micrograph of MCZSp material after corrosion (P.C. – protective coating; R.Z. – reaction zone)

**Tab. 2** Examples of chemical compositions identified by EDS in the points marked in Fig. 6 (C: CaO; A: Al<sub>2</sub>O<sub>3</sub>; S: SiO<sub>2</sub>; F: Fe<sub>2</sub>O<sub>3</sub>; Z: ZrO<sub>2</sub>)

Element	Points at Fig. 6				
	1 C <sub>3</sub> S	2 C <sub>3</sub> A	3 C <sub>4</sub> AF	4 C <sub>2</sub> S	5 C <sub>7</sub> A <sub>3</sub> Z
	[atomic-%]				
O	49,8	48,4	47,8	57,2	48,3
Mg	1,6	–	1,9	1,2	2,1
Al	0,9	18,5	15,8	1,9	19,7
Si	14,5	2,5	4,5	14,2	2,2
Zr	–	–	–	–	3,1
Ca	33,2	29,5	23,2	25,5	22,6
Fe	–	1,1	6,8	–	2,0

**Tab. 3** Summary of the obtained results

Refractory Material	Phase Composition	Open Porosity	Stability of Protective Cement Clinker Coating	New Phase Formation during Corrosion	Reaction Zone in the Material
MgO–CaZrO <sub>3</sub>	MgO CaZrO <sub>3</sub>	17,1	unstable	no	wide
MgO–CaZrO <sub>3</sub> +4 vol.-% MgAl <sub>2</sub> O <sub>4</sub>	MgO CaZrO <sub>3</sub> MgAl <sub>2</sub> O <sub>4</sub>	15,7	stable	yes	limited

sisted of MgO grains. The space between these grains was filled with solid solution of C<sub>3</sub>A – point 2, C<sub>4</sub>AF – point 3, and C<sub>2</sub>S – point 4. There was no presence of MgAl<sub>2</sub>O<sub>4</sub>. A new crystalline component developed: C<sub>7</sub>A<sub>3</sub>Z – point 5. In the material without MgAl<sub>2</sub>O<sub>4</sub>, C<sub>7</sub>A<sub>3</sub>Z was not formed. The thickness of the reaction zone in the material without MgAl<sub>2</sub>O<sub>4</sub> was three times higher.

## Discussion

MCZ and MCZSp materials were obtained at 1580 °C. The XRD analysis indicated that no new phases have developed. This is due to the fact that MgO, CaZrO<sub>3</sub>, and MgAl<sub>2</sub>O<sub>4</sub> are compatible with each other up to 1580 °C. Furthermore, the materials were obtained practically without the presence of a liquid phase. The liquid phase appears at 2050 °C in the MgO–CaZrO<sub>3</sub> system [10] and at 1650 °C in the CaZrO<sub>3</sub>–MgAl<sub>2</sub>O<sub>4</sub> system [11]. The source of the liquid phase could be the contamination from magnesia clinker.

The process of obtaining both materials proceeded through sintering in a solid phase. Both materials were characterized by similar microstructure. Introduction of fine-grained MgAl<sub>2</sub>O<sub>4</sub> reduced the open porosity from 17,1 % to 15,7 %. Moreover, fine-grained MgAl<sub>2</sub>O<sub>4</sub> filled the pores with a mean size

of 30 µm presented in the MCZ material, and thus a new population of smaller pores appeared in MCZSp material. The introduction of MgAl<sub>2</sub>O<sub>4</sub> also influenced sintering and allowed to obtain a more compacted microstructure. The corrosion mechanism of the MCZ material can be regarded as a corrosive mechanism involving liquid phase formation. The liquid phase penetrates the material along the grain boundaries, microcracks and pores with the simultaneous dissolution of MgO and CaZrO<sub>3</sub> developed. In addition to the presented process, MCZSp corrosion is also related to a chemical reaction that results in the formation of a new crystalline phase: C<sub>7</sub>A<sub>3</sub>Z.

C<sub>7</sub>A<sub>3</sub>Z is formed by the lack of co-stability of MgAl<sub>2</sub>O<sub>4</sub> with C<sub>3</sub>S and C<sub>3</sub>A and the reaction with CaZrO<sub>3</sub>. MgAl<sub>2</sub>O<sub>4</sub> takes part in liquid formation with cement clinker phases, in which CaZrO<sub>3</sub> is soluble, afterwards C<sub>7</sub>A<sub>3</sub>Z crystallized from the liquid phase. MgAl<sub>2</sub>O<sub>4</sub> was not resistant to the corrosive effects of cement clinker, but its small amount was conducive to inhibit the liquid phase penetration into the material. This process significantly reduced corrosion. This knowledge allows to optimise the composition and improve materials properties and so to increase their working time. The summary of the obtained results is presented in Tab. 3.

## Conclusions

Simultaneous introduction of CaZrO<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> in relatively small amounts up to 4 vol.-% into magnesia refractory materials improved their properties. Their presence improved resistance of magnesia refractories to chemical corrosion caused by cement clinker. On the surface of magnesia materials containing CaZrO<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub>, a stable protective coating developed and the reaction zone was limited. The optimization of the basic bricks by careful design of phase combinations due to high-performance microstructure development improved the properties of refractory lining of cement rotary kiln. The use of CaZrO<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> with the right particle size and in the right quantities allowed to obtaining deliberately-designed corrosion resistance properties.

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