

THE INFLUENCE OF SiC ADDITION ON CORROSION RESISTANCE OF MONOLITHIC REFRACTORIES BASED ON $\text{Al}_2\text{O}_3\text{-SiO}_2$

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VPLYV PRÍDAVKU SiC NA KORÓZNU ODOLNOSŤ ŽIAROBETÓNŮV NA BÁZE $\text{Al}_2\text{O}_3\text{-SiO}_2$

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Abstrakt

Moderné zariadenia na spaľovanie komunálneho odpadu patria k dôležitým prvkom ochrany životného prostredia. Spaľovaním odpadu vzniká teplo, ktoré sa odovzdáva výmenníkovým systémom. Dochádza k vzniku pary, ktorú je možné dodávať do energetických sietí alebo z nej vyrábať elektrickú energiu. Ďalšou výhodou spaľovania je významné redukovanie množstva komunálneho odpadu ukladaného na skládky. Spaľovanie komunálneho odpadu spôsobuje množstvo problémov v zariadeniach, ktoré spaľujú tento typ odpadov. Jeden z problémov je korózia žiaruvzdorných vymuroviek troskou a plynnou atmosférou, ktoré vznikajú počas spaľovacieho procesu. Žiaruvzdorné vymurovky sa počas prevádzky v spaľovniach komunálneho odpadu opotrebúvajú a znehodnocujú. Sú vystavené pôsobeniu vnútorného agresívneho prostredia, ktorému musia odolávať. Vysoká teplota, mechanické a hlavne chemické opotrebenie nepriaznivo vplyvajú na životnosť vymurovky. Žiaruvzdorné materiály s obsahom karbidu kremíka majú dobrú koróznú odolnosť a úspešne sa používajú ako vymurovka v spaľovniach komunálneho odpadu. Dva typy žiarobetónov na báze $\text{Al}_2\text{O}_3\text{-SiO}_2$ s obsahom 75 % a 25 % karbidu kremíka boli vystavené troske zo spaľovne o zložení $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-X}$ pri teplote 1250 °C. Pre posúdenie vplyvu troskovej taveniny na koróziu žiarobetónov sa zvolila statická korózná téglíková skúška. Predpísanou technológiou sa pripravila žiarobetónová zmes, ktorá sa naliala do formy. Vyrobili sa valcovité vzorky, ktoré mali v strede otvor. Vzorky sa sušili podľa určenej krivky sušenia, naplnili koróznym médiom a vložili do laboratórnej pece. Na určenie korózných mechanizmov bola použitá chemická analýza, optický mikroskop a semikvantitatívna EDX analýza.

Abstract

The modern equipments for combustion of municipal waste are part of mayor importance in protection the environment. Process of burning the waste leads to heat rising, which transmits by heat exchanger in the technology during creation of water vapour, which is possible to serve into energetical nets or to produce electrical energy. Another advantage of combustion is significant reduction of municipal waste and inhibition of accumulation of waste to a waste dumps. The combustion of municipal waste leads to quite a number of problems in the equipments which burn this type of waste. One of the serious problems is a corrosion of linings by slag and gas atmosphere which arise during combustion process. The refractory linings usually wears down and depreciates during the service in the incinerators of the

municipal waste. The linings are influenced by inner aggressive atmosphere to which have to resist. High temperature, mechanical and mostly chemical wear influences unfavourable the service life of lining. Monolithic refractories with silicon carbide content have good slag corrosion resistance and then they are successfully used in furnaces linings for incineration of municipal waste. Two refractory castables based on $\text{Al}_2\text{O}_3\text{-SiO}_2$ with 75 % and 25 % of SiC were exposed to one type of real slag from incineration of municipal waste with content $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-X}$ at temperature 1250 °C. Slag corrosion is caused by slag penetration into the castables at high temperature. Chemical analysis, optical microscopy and semiquantitative EDX analysis were used to determine the corrosion mechanisms and rates of these materials.

Key words: refractory castable, silicon carbide, static corrosion test, slag, incinerator of municipal waste

1. Introduction

The modern equipments for combustion of municipal waste are part of mayor importance in protection the environment. The incinerators of municipal waste are usually grate aggregates which generally operate at temperatures in the range of 800-1300 °C. They are made of consistent sloping movable grates which move or rotate [1].

The municipal waste changes with development of the human society, the plastic material increases, which also causes corrosive stress of these equipments, mainly in the areas of using refractory materials.

The aim of present contribution is based on the observation of unshaped refractory materials with slag meltings. The static corrosion tests were made on refractory castables with a different content of silicon carbide. As a corrosion medium, the real slag from incineration of municipal waste (company KOSIT, Inc. Košice) was used.

2. Experimental

During corrosion tests, two types of low cement castables with different content of SiC were used (Table 1).

As a corrosion medium, a slag prepared of the real slags from incineration of municipal waste (it was taken out in different seasons spring-autumn-winter) was prepared. The average chemical composition of the slag is shown in Table 2 (slag TS). The fusing point of corrosion medium is 1180 °C and it was determined by using the high temperature microscope Leitz-Wetzlar [2].

Table 1 Chemical composition and properties of refractory castables

		Refractory castable A	Refractory castable B
chemical analysis, [%]	SiC	75	25
	Al_2O_3	18	37
	SiO_2	5	32
	Fe_2O_3	0.5	1.5
	CaO	1.7	2
apparent porosity, [%],	after 800 °C	15	15
bulk density, [$\text{kg}\cdot\text{m}^{-3}$],	after 110 °C	2530	2380
	after 800 °C	2510	2370
permanent linear charge, [%],	after 800 °C	-0.1	-0.2
thermal conductivity, [$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$],	after 400 °C	4.81	3.07
	after 800 °C	5.51	2.97

The static corrosion test was realized for influence determination of slag melting on corrosion of refractory castables. The refractory mixture was prepared and flown into the form by regular technology. The cylindrical shaped specimens with dimensions of 12 cm diameter and 7 cm height were prepared and same cylindrical inlet with dimensions of 4 cm diameter and 3 cm height was made in the centre of each sample. The samples were dried for 26 hours according to given drying curve with temperature at 120°C /6h and 420°C/4h.)

Prepared samples were filled by corrosion medium and got inside the furnace. The heating temperature was 1250 °C for a period of 10 hours. The analysis of corrosion tests were made by:

- chemical analysis (AAS Perkin-Elmer 3100),
- macro and microscopic observation (light microscope NEOPHOT 32),
- semiquantitative EDX analysis (scan microscope JEOL 35 CF/LINK).

3. Results and discussion

Using chemical analysis the composition of slags after corrosion experiments were determined (Table 2). The slag composition after corrosion test for sample A is signed as A-1 and B-1 for sample B.

Table 2 Chemical composition of slags [wt.%]

Compound Slag	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O
TS	1.72	4.44	39.6	11.55	24.21	2.75	1.36	1.74	0.72
A - 1	-	6.9	44.28	16.59	24.79	2.65	1.65	1.93	1.1
B - 1	-	4.07	45.42	18.31	25.40	2.43	1.59	1.51	1.07

Chemical reactions between slag parts and refractory castable run during corrosion test, which is evident from the results. It leads to increasing of SiO₂ and Al₂O₃ (less) in the slag. SiO₂ and Al₂O₃ are main parts of refractory castable bond. A thin layer (cca 1-2 mm) of reaction melting was visible at the refractory castable – slag contact. This melting was optically different in comparison to residual slag in the sample. The semiquantitative EDX analysis of the reactive layer is documented in Fig. 5, 6 and it was obtained during observation of the specimens using scan microscope.

Fig. 1. represents the macrostructures of the cross-section views of samples after a corrosion test. Table 3 represents the penetration depths of slag into a samples shard and the widths of particular penetration zones. In both cases, the reaction zone of corrosion products was created in the shard, at the refractory castable – slag contact. Observing the sample A, three penetration zones with different penetration depths were found and were good visible. In the case of sample B, two penetration zones were observed, but the interface wasn't so clear.

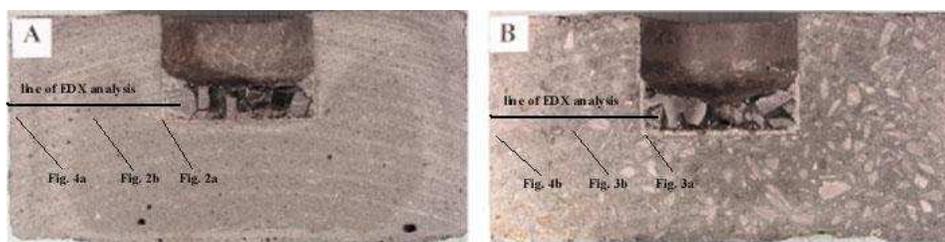


Fig.1 Macrostructures of refractories after test (magn. cca 0.6×)

Table 3 Penetration depth of slags to specimens

Specimen			A [mm]	B [mm]
Reaction zone 1	wall	average	0.79	0.92
		range	0 – 0.93	0 – 1.65
	bottom	average	0.55	1.05
		range	0 – 0.83	0 – 1.24
Penetration zone 2	wall	average	6.46	16.5
		range	0.93 – 11.75	1.65 – 19.66
	bottom	average	1.86	20.26
		range	0.83 – 2.372	1.24 – 27.72
Penetration zone 3	wall	average	15.98	14.71
		range	0.72 – 23.08	14.3 – 32.17
	bottom	average	26.56	6.74
		range	1.44 – 30.51	18.28 – 27.09
Penetration zone 4	wall	average	28.35	-
		range	15.77 – 32.99	-
	bottom	average	29.59	-
		range	27.32 – 30.10	-

Figs. 2.a and 3.a represent the microstructures of samples A and B after corrosion test using second light. From the microstructures a refractory castable – slag interface is visible as a part of wall and bottom of sample. The reaction layer of slag with other crystalline structure such slag has in the volume of crucible is also visible. The black grains represent a SiC, white-grey parts represent the grains of chamotte and a bond saturated with parts of slag.

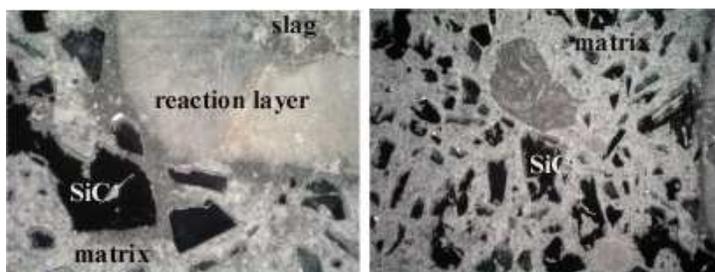


Fig.2 Specimen A: a.) reaction zone (polarised light, magn. 63×) b.) penetration zone (polarised light, magn. 25×)

The chemical reaction runs between the parts of slag and matrix, SiC grains and chamotte in the impregnated part of refractory castable shard (Fig. 2.b and 3.b). The corrosion of SiC grains creates local and foveal disturbances of the grain. The darker layer which corresponds to a diffusion of some slag parts (probably Fe, Ti and K) is visible on the surface of aggregate grains.

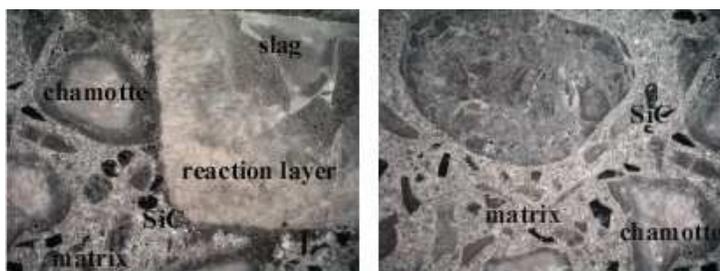


Fig.3 Specimen B: a.) reaction zone (polarised light, magn.63×) b.) penetration zone (polarised light, magn. 25×)

Fig. 4 represents a microstructure of primary shard of refractory castable. The grains of SiC are corroding by oxygen in this part of material and it diffuses into a shard of refractory castable. The local corrosion is observed on the surface of SiC grains. From thermodynamic analysis of the system and following the results of EDX analysis the reactions (1) – (3) are supposed.

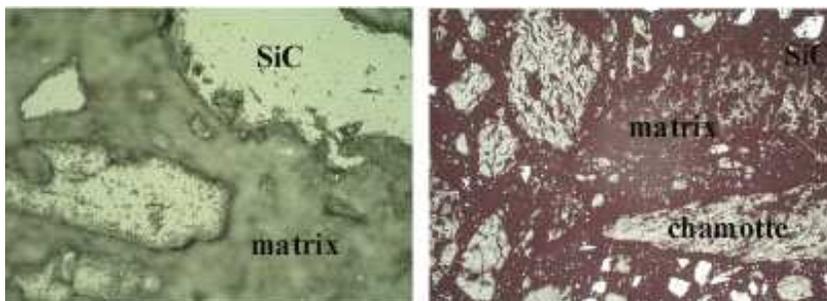
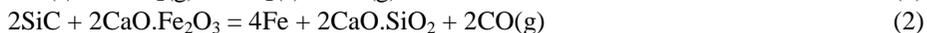
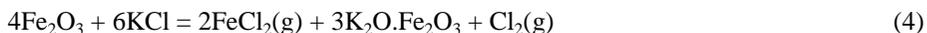


Fig.4 Primary structure: a.) specimen A (magn. 63×) b.) specimen B (magn. 63×)

Figures 5 – 6 shows the results of EDX analysis (JEOL 35 CF/LINK – analysable surface approximately 100x100 μm). Analysis determined the melting of the refractory concrete basic components (SiO₂ and Al₂O₃) into the slag. The reaction part of the slag of high concentration of the calcium was created at the slag – refractory concrete interface. We suppose it is pseudo wollastonit in the system CaO-SiO₂-Al₂O₃ [3].

The slag melting penetrated into the castable A and B, approximately 2 mm of depth from the slag – refractory concrete interface. Comparing the experimental results it is evident that the corrosion process of the specimens A, B has a different course. A strong difference in content of SiC in the specimens influence the character of the atmosphere in the masonry. The high content of SiC and reducing conditions in the impregnated area in the specimen A suppress the diffusion of Cl and K. In the impregnated layer of the specimen B, also in the outer edge of the specimen A run over to intensive diffusion and chemical reactions between the slag elements (e.g. Cl, Fe, K), according to reaction (4):



From the results of the local microanalysis it is evident that ions Na, Mg, Ca do not diffuse into the brick and their content in the masonry is balanced. We suppose that the chloride in the slag is present mainly in the form of NaCl and KCl. During the corrosion actions the reaction (5) can run over.



SiC which is present in the specimens, made by oxygen from the furnace atmosphere and from the oxides of the slag, reacts according to reactions (1)-(3). The results of the EDX analysis of SiC grain and its boundaries between the slag and refractory material from both specimens are shown in table 4.

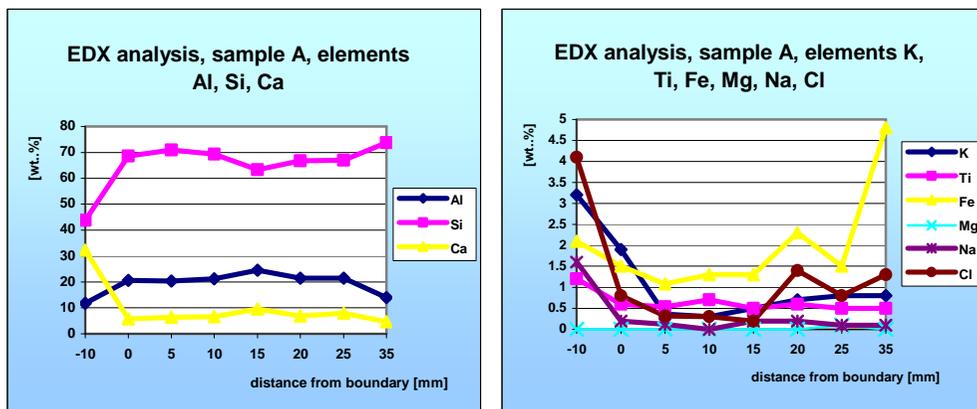


Fig.5 EDX analysis, sample A

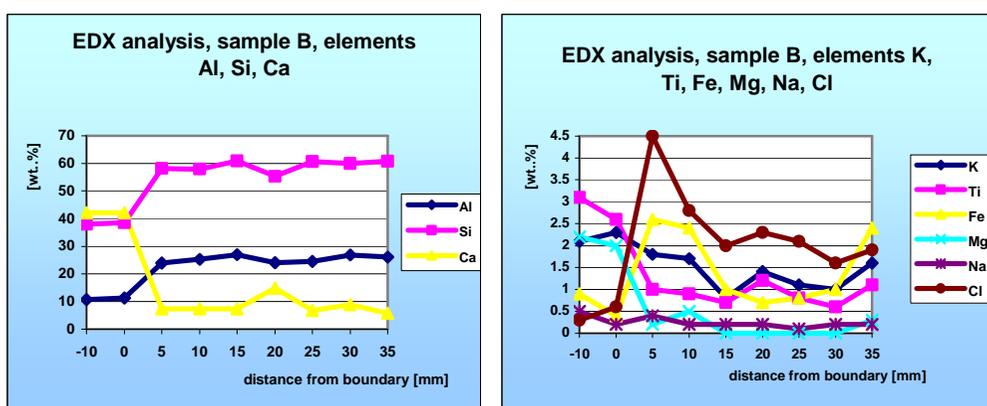


Fig.6 EDX analysis, sample B

Table 4 EDX analysis of SiC grains and boundary of SiC grains [wt.%]

	Chem. elements	Al	Si	K	Ca	Ti	Fe	Mg	Na
Sample A	grain SiC	0	99,5	0	0	0,3	0	0,2	0
Sample B		0	99,8	0	0	0,1	0	0	0
Sample A	boundary of SiC grain	15,7	50,6	2,3	26,1	1,3	1,6	1,2	1,2
Sample B		3,5	86,6	0,9	3,2	0,1	3,1	2,6	0

4. Conclusions

The aim of the contribution is to describe an interaction between a slag from municipal waste with LCC refractory castables with different content of SiC. After chemical analysis of slags (Table 2) is evident that the parts of slag and refractory castables react together. In both refractory castables, a reaction layer at the slag – refractory castable contact was created in the slag with a visually different crystalline structure, it is probably crystallized pseudo wollastonite.

Using a macroscopical observation and evaluation, a three penetrated zones in sample A of different thickness and evidently separated were observed. In the sample B, two

impregnated zones of fluent passing were observed. Comparing the depth of penetration, the sample A is more preferable. From macroscopical observation, a reduction of metallic iron in a form of metal drops in a slag occurs, which were visible at the slag surface and in the reaction part at the contact surface of slag – refractory concrete.

Microscopical observations and EDX analysis showed the slag intersection into crock castable through the matrix. In the crock, a corrosion of SiC grains by oxygen and slag oxides were observed. On the surface of the SiC grains a point corrosion was created, the reaction products were drops of metal iron and SiO₂ layer, or complex silicates of SiO₂-Al₂O₃-CaO system.

The results confirmed the assumptions of a positive influence of SiC addition into concrete to increase their chemical resistance towards the oxygene slags from the process of combustion of the municipal waste.

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