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Ceramics International 36 (2010) 1877–1885

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Chemical corrosion of basic refractories by cement kiln materials

Jacek Szczerba *

AGH – University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Cracow, Poland

Received 9 November 2009; received in revised form 25 February 2010; accepted 18 March 2010
Available online 27 April 2010

Abstract

The study of basic refractories corrosion by cement kiln materials was carried out with powder tests and coating tests at the typical temperature range of the sintered material in the transition zone and the sintering zone (1200–1450 °C). The tested basic refractories were magnesia-spinel (MSp) and magnesia–zirconia (MZ) refractory bricks. The industry cement kiln materials were rich of sulphur and chlorine. The microstructures of the as-delivered and tested samples were researched by XRD and SEM–EDS techniques. The new phases detected in the samples with MSp (with and without ZrO_2) bricks after tests at the temperature of 1200 °C were binary ($C_{12}A_7$ t_{mp} – 1392 °C, $CaZrO_3$: t_{mp} – 2345 °C)[1]: and ternary (C_2AS: t_{mp} – 1593 °C or C_3MS_2: t_{dp} – 1573 °C) phases. After tests at the temperature of 1300 °C and higher, ternary phases of C_7A_3Z (t_{mp} – 1550 °C) and $CaZrO_3$ and quaternary phases Q-$C_{20}A_{13}M_3S_3$ or $C_6A_4(M,f)S$ (t_{dp} – 1380 °C) were detected. The $C_3A_3{\cdot}CaSO_4$ phase was formed in the samples after the corrosion tests performed up to the temperature of 1300 °C. The new phases formed in the sample with the MZ bricks were clinker phases (β-C_2S, C_3A and $C_2(A,F)/C_4AF$) and the C_7A_3Z phase.

Keywords: B. Electron microscopy; C. Corrosion; Basic refractories; Cement kiln; Microstructure; XRD

1. Introduction

The secondary and subordinate phases of basic refractory bricks in the sintering zone of cement rotary kilns are corroded in the first instance by the cement clinker phases (C_3S, C_2S, C_3A, C_4AF and liquid phase) [1–3]. This depends on the temperature. The length of the sintering zone of cement rotary kilns is usually identified by the presence of the liquid phase in the clinker [4,5]. A liquid phase in the clinker appears at the zero-point of the C_3S–C_2S–C_3A–C_4AF subsystem of the CaO–SiO_2–Al_2O_3–Fe_2O_3 system at the temperature of 1338 °C [6]. The liquid phase which can appear earlier, at the temperature of ca. 1280 °C, is related to the eutectic in the C_2S–$C_{12}A_7$–$C_2(A,F)$ subsystem. The presence of MgO and R_2O (R = K, Na) decreases the temperature of liquid phase appearance to 1260 °C [7]. Yet an earlier liquid phase may appear and could be related to eutectic of CF–CF_2 at the temperature of ca. 1200 °C.

Presently, the magnesia-spinel bricks can be observed among the basic refractories to be used in the sintering zone of cement rotary kilns [8–10]. The present research was undertaken in order to better recognize the new phases formation as a result of the chemical corrosion reaction between the phases from the basic bricks (MSp and MZ) and the phases from the cement clinker.

The research was carried out with powder tests and coating tests at typical temperatures of the sintered cement material in the transition zone and the sintering zone (1200–1450 °C). The refractory materials were the magnesia-spinel bricks and the magnesia–zirconia bricks. The industry cement materials (rich in sulphur and in chlorine), were the hot kiln meal taken from the precalciner cement kiln, and the Portland clinker obtained afterwards.

2. Experimental procedure

2.1. Materials

Nowadays, in cement kilns, parallel to traditional fuels and raw materials, alternative (secondary) fuels and raw materials are used. Their utilization may influence the heat balance and increase of chloride and sulphate or alkali oxides present in the

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* Tel.: +48 12 6172501.
E-mail address: jszczerb@agh.edu.pl.

[1] C-CaO; A-Al_2O_3; S-SiO_2; M-MgO; F-Fe_2O_3; Z-ZrO_2; f-FeO; t_{mp} – melting point; t_{dp} – disintegration point.

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doi:10.1016/j.ceramint.2010.03.019

Table 1
The standard chemical and physical average values of tested basic bricks.

	MSp type I	 II	 III	 IV	MZ type I	 II
Physical properties[a]						
BD, g/cm^3	~2.94	~2.99	~2.91	~2.9	~3.0	~3.1
OP, %	14–16	14–16	16–18	~18	~17	~16.5
CCR, MPa	50–70	40–60	50–70	~40	~58.0	~45.0
Chemical composition, wt.%						
SiO_2	0.3	0.4	1.1	0.9	0.3	0.3
CaO	0.9	0.8	0.6	0.6	4.5	5.5
Al_2O_3	5.5	12	12.6	7.0	0.2	0.2
Fe_2O_3	0.5	0.4	1.9	1.3	0.4	0.2
ZrO_2	–	2.7	–	–	8.0	11.0
MgO	92.1	82.7	82.1	89.5	86.0	82.0

[a] BD – bulk density; OP – open porosity; CCR – cold crashing strength.

Table 2
Volatile components of materials from cement kiln.

Component	Hot kiln meal	Portland clinker
K_2O	1.7	1.1
Na_2O	0.1	0.1
SO_3	4.9	2.5
Cl^-	3.5	–

process. Fuels combustion is conducted with an air extent. It assures that the process of cement clinker firing goes generally in an oxidizing atmosphere. Disturbances of fuel firing process may be responsible for appearance of the local areas with reducing conditions. The crucial for the proper course of cement clinker firing process is assuring the balance between alkali oxide and sulphur content. This balance is described as an alkali-sulphate ratio $(ASR = (K_2O/94 + Na_2O/62 - Cl_2/71)/(SO_3/80))$. It is commonly accepted that optimal ASR value should be situated in the range of 0.8–1.2. This determined the choice of precalciner material and clinker cement taken from the same precalciner cement kiln as materials for investigations.

The tested materials were the magnesia-spinel (MSp) and the magnesia–zirconia (MZ) refractories (Table 1) the hot kiln meal (rich in sulphur and chlorine) and the Portland clinker (rich in sulphur) (Table 2) taken from the same precalciner cement kiln. The magnesia-spinel materials were manufactured with magnesia clinker and fused spinel (MSpI, MSpII and MSpIII) or spinel clinker (MSpIV). The MSpII brick contained a zirconia addition. The magnesia–zirconia bricks were prepared with magnesia clinker and calcium zirconate clinker.

The microstructure of the tested magnesia-spinel bricks showed periclase aggregates (sintered grains) and spinel aggregates (fused or sintered grains) surrounded by the

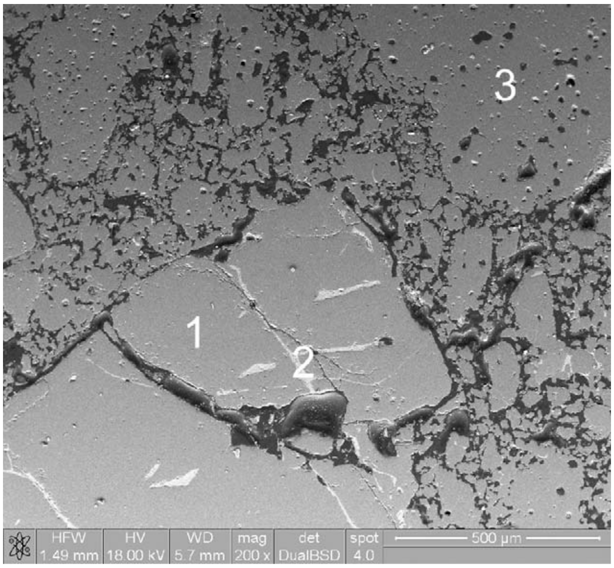


Fig. 1. MSpI brick (Table 1). Magnesia clinker and spinel aggregates surrounded by a periclase groundmass and pores (black spots). 1 – fused spinel; 2 – CA_{ss}; 3 – sintered magnesia.

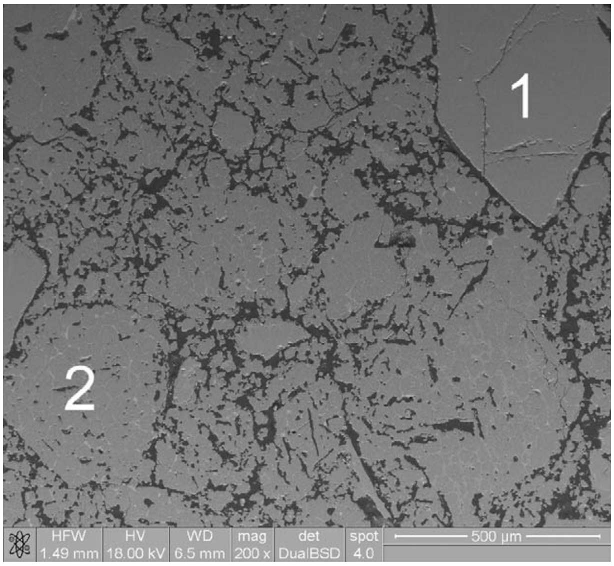


Fig. 2. MSpIII brick (Table 1). Magnesia clinker and spinel aggregates surrounded by a periclase groundmass and pores (black spots). 1 – sintered spinel; 2 – sintered magnesia.

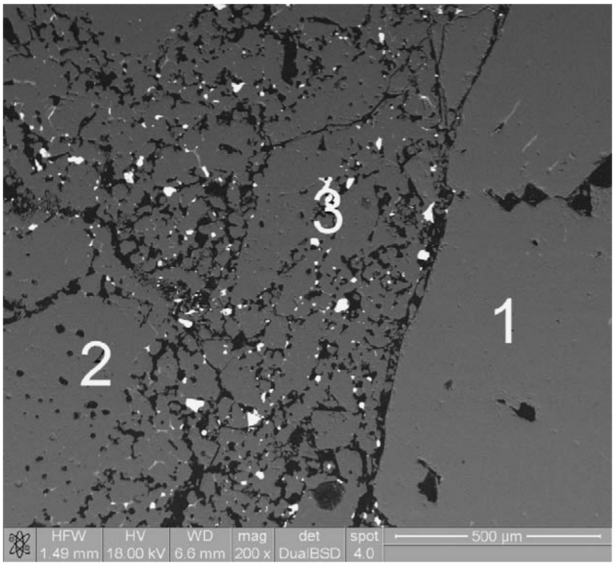


Fig. 3. MSpII brick (Table 1). The stabilized ZrO_2 (3) between the periclase grains of the groundmass surrounded of magnesia clinker (2) and spinel (1) aggregates. Black spots are pores.

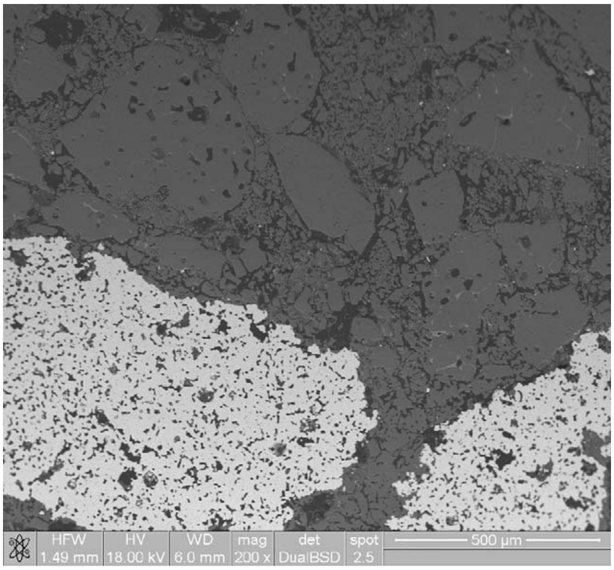


Fig. 5. MZ II brick (Table 1). Sintered magnesia (grey) and sintered calcium zirconate (white) aggregates surrounded by the periclase groundmass and pores (black spots).

periclase groundmass (Figs. 1 and 2). The subordinate phases as the silicate phases β-$Ca_2[SiO_4]$ (C_2S), $Ca_3Mg[SiO_4]_2$ (C_3MS_2), $CaMg[SiO_4]$ (CMS), $Mg_2[SiO_4]$ (M_2S) and the calcium aluminate phase $CaAl_2O_4$ (CA), depending on the CaO/SiO_2 and the CaO/Al_2O_3 molar ratios, were homogeneously distributed between periclase grains.

Dicalcium silicate β-$Ca_2[SiO_4]$ and calcium aluminate $CaAl_2O_4$ were the bonding phases of MSpI. The bonding phases of MSpII were merwinite $Ca_3Mg[SiO_4]_2$ and monticellite $CaMg[SiO_4]$. Besides silicates, stabilized ZrO_2 was homogeneously distributed in the periclase groundmass of MSpII brick (Fig. 3). Forsterite $Mg_2[SiO_4]$ and monticellite $CaMg[SiO_4]$ were the bonding phases of MSpIII and MSpIV. Magnesio-ferrite $MgFe_2O_4$ (MF) could be seen as the inclusions in periclase grains of the magnesia-spinel III and IV bricks richer in the Fe_2O_3 (Fig. 4).

The microstructure of the magnesia–zirconia MZI brick shows periclase sintered grains and calcium zirconate sintered

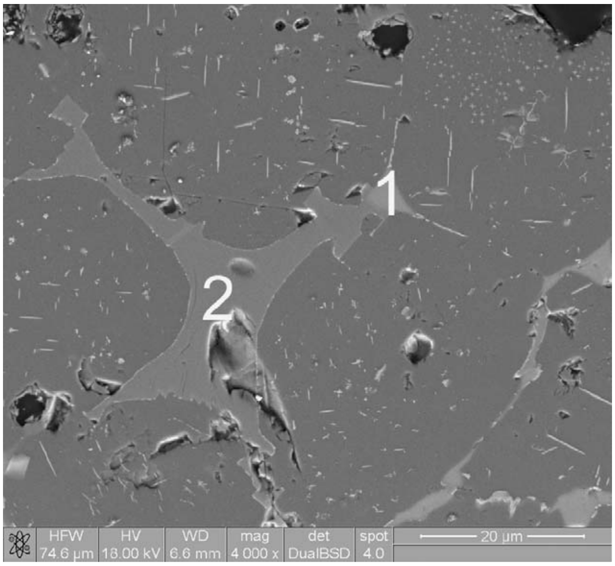


Fig. 4. MSpIII brick (Table 1). Magnesia-spinel (MA – 2) as an interstitial substance with subordinate silicate M_2S (1) between the periclase grains and the inclusions of solid solution MF in the periclase grains. Black spots are pores.

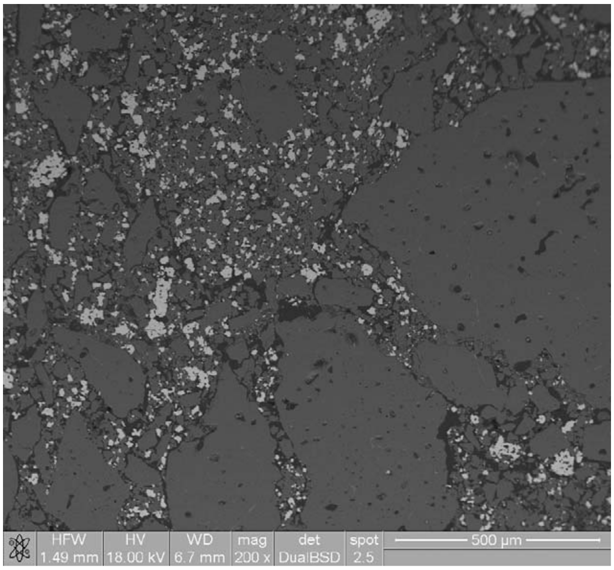


Fig. 6. MZ I brick (Table 1). The calcium zirconate (white) between the periclase (grey) grains of the groundmass surrounded of sintered magnesia aggregates. Black spots are pores.

grains surrounded by the periclase groundmass (Fig. 5). Contrary to this, the microstructure of magnesia–zirconia MZII brick showed periclase sintered grains surrounded by the periclase and calcium zirconate groundmass (Fig. 6). The subordinate phases, such as β-$Ca_2[SiO_4]$ and $Ca_3Mg[SiO_4]_2$ silicate phases, were homogeneously distributed between periclase grains.

The phases of the hot kiln meal identified by the X-ray analysis were belite β-C_2S, mayenite $Ca_{12}Al_{14}O_{21}$ ($C_{12}A_7$), anhydrite $CaSO_4$, sylvine KCl and the remains of quartz SiO_2 and calcite $CaCO_3$. The main phases of the Portland clinker were alite $Ca_3[SiO_4]O$ (C_3S), belite β-C_2S, calcium aluminate $Ca_3Al_2O_6$ (C_3A) and calcium alumino-ferrite phase Ca_2AlFeO_5 (C_4AF).

2.2. Sample preparation and analysis technique

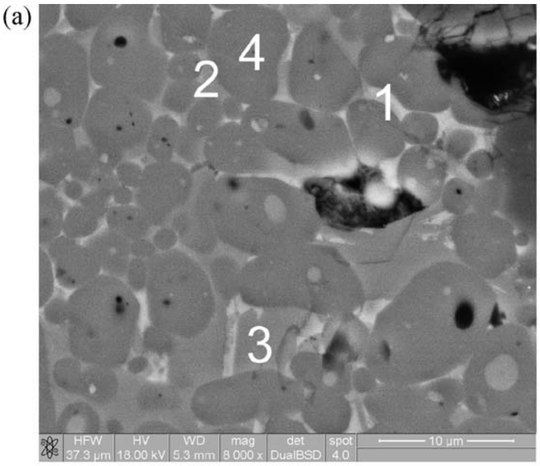
The powder tests were carried out with mixes of brick (MSpI, MSpII and MZII) to hot kiln meal or Portland clinker, with a mass ratio 3:1. The tested materials were ground below 0.063 mm. Pellets, 20 mm in diameter and 10 mm in height, were pressed at 100 MPa. The samples with the hot kiln meal were heated up to 1200 °C and those with Portland clinker to 1300 and 1400 °C with a 2 h soaking time at each temperature and cooled down together within the laboratory electric furnace. The phases were identified by XRD analysis.

The coating tests were carried out with bricks disks (30 mm in diameter and 20 mm in height) covered with powder (below 0.063 mm) of hot kiln meal or Portland clinker. The surface of each disks was polished before being pressed with the hot kiln meal or the Portland clinker, in the mold of 50 mm diameter, under a pressure of 50 MPa. The samples with the hot kiln meal were heated up to the temperature of 1300 °C, and the samples with the Portland clinker were heated up to the temperature of 1450 °C with 5 h soaking time at each temperature and cooled down together with the laboratory electric furnace. Then, the prepared microsections were observed by scanning electron microscopy (SEM) equipped with EDS chemical microanalyser.

3. Results and discussion

3.1. The powder tests

The new phases formed as a result of chemical reactions between components of the hot kiln meal and components of basic bricks at the powder tests were the calcium sulphate aluminate $Ca_4Al_6O_{12}(SO_4)$ ($C_3A_3 \cdot CaSO_4$) (in the samples of



(b) $C_6A_4(M,f)S$ (point 3)

(c) $C_3A_3 \cdot CaSO_4$ (point 4)

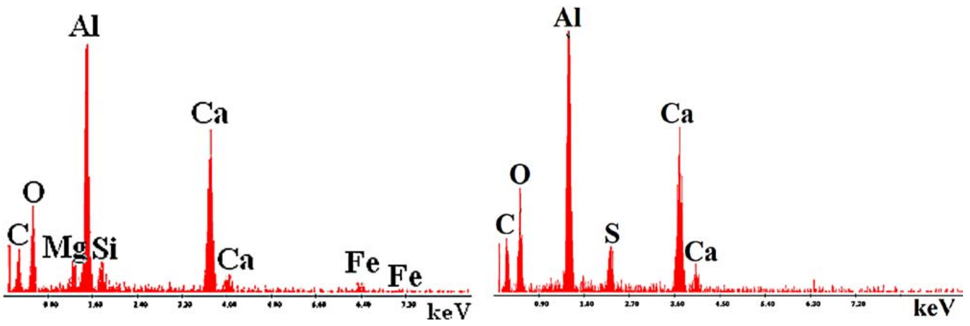


Fig. 7. The $C_3A_3 \cdot CaSO_4$ (4) phase surrounded by calcium aluminates phases: $C_6A_4(M,f)S$ (2, 3) and $C_2(A,F)$ (1): (a) SEM image; (b) EDS analysis suggesting the presence of $C_6A_4(M,f)S$ phase (point 3-SEM image); (c) EDS analysis suggesting the presence of $C_3A_3 \cdot CaSO_4$ phase (point 4-SEM image).

Table 3
Identified phases by XRD analysis of mixes of a brick and the hot kiln meal. Temperature of 1200 °C.

Brick	Phases
MSpI	MgO, β-Ca_2SiO_4, C_3MS_2, $C_{12}A_7$, $C_3A_3{\cdot}CaSO_4$
MSpII	MgO, β-Ca_2SiO_4, $CaZrO_3$, $MgAl_2O_4$, $C_{12}A_7$, $C_3A_3{\cdot}CaSO_4$
MZII	MgO, $CaZrO_3$, β-Ca_2SiO_4, C_4AF, $C_3A_3{\cdot}CaSO_4$, C_3A

MSpI, MSpII and MZ) and calcium zirconate $CaZrO_3$ (in the samples of MSpII and MZ) (Table 3). The primary phases of the spinel and the zirconia from the magnesia-spinel bricks have disappeared. The formation of the $C_3A_3{\cdot}CaSO_4$ phase was probably due to the reactions between the spinel from the bricks and phases from the hot kiln meal (e.g. $CaSO_4$ and CaO) or between the hot kiln meal: $CaSO_4$, $Ca_3Al_2O_6$, CaO and SiO_2 and ZrO_2 from the MZ brick, according to the following equations:

$$CaSO_4 + 3CaO + 3MgAl_2O_4 \rightarrow Ca_4Al_6O_{12}(SO_4) + 3MgO \quad \text{(I)}$$

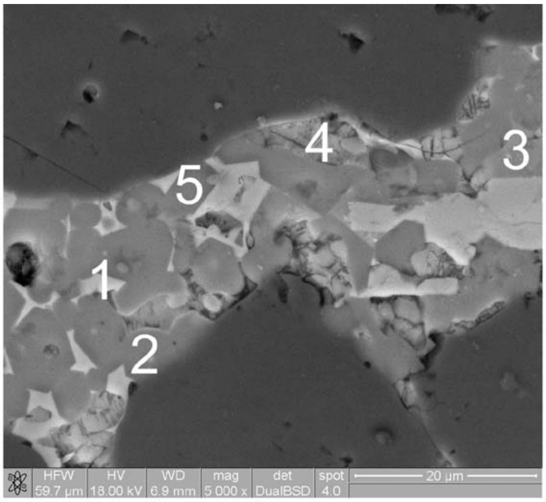
$$CaSO_4 + Ca_3Al_2O_6 + 7SiO_2 + CaO + 2ZrO_2 \rightarrow Ca_4Al_6O_{12}(SO_4) + 7Ca_2[SiO_4] + 2CaZrO_3 \quad \text{(II)}$$

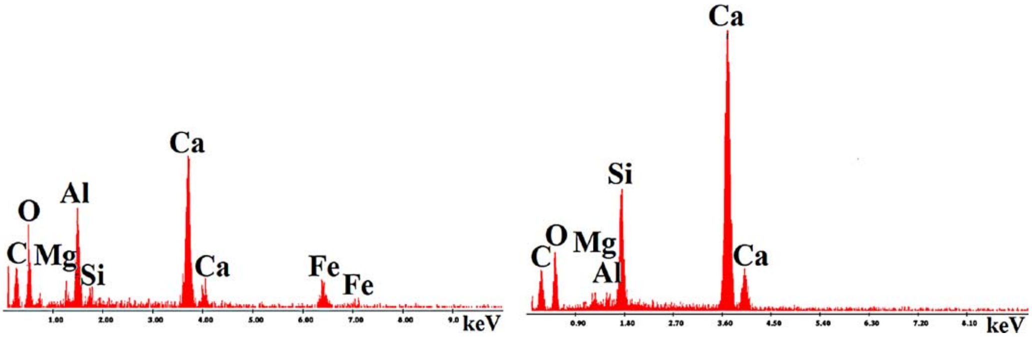
The $C_3A_3{\cdot}CaSO_4$ phase is stable up to the temperature of 1350 °C [12]. The $CaZrO_3$ is the result of the chemical reaction between the zirconia from the MSpII brick and the CaO oxide from the hot kiln meal. Silicate and aluminate phases found in the samples were compatible with the periclase [13].

The new phases formation was a result of chemical reactions between components of the Portland clinker and components of basic bricks at the powder tests—the calcium aluminate $C_{12}A_7$, the calcium sulphate aluminate $Ca_4Al_6O_{12}(SO_4)$ ($C_3A_3{\cdot}CaSO_4$), calcium zirconate $CaZrO_3$ and the $C_{20}A_{13}M_3S_3$ phase, at the applied temperature of 1300 °C (Table 4). The quaternary $C_{20}A_{13}M_3S_3$ phase is also a new phase at the tested temperature of 1400 °C (Table 4). This phase was reported in the previous investigations, which were carried out with the mixtures of the cement clinker and the sintered spinel [2]. The primary phases of the spinel and the zirconia from the magnesia-spinel bricks and the silicate C_3S phase and the C_3A phase from the Portland clinker disappeared. Silicate and aluminate phases found in the samples were compatible with the periclase [13].

The formation of calcium sulphate aluminate in the samples with the Portland clinker at the temperature of 1300 °C took place, probably due to the reactions between spinel from the

(a)




(b) $C_2(A,F)$ (point 1)

(c) β-C_2S (point 4)

Fig. 8. The tabular form of the $C_3A_3{\cdot}CaSO_4$ (2, 5), the alumino-ferrites: $C_2(A,F)$ (1) and $C_6A_4(M,f)S)$ (3) and the silicate β-C_2S (4) as interstitial substances between periclase grains (dark grey): (a) SEM image; (b) EDS analysis suggesting the presence of $C_2(A,F)$ phase (point 1-SEM image): (c) EDS analysis suggesting the presence of β-C_2S phase with Mg and Al admixtures (point 4-SEM image).

Table 4
Identified phases by XRD analysis of mixes of a brick and Portland clinker.

Brick	Phases
Temperature of 1300 °C	
MSpI	MgO, β-Ca_2SiO_4, $C_{12}A_7$, $C_3A_3{\cdot}CaSO_4$, C_3A, C_4AF
MSpII	MgO, β-Ca_2SiO_4, $CaZrO_3$, $MgAl_2O_4$, $C_{20}A_{13}M_3S_3$, $C_{12}A_7$, $C_3A_3{\cdot}CaSO_4$, C_4AF
MZII	MgO, $CaZrO_3$, Ca_3SiO_5, C_3A, C_4AF
Temperature of 1400 °C	
MSpI	MgO, β-Ca_2SiO_4, $C_{12}A_7$, C_4AF
MSpII	MgO, β-Ca_2SiO_4, $CaZrO_3$, $MgAl_2O_4$, $C_{20}A_{13}M_3S_3$, C_4AF
MZII	MgO, $CaZrO_3$, Ca_3SiO_5, C_3A, C_4AF

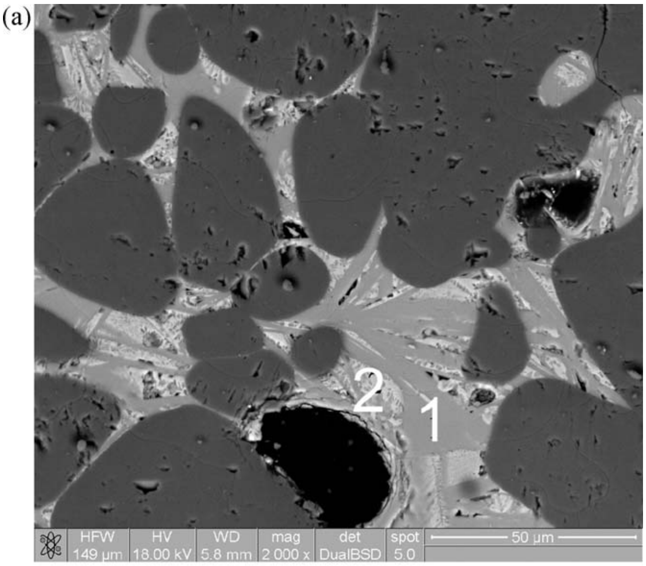
bricks and C_3S and C_3A phases and the SO_3 oxide, which could form K_2SO_4 and $CaSO_4$ and could dissolved in the cement phases [4], from the clinker, in the presence of the liquid phase (*L*), according to the following equations:

$$4Ca_3SiO_5 + 3MgAl_2O_4 + SO_3 \rightarrow Ca_4Al_6O_{12}(SO_4) + 4Ca_2SiO_4 + 3MgO \qquad \text{(III)}$$

or

$$Ca_3Al_2O_6 + Ca_3SiO_5 + 2MgAl_2O_4 + SO_3 \rightarrow Ca_4Al_6O_{12}(SO_4) + Ca_2SiO_4 + MgO \qquad \text{(IV)}$$

The $C_3A_3{\cdot}CaSO_4$ phase was reported in some of the used magnesia-spinel bricks taken from burning and transition zones of rotary cement kilns [14,15].



(b) C_6A_4(M,f)S (point 1)

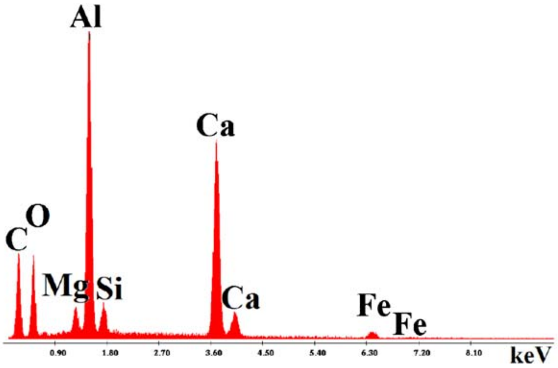
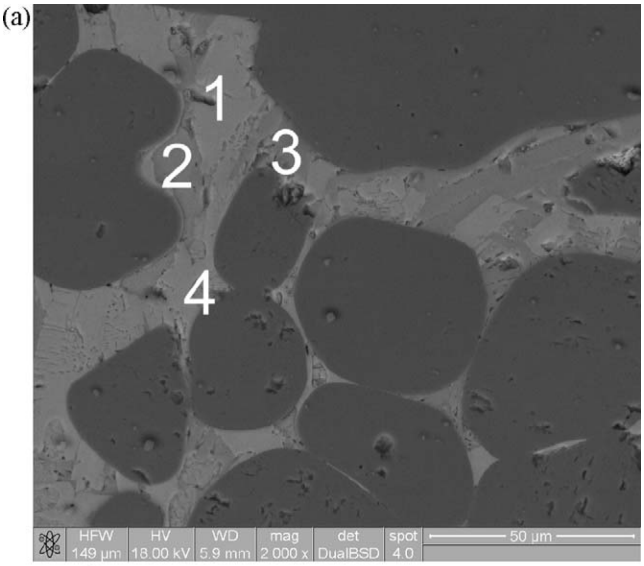


Fig. 9. The elongated crystals of the C_6A_4(M,f)S phase (1) and the C_6A_2F phase (2) as interstitial substances between periclase grains (dark grey). Black spots are pores. (a) SEM image; (b) EDS analysis suggesting the presence of C_6A_4(M,f)S phase (point 1-SEM image).



(b) C_3A (point 2)

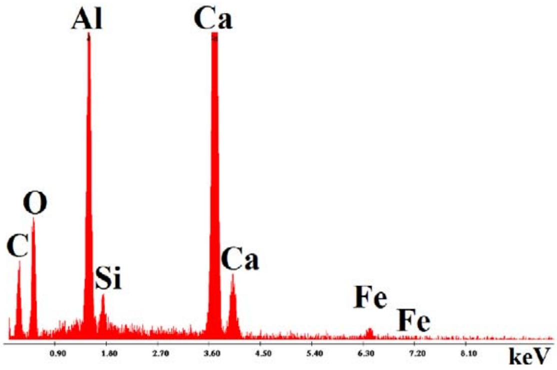


Fig. 10. Between periclase grains (dark grey) are the aluminates C_6A_2F (1), C_3A (2) and C_6A_4(M,f)S (3) phases and the β-Ca_2SiO_4 phases (4): (a) SEM image; (b) EDS analysis suggesting the presence of C_3A phase with Si and Fe admixtures (point 2-SEM image).

3.2. The coating tests

The new phases formation, in the bricks in the coating tests with the hot kiln meal at 1300 °C were mayenite $C_{12}A_7$, calcium alumino-ferrite $C_2(A,F)$, calcium sulphate aluminate $C_3A_3 \cdot CaSO_4$ and the quaternary $Ca_6Al_8(Mg,Fe)SiO_{23}$ ($C_6A_4(M,f)S$) phase (Figs. 7 and 8). The primary subordinated phases of the bricks disappeared. The corrosion reaction at the tested temperature could proceed in the presence of the liquid phase.

The formation of the $C_3A_3 \cdot CaSO_4$ phase could proceed in the analogous way as the chemical corrosion reactions according to Eq. (I). The $C_3A_3 \cdot CaSO_4$ phase and calcium aluminates (C_3A, $C_{12}A_7$ and CA) were compatible up to 1350 °C, the temperature of disintegration point of calcium sulphate aluminate, of the $CaO–CaAl_2O_4–CaSO_4$ system [12].

The ($C_6A_4(M,f)S$) phase was also a new one in the magnesia-spinel bricks as the product of the reaction with Portland clinker at the temperature of 1450 °C (Figs. 9 and 10). Besides Parker's phase, others phases, such as the aluminate $Ca_6Al_2FeO_{15}$ (C_6A_2F) phase and the C_3A phase and the silicate β-Ca_2SiO_4 phase (Fig. 10) could be formed. The primary subordinated phases of the bricks disappeared.

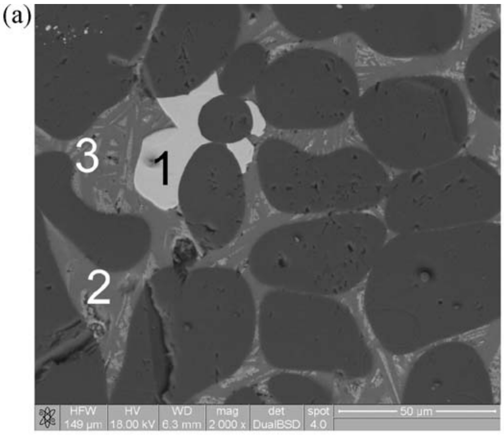
The presence of ($C_6A_4(M,f)S$) phase, besides other calcium aluminates C_3A, $C_{12}A_7$ and C_6A_2F/C_4AF, was probably due to the high temperature dissociation of Fe_2O_3 under low oxygen partial pressure [11]. The $C_6A_4(M,f)S$ phase, melting incongruently at the temperature of 1380 °C [16], was found in the post-mortem magnesia-spinel bricks [15]. The other quaternary phase Q-$C_{20}Al_{26}Mg_3O_{68}$ which was identified by the XRD analysis in the sample of the powder tests (Table 4) and in the previous research of corrosive reaction, which were carried out with the mixtures of the clinker with the spinel (MA) [2], was not found in the coating tests.

Besides the aluminate phases, the high-refractory calcium zirconate (CZ) and the calcium zirconium aluminate $Ca_7Al_6ZrO_{18}$ (C_7A_3Z) could be formed in the magnesia-spinel bricks as the reaction products with the hot kiln meal (at 1300 °C) and the Portland clinker (at 1450 °C) (Fig. 11) as new phases in the magnesia-spinel bricks with the ZrO_2 oxide.

The ternary $Ca_7Al_6ZrO_{18}$ (C_7A_3Z) phase was also a new phase formed at the contact zone of the magnesia–zirconia bricks, with the hot kiln meal and the Portland clinker (Fig. 12).

The new phases in the tested bricks are a calcium sulphate aluminate, binary, ternary and quaternary phases of calcium aluminates and calcium alumino-ferrites and silicate phases.

The formation of the calcium sulphate aluminate ($C_3A_3 \cdot CaSO_4$) was due to the presence of sulphur in the hot kiln meal and the Portland clinker. The formation of the quaternary phase of the calcium alumino-ferrites ($C_6A_4(M,f)S$) was due to a dissociation of the Fe_2O_3 oxide [11], at a high temperature.



(b) $CaZrO_3$ (point 1)

(c) C_7A_3Z (point 3)

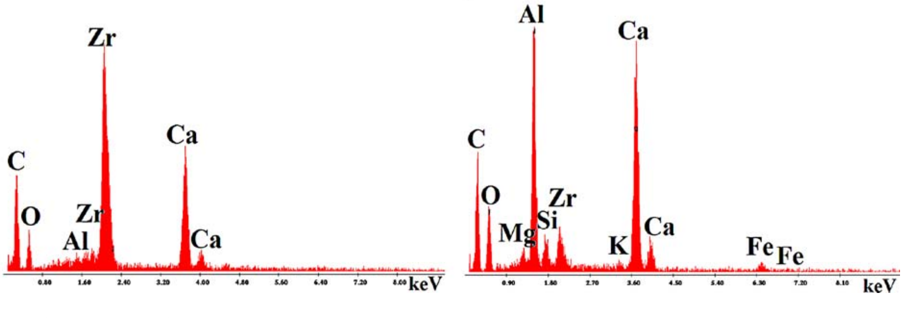
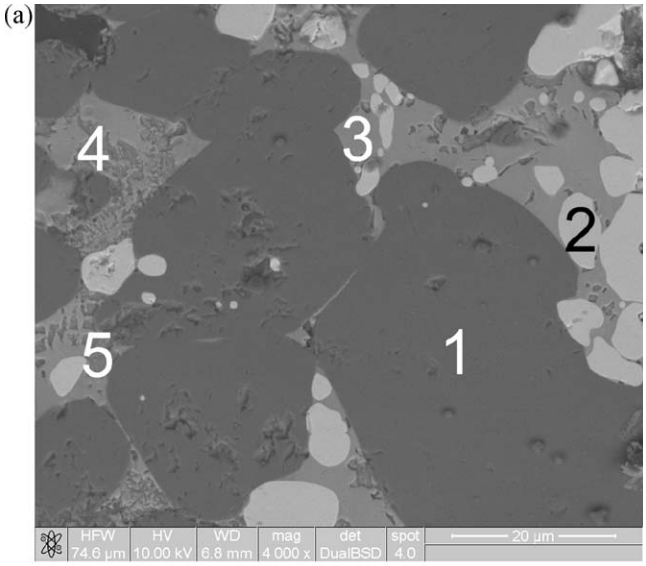


Fig. 11. The elongated crystals of the $C_6A_4(M,f)S$ phase (2) and the C_7A_3Z phase (3) as interstitial substances between periclase grains (dark grey) and calcium zirconate grains (1): (a) SEM image; (b) EDS analysis suggesting the presence of $CaZrO_3$ phase with Mg, Si, Fe and K admixtures (point 1 – SEM image); (c) EDS analysis suggesting the presence of C_7A_3Z phase with Mg, Si, Fe and K admixtures (point 3 – SEM image).



(b) C_7A_3Z (point 5)

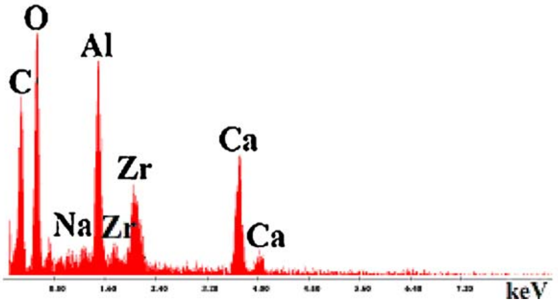


Fig. 12. The periclase crystals (1) surrounded by the calcium zirconate (2) and the aluminates: the C_3A (3) phase and the C_7A_3Z phase (4, 5): (a) SEM image; (b) EDS analysis suggesting the presence of C_7A_3Z phase with Mg, Si, Fe and K admixtures (point 5 – SEM image).

4. Summary and conclusions

The investigation of corrosion of basic refractories in the presence of the precalciner material, rich in sulphur, and Portland clinker taken from the precalciner cement kiln were made at 1200, 1300, 1400 and 1450 °C.

The new phases formation as a result of chemical reactions in the tested samples with MSp bricks were binary phases ($C_{12}A_7$: t_{mp} – 1392 °C, $CaZrO_3$: t_{mp} – 2345 °C) and ternary phases (C_2AS: t_{mp} – 1593 °C or C_3MS_2: t_{dp} – 1573 °C) after the tests at the temperature of 1200 °C and ternary phases of C_7A_3Z (t_{mp} – 1550 °C) and $CaZrO_3$ and quaternary phases Q-$C_{20}A_{13}M_3S_3$ or $C_6A_4(M,f)S$ (t_{dp} – 1380 °C) after the tests in the temperature range of 1300–1450 °C. The Q-$C_{20}Al_{26}Mg_3O_{68}$ phase was identified by the XRD analysis in the sample of the powder tests. But the $C_6A_4(M,f)S$ phase was formed in the samples of the coating tests and in the post-mortem MSp bricks by SEM–EDS analysis. The new $C_3A_3{\cdot}CaSO_4$ phase (t_{dp} – 1350 °C) was formed in the sample of the corrosion tests up to the temperature of 1300 °C. The formation of calcium sulphate aluminate ($C_3A_3{\cdot}CaSO_4$) is due to the presence of sulphur in the cement kiln materials. The quaternary phase formation of the calcium alumino-ferrites ($C_6A_4(M,f)S$) is due to the high temperature dissociation of the Fe_2O_3 oxide. The new phases formation in the sample with the magnesia–zirconia bricks are clinker phases (β-C_2S, C_3A and $C_2(A,F)/C_4AF$) and the C_7A_3Z phase. The formation of the $CaZrO_3$ and the C_7A_3Z phases were the result of the chemical reaction between the zirconia from the bricks and the CaO oxide from the cement kiln materials. Silicate and aluminate phases found in the samples are compatible with the periclase.

In the system: cement kiln materials—magnesia-spinel bricks the appearance of a binary, ternary and quaternary aluminates phases was detected. These phases have appeared as a result of the chemical reaction between the phases present in cement kiln materials (e.g. CaO, $CaSO_4$, Ca_3SiO_4, $Ca_3Al_2O_6$) and $MgAl_2O_4$ from refractories.

The presence of sulphur in cement kiln materials was the reason of $Ca_4Al_6O_{12}(SO_4)$ creation at 1200 and 1300 °C. At higher temperatures this phase was not detected, due to its disintegration [12]. The presence of $Ca_4Al_6O_{12}(SO_4)$ was detected in post-mortem magnesia-spinel bricks taken from the transition zone of the cement rotary kilns [17].

Zirconia in magnesia-spinel bricks determined the creation of high-refractory $CaZrO_3$ phase and aluminate $Ca_7Al_6ZrO_{18}$ phase.

In the system of magnasia-zirconia bricks and cement kiln materials the new phase was aluminate $Ca_7Al_6ZrO_{18}$ which appeared as the result of chemical reaction between $CaZrO_3$ from bricks and phases of cement kiln materials.

On the basis of the conducted tests some practical conclusions can be drawn. The most important one is the statement that an application of alternative, rich in sulphur fuels in the cement kilns intensifies the chemical corrosion of the spinel phase in basic refractories. It leads to the creation of low-melting aluminate phases ($Ca_{12}Al_{14}O_{21}$, $Ca_3Al_2O_6$, $Ca_6Al_8(Mg,Fe)SiO_{23}$ or $Ca_{20}Al_{26}Mg_3SiO_{68}$) and calcium sulphate aluminate $Ca_4Al_6O_{12}(SO_4)$.

The presence of ZrO_2 and $CaZrO_3$ in magnesia refractory products should improve their resistance to chemical corrosion caused by cement clinker.

Acknowledgement

The work was partially supported by the grant no. N R15-0014-06 of the Polish Ministry of Science and Higher Education.

References

[1] W. Polesnig, W. Zednicek, The behaviour of basic refractory lining materials in oil- and coal-fired rotary kilns in the cement industry, Interceramics (special issue) (1984) 49–53.

[2] G.E. Gonçalves, L.R.M. Bittencourt, The mechanism of formation of mayenite ($C_{12}A_7$) and the quaternary phase Q ($Ca_{20}Al_{26}Mg_3Si_3O_{68}$) of the system CaO–MgO–$Al_2O_3$–$SiO_2$ in magnesia-spinel bricks used in the burning and transition zones of rotary cement kilns, in: Proceedings of the 8th UNITECR'03, Tokyo, Japan, (2003), pp. 138–141.

[3] J. Szczerba, The mechanisms of new phases formation in basic refractories in reaction with sintering cement clinker, Ceramika/Ceramics 102 (2008) 151–170.

[4] W. Kurdowski, Chemia Cementu/The Chemistry of Cement, Wydawnictwo Naukowe PWN, Warszawa, 1991, pp. 27–112.

[5] J. Szczerba, The effect of cement kiln service environment on the corrosion of magnesia-spinel materials, Ceramika/Ceramics 88 (2005) 110–122.

[6] H. Kühl, Zement Chemie/The Chemistry of Cement, Verlag Technik Gmbh, Berlin, 1951.

[7] F.M. Lea, The Chemistry of Cement and Concrete, Chemical Publ. Comp. Inc., New York, 1972.

[8] P. Bartha, The cement rotary kiln and its refractory lining, Interceramics 53 (2004) 14–17 [Refractories Manual–Special Edition].

[9] G.E. Gonçalves, A.K. Duarte, P.O.R.C. Brant, Magnesia-spinel brick for cement rotary kilns, Am. Ceram. Soc. Bull. 72 (2.) (1993) 49–54.

[10] M. Ohno, K. Tokunaga, Y. Tsuchiya, Y. Mizuno, H. Kozuka, Applications of chrome-free basic bricks to cement rotary kilns in Japan, in: Proceedings of the 8th UNITECR'03, 2003, pp. 27–31.

[11] E.M. Levin, C.R. Robbins, H.F. McMurdie, Phase Diagrams for Ceramists, The American Ceramic Society, USA, 1969, p. 5. (Fig. 2070).

[12] R. Turriziani, F. Massazza, Ann. Chim. (Rome) 56 (1966) p1180.

[13] E.M. Levin, C.R. Robbins, H.F. McMurdie, Phase Diagrams for Ceramists, The American Ceramic Society, Inc., USA, 1964/1969.

[14] H.J. Klischat, P. Bartha, Progress in performance behaviour of basic bricks by innovative raw material selection, in: Proceedings of the 7th UNITECR'01, 2001, pp. 631–641.

[15] J. Szczerba, Examples of changes in magnesia spinel bricks after working in cement dry-process kilns using alternative fuels, in: Proceedings of the 1st Global Refractories for Cement & Lime Conference & Exhibition, London, (2007), pp. 4.1–4.8.

[16] R.H. Bogue, The Chemistry of Portland Cement, Reinhold Publishing Corporation, New York, 1955, pp. 355–364.

[17] J. Szczerba, Changes in basic brick from preheater cement kilns using secondary fuels, Ind. Ceram. 29 (2009) 19–30.