Corrosion of Al_2SiO_5–SiC and Al_2SiO_5–$ZrSiO_4$ Refractories in the Corroding Medium of the External Heat Exchanger of Cement Kiln

EIRICH AWARD 2013

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The paper presents the results regarding changes in the chemical (XRF, chloride Cl^- and sulphur SO_3 content), phase (XRD, FT-IR) compositions and microstructure (SEM/EDS) of Al_2SiO_5–SiC and Al_2SiO_5–$ZrSiO_4$ refractories under the influence of the selective interaction between the refractory phases of brick and corrosive solids, liquids and vapours present in a corrosive environment of the cement cyclone preheater. Reactions of the SiC or $ZrSiO_4$-containing andalusite refractory bricks with the components of a corroding medium in the external heat exchanger of cement kiln at 1000 ± 100 °C were discussed.
The calcium-rich hot kiln meal moving in a counter-current relative to the furnace gas reacted with a refractory component of the both ceramic materials. The Al_2SiO_5–SiC refractory brick was constantly affected by the corrosive agents in gaseous form such as K^+/K_2O, SO_2, CO_2 and Pb vapor. According to the XRD and SEM/EDS examinations it has been found that the initial phase of refractory brick were disappeared and the new phases were formed. Mainly, potassium aluminosilicates, calcium aluminosilicates, $CaSiO_3$, Ca_2SiO_4, $K_2Si_4O_9$, $Ca_2PbSi_3O_9$, spurrites $2Ca_2SiO_4 \cdot CaCO_3$ and $2Ca_2SiO_4 \cdot CaSO_4$ and also KCl were identified in the corroded Al_2SiO_5–SiC refractory brick. Andalusite refractory brick containing $ZrSiO_4$ was subjected to corrosion by Ca^{2+}/CaO, K^+/K_2O, Pb vapor and Cl^-. Post-mortem examination of the corroded brick enabled the identification of potassium aluminosilicates, calcium aluminosilicates, $Ca_3ZrSi_2O_9$, $CaZrO_3$, $Ca_{12}Al_{14}O_{32}Cl_2$, Ca_2SiO_4 and KCl as the predominant corrosion products.

1 Introduction

Nowadays, the aluminosilicate refractories both shaped and unshaped, especially low and ultralow cement refractory concretes are widely applied in kiln installations of the cement industry (external heat exchanger, precalciner cement kilns, cement rotary kiln, coolers) below temperature of 1250 °C. Utilization of raw materials and alternative fuels rich in chlorine, sulfur and phosphorus, alkali oxides and heavy metals causes of the corrosion process of refractories [1–4]. With this in mind, it becomes necessary to find new solutions of modification of aluminosilicate refractories, which is forced first of all by increasing the alternative fuels usage rate in the production of Portland cement clinker [5]. There is no research in the literature as yet that shows the mechanism corrosion of andalusite-based refractories modified by addition of SiC or $ZrSiO_4$.
Hence, the main purpose of this study was to indicate which of the components present in the in the corroding medium of the external heat exchanger of cement kiln included in the atmosphere (oxides – CO_2, CO, SO_2, H_2O, K_2O, Na_2O, NO_x, ions – Cl^-, K^+, Na^+, OH^-, H^+ and heavy metal vapors – Se, Bi, Pb, Tl, Cd, Hg, Rb and Cs) and the calcium-silicon-aluminium-iron-magnesium-potassium-sodium-sulphur and chlorine-rich hot kiln meal moving in a counter-current relative to the furnace gas reacted with a refractory component of the Al_2SiO_5–SiC and Al_2SiO_5–$ZrSiO_4$ refractory bricks.

2 Experimental procedure

The andalusite-silicon carbide and andalusite-zircon refractory bricks were manufactured under industrial conditions with the andalusite, zircon sand/or SiC, calcined bauxite and refractory clay as raw materials. During mixing the phosphoric acid was added. The sample was formed in the shape of rectangular prism with the dimensions of (length × width × thickness) 230 mm × 114 mm × 40 mm under pressure of 120 MPa and fired at 1200 °C. The corrosion test was carried out under industrial conditions at temperature about 1000 ± 100 °C. The corrosive components

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Keywords: corrosion, external heat exchanger of cement kiln, andalusite refractories, SiC, $ZrSiO_4$

Received: 31.05.2013
Accepted: 24.09.2013

Tab. 1 **The chemical and phase compositions of as-delivered and corroded Al_2SiO_5-SiC refractory bricks**

Analysis		As-delivered Al_2SiO_5–SiC Brick	Reaction Zone Near the Interface of the Corroded Al_2SiO_5–SiC Brick
Chemical Composition			
Loss on Ignition (L.o.I.) [%] at 750 °C		0,21	1,08
SiC content [%]		31,9	28,3
SiO_2 content [%]		19,7	19,7
Free carbon content [%]		0,20	0,30
Oxide composition [mass-%]	Al_2O_3	40,9	35,1
	Fe_2O_3	0,93	0,86
	CaO	0,17	2,78
	K_2O	0,30	6,07
	P_2O_5	2,87	2,23
	TiO_2	0,34	0,30
	ZrO_2	0,52	0,03
	others	1,87	3,19
Chloride, Cl^- content [%]		0,009	0,799
Sulphur, SO_3 content [%]		0,09	0,06
Phase Composition			
Qualitative XRD phase-analysis		Al_2SiO_5, SiC, Al_2O_3, SiO_2 cristobalite and quartz, mullite solid solution	Al_2SiO_5, SiC, $KAlSiO_4$, SiO_2 quartz, $KAlSi_2O_6$, $AlPO_4$, KCl, mullite solid solution
FT-IR analysis		Al_2SiO_5, Al_2O_3, SiO_2 cristobalite and quartz, mullite, $AlPO_4$	Al_2SiO_5, Al_2O_3, SiO_2 cristobalite and quartz, mullite, $AlPO_4$, $KAlSiO_4$, $KAlSi_2O_6$, $Ca_2Al_2SiO_7$, $CaAl_2Si_2O_8$

affected all surfaces of the thin-walled refractory bricks attached to a chrome steel. The examined refractory bricks was located in the external heat exchanger (4 degree cyclone pre-heater) of Polish cement plant and exposed in its environmental conditions during 8 months. This paper presents the results regarding changes in the chemical (XRF, chloride Cl^- and sulphur SO_3 content), phase (XRD, FT-IR) compositions and microstructure (SEM/EDS) of Al_2SiO_5–SiC and Al_2SiO_5–$ZrSiO_4$ refractories under the influence of the selective interaction between the refractory phases of brick and corrosive agents. The investigations of chemical and phase composition were carried out on 8 mm thick (a thin layer (reaction zone) adjacent to the brick interface) samples received from both Al_2SiO_5–SiC and Al_2SiO_5–$ZrSiO_4$ corroded bricks. The prepared microsections after the corrosion test were analyzed by means of the scanning electron microscope (*FEI* Nova Nano SEM 200) equipped with an EDS microanalysis detector (EDAX *Genesis*). Direct observations of fracture in a post-mortem Al_2SiO_5–SiC and Al_2SiO_5–$ZrSiO_4$ materials in the SEM were also done. The reference, uncorroded materials were also investigated using all of the above-mentioned methods.

3 Results and discussion

3.1 Post-mortem investigation of Al_2SiO_5–SiC refractory brick

At this point the reactions of the SiC-containing andalusite refractories with the components of a corroding medium in the external heat exchanger of cement kiln at 1000 ± 100 °C are discussed. According to the XRF, XRD, FT-IR (Tab. 1) and SEM/EDS investigations the main corrosive agents in an external heat exchanger were agents in gaseous form – K^+/K_2O, SO_2, CO_2 and Pb vapor. The CaO-rich hot kiln meal moving in a counter-current relative to the furnace gas also reacted with a refractory component of the ceramic materials.

It has been found that the initial phase of refractory brick – Al_2SiO_5 was disappeared and the new phases were formed. The post mortem X-ray diffraction, SEM/EDS and FT-IR analyses of the corrosion products revealed that potassium aluminosilicates (i.e. $KAlSi_2O_6$ and $KAlSiO_4$) and calcium aluminosilicates (i.e. $CaAl_2Si_2O_8$ and $Ca_2Al_2SiO_7$) were formed in the corroded refractory brick. The highest K_2O and CaO oxides concentrations observed in the near-surface zone of the corroded Al_2SiO_5–SiC refractory brick resulted in the domination of the thermodynamically stable phases i.e. $KAlSiO_4$ and $Ca_2Al_2SiO_7$.

According to FT-IR results, characteristic infrared absorption bands of the corrosion products like calcium aluminosilicates, both $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ unidentified by XRD were easily found in the decomposed FT-IR spectrum of corroded material.

EDS X-ray microanalysis has shown that kalsilite, $KAlSiO_4$ forms an outer ring around unreacted andalusite grain core (Fig. 1). As a

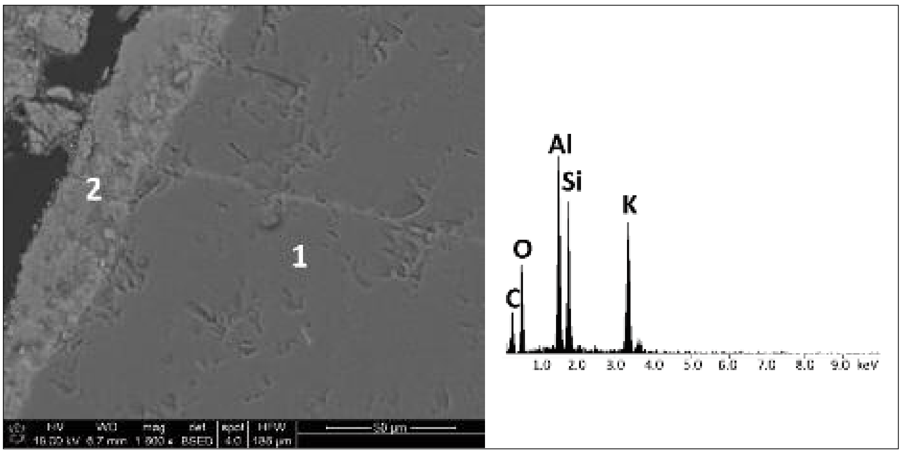

Fig. 1 **SEM micrograph of the reaction zone near the interface of the corroded Al_2SiO_5-SiC brick; 1 – Al_2SiO_5, 2 – $KAlSiO_4$ (Spot 2 – EDS analysis – Fig. 1a)**

result of diffusion potassium ions through the corrosion product, the continuous consumption of andalusite grain takes places. The total reaction equation of the kalsilite, $KAlSiO_4$ phase formation can be written as follows:

$$2(Al_2O_3 \cdot SiO_2) \text{ (andalusite)} + K_2O \rightarrow K_2O \cdot Al_2O_3 \cdot 2SiO_2 \text{ (kalsilite)} + Al_2O_3 \quad (1)$$

The obtained results of SEM and EDS studies confirmed that the transient intermediate compounds ($KAlSi_2O_6$ and $CaAl_2Si_2O_8$) have been found as the dominant phases at the lower concentration of two main corrosive agents i.e. K_2O and CaO oxides in the deeper part of the corroded Al_2SiO_5–SiC refractory brick.

Moreover, the secondary phases i.e. $CaSiO_3$, Ca_2SiO_4, $K_2Si_4O_9$, $Ca_2PbSi_3O_9$, spurrites $2Ca_2SiO_4 \cdot CaCO_3$ and $2Ca_2SiO_4 \cdot CaSO_4$ were also detected in microareas of SiC or Al_2SiO_5 of the corroded refractory brick. The formation of some compounds was preceded by the oxidation of SiC. A post-mortem study of used Al_2SiO_5–SiC refractory bricks allowed the identification of Cr, S, K, Ca, Cl, O, Al, Si, Fe or P – bearing compounds, such as $Ca_3(PO_4)_2$, $KCa(PO_3)_3$, $K_2Ca(Cr,S)_2O_8$, $CaCr_2O_4$-$CaFe_2O_4$ s.s., $Ca_3(Cr,Al)_2(SiO_4)_3$, $CaCrO_4$ and KCl. The above-mentioned phases were identified in the corroded Al_2SiO_5–SiC refractory brick by SEM/EDS.

3.2 Post-mortem investigation of Al_2SiO_5–$ZrSiO_4$ refractory brick

According to the XRF, XRD, FT-IR and SEM/EDS investigations the corroded $ZrSiO_4$-containing andalusite refractory brick was subjected to corrosion by K^+/K_2O, Ca^{2+}/CaO, Pb vapor and Cl^- corrosive agents present in the corroding medium of the cement cyclone preheater. The XRF analysis of Al_2SiO_5–$ZrSiO_4$ after corrosion test showed elevated levels of potassium and calcium oxides in comparison with initial refractory material (Tab. 2). The new phases formed as a result of chemical reactions between both component of the hot kiln meal and gaseous phase, with components of modified aluminosilicate refractory material were found by XRD: kalsilite $KAlSiO_4$, leucite $KAlSi_2O_6$, gehlenite $Ca_2Al_2SiO_7$ and also KCl (Tab. 2).

According to FT-IR results (Tab. 2), characteristic infrared absorption bands of the intermediate corrosion products i.e. orthoclase $KAlSi_3O_8$ and anorthite $CaAl_2Si_2O_8$ unidentified by XRD were found in the decomposed FT-IR spectrum of corroded material.

It has been also found that the calcium silicate, Ca_2SiO_4 phase occurred due to the transformation of Al_2SiO_5 into $Ca_2Al_2SiO_7$ and finally into Ca_2SiO_4 and $Ca_{12}Al_{14}O_{33}$ under the influence of CaO. The aluminate phase has been subjected to chlorine-reaction to calcium chloroaluminate, $Ca_{12}Al_{14}O_{32}Cl_2$ formation (Fig. 2). This can be represented by the following chemical equations:

$$Al_2SiO_5 + 2CaO \rightarrow Ca_2Al_2SiO_7 \text{ (gehlenite)} \quad (2)$$

$$7Ca_2Al_2SiO_7 + 12CaO \rightarrow Ca_{12}Al_{14}O_{33} + 7Ca_2SiO_4 \quad (3)$$

Tab. 2 **The chemical and phase compositions of as-delivered and corroded Al_2SiO_5–$ZrSiO_4$ refractory bricks**

Analysis		As-delivered Al_2SiO_5–$ZrSiO_4$ Brick	Reaction Zone Near the Interface of the Corroded Al_2SiO_5–$ZrSiO_4$ Brick
Chemical Composition			
L.o.I. [%]		0,09	1,0
Oxide composition [mass-%]	SiO_2	37,3	34,3
	Al_2O_3	49,2	43,6
	Fe_2O_3	0,96	0,76
	CaO	0,16	3,28
	K_2O	0,26	4,18
	P_2O_5	2,32	2,41
	TiO_2	0,38	0,38
	ZrO_2	9,20	10,40
	others	0,16	0,56
Chloride, Cl^- content [%]		0,007	0,149
Sulphur, SO_3 content [%]		0,06	0,13
Phase composition			
Qualitative XRD phase-analysis		Al_2SiO_5, $ZrSiO_4$, Al_2O_3, SiO_2 cristobalite and quartz, mullite solid solution	Al_2SiO_5, $ZrSiO_4$, SiO_2 quartz, Al_2O_3, $KAlSiO_4$, KCl, $KAlSi_2O_6$, $Ca_2Al_2SiO_7$
FT-IR analysis		Al_2SiO_5 , $ZrSiO_4$, Al_2O_3, SiO_2 cristobalite and quartz, mullite, $AlPO_4$	Al_2SiO_5, $ZrSiO_4$, Al_2O_3, SiO_2 cristobalite and quartz, mullite, $AlPO_4$, $KAlSi_3O_8$, $KAlSi_2O_6$, $KAlSiO_4$, $Ca_2Al_2SiO_7$, $CaAl_2Si_2O_8$, Ca_2SiO_4

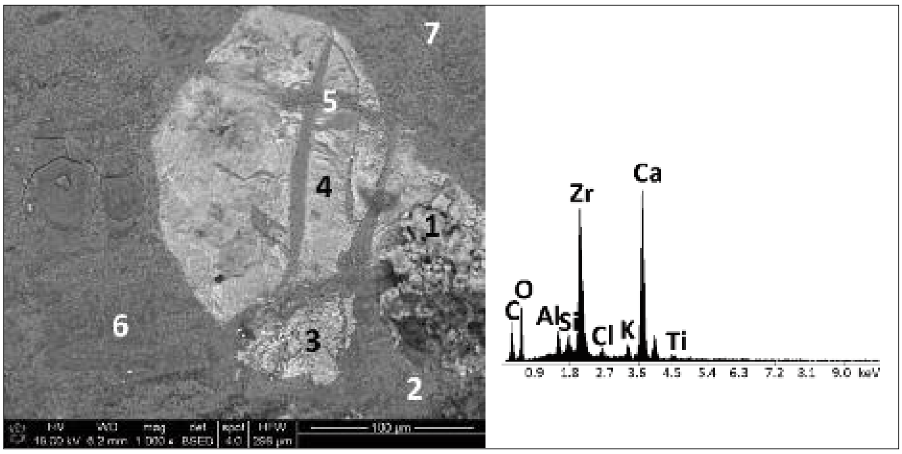

Fig. 2 **SEM backscatter image of the corroded Al_2SiO_5–$ZrSiO_4$ brick (interface); 1 – KCl, 2, 5, 7 – Ca_2SiO_4, 3 – $CaZrO_3$ (Spot 3 – EDS analysis – Fig. 2a), 4 – $Ca_3ZrSi_2O_9$, 6 – $Ca_{12}Al_{14}O_{32}Cl_2$**

According to the SEM-EDS results, calcium oxide from the solid particles of a hot kiln meal reacted in the microareas of Al_2SiO_5 and $ZrSiO_4$ grains to formation of the $CaO–Al_2O_3–SiO_2$ phases identified by XRD and FT-IR and the compounds occurring in the $CaO–SiO_2–ZrO_2$ system identified by SEM/EDS.

On the spot of initial zircon grain, the new phases were formed. In the reacted zircon grain with a laminar structure, diversification of the chemical composition was found by means of SEM and EDS methods. Studies have shown that the formation of the transient ternary phase – baghdadite, $Ca_3ZrSi_2O_9$ and the thermodynamically stable binary compound – calcium zirconate, $CaZrO_3$ took place (Fig. 2). This fact may indicate the process of counter-diffusion of Ca^{2+} ions towards $ZrSiO_4$ grain core and Si^{4+} ions towards the refractory matrix whereas Zr^{4+} ions remain immobile. Hence, dicalcium silicate Ca_2SiO_4 and $Ca_{12}Al_{14}O_{32}Cl_2$ were also detected (Fig. 2).

Moreover, according to the SEM/EDS analysis, the formation of potassium aluminosilicates is accompanied by separation of undoped α-Al_2O_3 hexagonal platelets. When $ZrSiO_4$ grain was attacked by potassium ions, decomposition of $ZrSiO_4$ and formation ZrO_2 took place.

$$2ZrSiO_4 + Al_2O_3 + K_2O \rightarrow 2KAlSiO_4 + 2ZrO_2 \qquad (4)$$

A post-mortem study of used $Al_2SiO_5–ZrSiO_4$ refractory brick allowed the identification of K, Ca, Pb, P, O, Cr, Fe, S, Cr, Cl, Al or Si – bearing compounds, such as $Ca_3(PO_4)_2$, $KCa(PO_3)_3$, $K(Ca,Pb)(PO_3)_3$, $K_4Pb(P_3O_9)_2$, Cr_2O_3, $(Cr,Fe)_2O_3$, K_2SO_4, $K_2(S,Cr)O_4$, $K_2Ca_2(SO_4)_3$, KCl, $Ca_2(Al,Si)(Al,Si,Cr)_2O_7$ and $(Cr,Al)_2O_3$ by SEM/EDS.

4 Summary and conclusions

Although, the cement industry is moving towards the use of alternative fuels to reduce environmental pollution, the utilization of alternative fuels has also a negative effect, in that it decreases the lifetime of refractory lining.

Doctoral thesis entitled „Corrosion of Al_2SiO_5–SiC and $Al_2SiO_5–ZrSiO_4$ refractories in the corroding medium of the external heat exchanger of cement kiln" concerns the effects of selective corrosion by the components of the environment gaseous phase and the CaO-rich hot kiln meal moving in a counter-current relative to the furnace gas with a refractory component of the ceramic materials. Studies have shown that the SiC-containing andalusite refractory material was subjected to reaction with Ca^{2+}/CaO, K^+/K_2O, SO_2, CO_2 and Pb vapor. Material containing $ZrSiO_4$ was subjected to corrosion by Ca^{2+}/CaO, K^+/K_2O, Pb vapor and Cl^-.

A post-mortem study of worn Al_2SiO_5–SiC and $Al_2SiO_5–ZrSiO_4$ refractory bricks allowed the identification of secondary phases and the reconstruction of the corrosion process.

Acknowledgement

This work is supported by the grant No. INNOTECH-K2/IN2/16/181920/NCBR/13 of the *National Centre for Research and Development*.

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