

THE DEGRADATION OF LINING OF ROTARY FURNACES IN THE PRODUCTION OF ZINC OXIDE

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Resume

This paper is closely connected with the complex problem of degradation relating to the refractories of rotary furnace linings in the production of zinc oxide. Zinc oxide can be produced by variety of ways, but the most common method of production which is used in Europe is indirect, i.e. pyrolytic combustion of zinc. This method is also called "French process" of manufacturing ZnO. But this mentioned method of preparation leads to the creation of the enormous amount of zinc slag including chemical complexes of elements Fe, Zn and Al. The mechanism of degradation of the lining leads to slag rests and it is closely connected with the mutual interaction of the aggressive agents with the components of the lining. This process creates a new undesired surface layer which increased the overall thickness of zinc slag. Stuck slag has the influence on rapid degradation of the linings and moreover it also decreases the production quality of ZnO. Analysis results introduced in this paper are significant information for minimizing of degradation of rotary furnaces.

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1. Introduction

Zinc oxide (ZnO) has been an important industrial material for centuries and is currently the subject of considerable new interest [1, 2]. ZnO is used by several 100 000 tons per year [2]. Zinc oxide is a white solid inorganic powder, non-flammable, stable and insoluble in water. Size can vary between 0.5 and 5 µm, but typical size is around 1 µm. Zinc oxide occurs in nature as mineral zincite. However, in most cases zinc oxide is obtained through a technical process from zinc [1, 3, 4]. Recent investigations reveal that zinc oxide convert sun's rays into chemical energy in a manner similar that of chlorophyll. Zinc oxide is the only inorganic material known to act in that manner [5].

Zinc oxide powder has traditionally been

used as a white pigment and as an additive to rubber. While it has largely been displaced as a pigment in paints, its usage in rubber remains very important [1]. Everyday items zinc or zinc compounds are used in paint pigments and coating, plastics, rubbers, cosmetics, medical etc. [3]. Indirect production of ZnO starts by melting of zinc and following oxidation with oxygen from the air in rotary furnaces [1]. French process is considered to be the fastest and most productive method for industrial production of ZnO [6], but according to the practical experience, this type of production ZnO is not optimal for utilization of the product in all technological applications. The production of ZnO is based on high speed of zinc vapour at speeds 0.1 Mach (30 m.s⁻¹) or higher and temperature is in the range from

1300 °C to 1400 °C. Sublimation temperature of ZnO is 1p725 °C [3]. The work is also focused on the enormous amount of slag material. It is closely connected with the previous work [7, 8], in which the primary material has been studied. Detailed investigation of waste material of zinc slag was studied in previous work [9].

The degradation of rotary linings (Fig. 1) can be caused different temperature gradients, aggressive action of zinc vapour and especially incorrect selection of refractory ceramics. The given problem is closely connected with the systematic approach to the assessment and proposal of suitable the ceramics refractories of lining for rotary furnaces during the production of zinc oxide.



Fig. 1. Cracks on the connecting channel in the manufacture of zinc oxide.
(full colour version available online)

2. Experiment

Study refractories have been chosen on the base of chemical composition (Tab. 1), physical and mechanical properties as well as technological process for the given materials.

Static (primary and secondary) corrosion tests have been used for analysis and evaluation of degradation measurement. Corrosion tests were performed at the high-temperature furnace (CEKSaSM, TnUAD in Trencin, Slovakia).

A holes (Ø 10 mm and depth about 50 mm) was bored into the sample of refractories and then the metallic zinc with the strictly specified amount (2.0 ± 0.001 g Zn) and the given chemical composition (Zn = 96.73 wt. %, Fe = 2.2 wt. %, Al = 0.5 wt. %, Ni = 0.29 wt. %, Pb = 0.0044 wt. %, Cu = 0.0096 wt. %, Cd = 0.0004 wt. %) was inserted and left to act. The tests were performed under static conditions without the influence of convection [10 - 12]. Prepared materials were heated gradually ($10 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) up to temperature 1400 °C and the whole process of heating took 120 and following 420 minutes.

The measurements were performed using the stereomicroscopic device NIKON SMZ 1500 (CVUT in Prague, Czech Republic), SEM - JSM 7600F (CVUT in Prague, Czech Republic) and X- Ray diffraction Brúcker 8, KalfaCo with Co-lamp (SAV Bratislava, Slovakia). Setting the measurement - time to step is set up in different cps (counts per second).

Table 1

Chemical composition of selected refractories (wt. %).

Refractories	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	SiC	MgO
Chamotte	-	1.6	41.0	53.5	-	-
MgO	1.6	0.5	0.2	0.6	-	97.0
Silicon Carbide	-	-	18.0	1.7	75.0	-

3. Experimental results

The zinc slag was gradually fed by products from reactions with refractory materials. During the primary test (at a temperature of 909 °C), the sudden reaction was observed - the sublimation of zinc was followed by oxidation with oxygen from the air. There was the conical arrangement of the zinc oxide on the surface of material based on MgO and chamotte fireclay (Fig. 2). It is important to point out that there was the zinc burning in the middle of the formed ZnO cone at temperature 1000 °C. Material based on SiC absorbed the ZnO powder.

Using X-ray diffraction (Fig. 3) for ZnO powder which was formed in a volcanic way, it has been found that the resulting compound contains only crystalline substances (Fig. 4), such as zinkit - ZnO (94 wt. %) and gahnit - ZnAl_2O_4 (6 wt. %). In the case of the samples of SiC and MgO, there was not the penetration by molten zinc but the given investigated area contained the zinc which was burned out (XRD analysis determined). In relation to chamotte sample, irreversible damage (infiltration) of material was occurred and it was caused by chemical reactions of chamotte with molten zinc.



Fig. 2. Formed zinc oxide on the surface of chamotte.
(full colour version available online)

The difference between primary and secondary corrosion test is connected with the different construction of samples of refractories (samples representing the substrate were covered by a layer of the same material as the substrate). The purpose of the structural changes of the previous measurements was to prevent the creation of zinc oxide by the volcanic effect. Prepared materials were heated gradually up to temperature 1400 °C and the whole process of heating took 420 minutes (Fig. 5).

There was a change of refractory material based on silicon carbide. Sintered cristobalite ($\beta\text{-SiO}_2$) was occurred on the surface of refractories

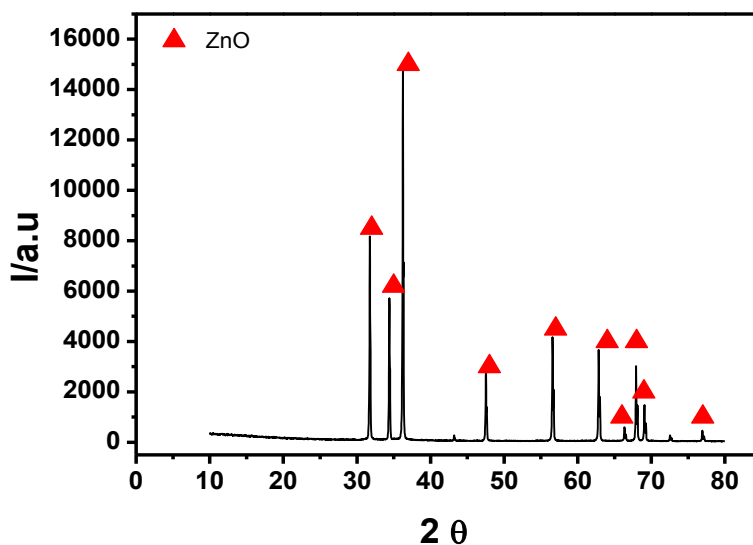


Fig. 3. The diffractogram of selected samples for formed zinc oxide.
(full colour version available online)



Fig. 4. Zincit, LOM.
(full colour version available online)

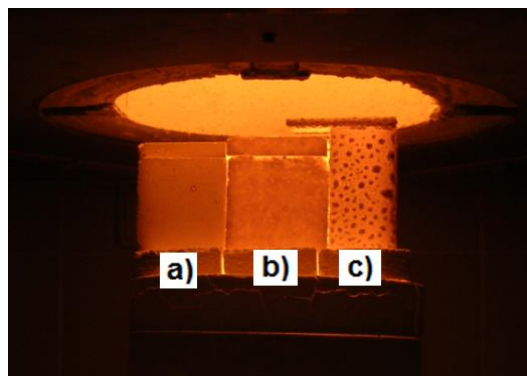


Fig. 5. Selected refractories in the elevator furnace with temperature 1,400 °C; a) chamotte, b) MgO, c) SiC.
(full colour version available online)

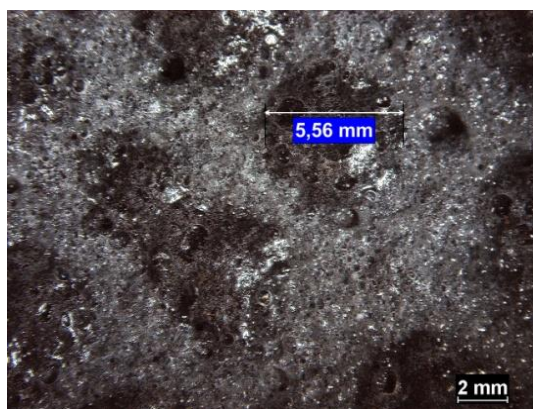


Fig. 6. The surface of refractory material (SiC-based) with created cristobalite after the secondary corrosion test, LOM.
(full colour version available online)

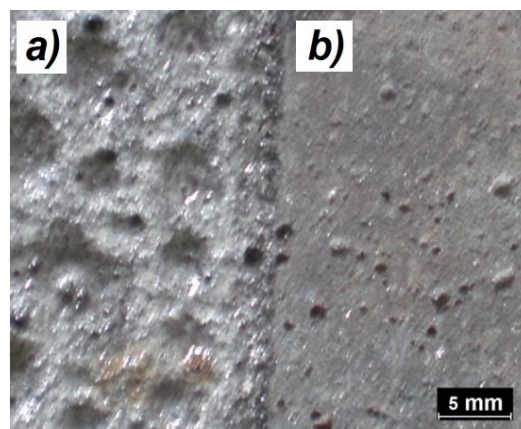


Fig. 7. The interface of refractory material (SiC-based) between a) original material before test and b) after test, SEM.
(full colour version available online)

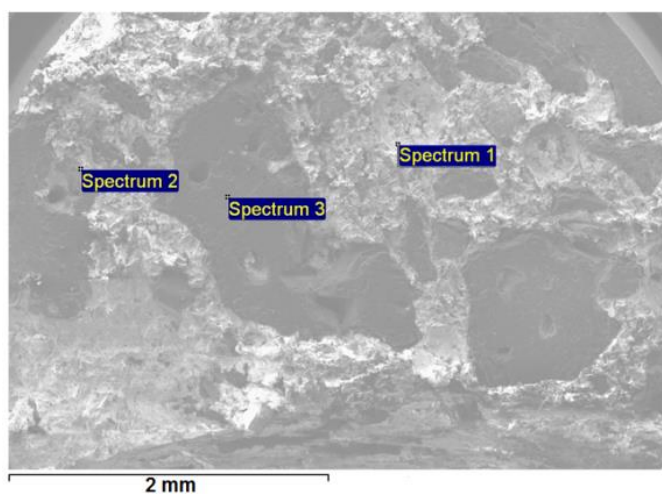


Fig. 8. EDX analysis of selected surface (SiC-based material), SEM.
(full colour version available online)

(SiC-based) (Fig. 6). The interaction of zinc with the refractory led to occurrence of willemite (Zn_2SiO_4) which was identified by XRD analysis. In Fig. 7 is detail of view interface refractory on the based SiC before and after the secondary corrosion test.

Not occurred to mutual influence refractory (based on MgO) with zinc in corrosion testing of refractory samples. During the corrosion tests, the influence of zinc on refractory material (based on SiC) was recognized. The mentioned fact was also proven by help of LOM, SEM investigations of the structures (Fig. 8). EXD analysis was also used for the investigation of surfaces (Tab. 2) and it also showed that there is the influence by zinc.

4. Conclusions

From the study, the following conclusions can be drawn:

- Temperature is important critical factor affecting the corrosion processes in the system refractory - melted zinc - atmosphere. Penetration rate of elements into matrix of refractory is increased exponentially with increasing temperature;

- Primary factor for selecting the most suitable refractory materials is a basic character of ceramic components compatible with the aggressive components of slag materials (for example molten zinc). In relation to material properties are primary knowledge of porosity, the phase interface, morphology and the grain size of the investigated material;

- Open porosity of refractories contributed to absorption of Zn into the matrix of given material;

- On the reaction surface of sample of MgO and SiC, there was the occurrence of minority physico-chemical reactions. Zinc in the form of dendrites was detected at the interface zinc/refractory. There was not the penetration of the slag into matrix of refractory materials as well as adhesive action on the microscopic level was not observed.

- Depending on the chemical composition, we can conclude that there is not influence of MgO materials on the quality of the produced ZnO. Zinc oxide was produced in the range of chemical concentrations which are suitable for its usage.

- Present Zn, ZnO and Fe not penetrated into the matrix of SiC-based refractories when they are in the contact with the surface of refractory material. The liquid slag is not penetrated into the study material;

- It can be pointed out that the used SiC-based refractories (75.0 wt. % SiC and the rest representing the 25 or 15 % can be oxides, such as Al_2O_3 , SiO_2) have impact on the mutual interaction between the alkaline and acids constituents.

- In case of application of MgO refractories, we recommend to keep conditions relating to the gradual temperature increase ($200\text{ }^\circ\text{C.h}^{-1}$) in the furnace and the finishing of the production cycle should be completed by gradual cooling;

- We recommend reducing the overall open porosity of the selected materials based on alkaline magnesium oxide while the maximum total value should be 12%. This is a sufficient level of porosity which is required to maintain resistance to thermal shocks as well as suitable insulation properties.

Table 2

EDX analysis of contains of elements (SiC-based sample is show in fig. 5) (wt. %).

Selected Spectrum	Ca	Zn	Al	O	Si
Spectrum 1	2.27	2.57	12.85	48.64	24.25
Spectrum 2	4.15	13.83	21.58	39.85	11.50
Spectrum 3	0.01	0.12	0.07	1.80	69.61
Sum. Spectrum	1.71	1.76	5.76	23.22	37.99

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