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Composition and microstructure of a periclase–composite spinel brick used in the burning zone of a cement rotary kiln

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Abstract

The composition and microstructure of a periclase–composite spinel brick used in the burning zone of a cement rotary kiln were investigated and compared to the original brick. The results indicate that cement clinker and alkali salts are two important agents that cause corrosion especially of the bonding phase of refractories in cement rotary kilns. When the molar ratio of alkalis to anions ((Na+K)/(Cl+2S)) is more than one, alkali salts accumulated in the pores, cracks and grain boundaries of the refractory but the severe corrosion of the bonding phase of the refractory did not occur in zones with lower temperatures. The interaction between the cement clinker and the refractory formed a liquid, which, together with alkali salts, improved sintering. The reaction between the cement clinker and the refractory formed a dense reaction layer. Cracks formed in the dense layer and extended through the boundary between the reaction and non-reaction (penetrated) layers by mechanical and thermal stress, which caused the spalling of the reaction and coating layer from the refractory. The recurrence of this process during service leads to degradation of the refractory.

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1. Introduction

Magnesia chrome bricks have been widely used in cement rotary kilns because of their excellent properties, such as high spalling resistance, increased corrosion resistance and stable coating adhesion [1–3]. However, toxic Cr⁶⁺ contributes to environmental pollution. Recently, attention has been focused on the development of chrome-free refractories to displace MgO–Cr₂O₃ refractories [4–7], such as MgO–CaO refractories, MgO–CaZrO₃ refractories, MgO–MgAl₂O₄ refractories and MgO–FeAl₂O₄ refractories [8–13].

The mechanism of MgO-CaO/MgO-CaZrO₃ corrosion by cement clinkers has been described by several researchers [14–16]. Briefly, it has been reported that the liquid phase in

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the clinker, which is predominately enriched in calcium, iron and aluminum, rapidly diffuses and preferentially reacts with spinel, calcium zirconate and magnesia in the bricks.

The mechanism of chemical corrosion of MgO–MgAl $_2$ O $_4$ refractories by cement clinkers has also been investigated [17–21]. Researchers discovered that calcium aluminate phases with the low melting points (such as 3CaO · Al $_2$ O $_3$, 12CaO · 7Al $_2$ O $_3$, and CaO · Al $_2$ O $_3$) are easily formed by reactions between MgAl $_2$ O $_4$ and cement clinker and reactions between MgO–MgAl $_2$ O $_4$ and alkali salts.

There have been several studies on the manufacture and properties of hercynite [22] and MgO–FeAl₂O₄ refractories [23–27]. However, there are few studies on the corrosion of MgO–FeAl₂O₄ bricks in cement rotary kilns.

The refractories in cement kilns are destroyed not only by the chemical corrosion of cement kiln materials but also by mechanical and thermal stress [28,29]. Studying the composition and morphology of the linings used in rotary kilns may provide additional information on refractory degradation. Stjernberg et al. [30] studied the chemical composition and morphology of deposited and lining materials in rotary kilns

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used for iron pellet manufacture and proposed possible refractory degradation mechanisms.

In this paper, the composition and microstructure of a periclase-composite spinel brick used in the burning zone of a cement rotary kiln were investigated, and degradation mechanisms for bricks used in cement rotary kiln are proposed.

2. Experimental procedure

2.1. The samples

The brick sample investigated was obtained from a cement rotary kiln that produces 2500 t a day, as shown in Fig. 1. The chemical composition of the cement clinker and coal ash are provided in Table 1. The main phases of the cement clinker were determined to be alite $\text{Ca}_3[\text{SiO}_4]O$ (C_3S), belite

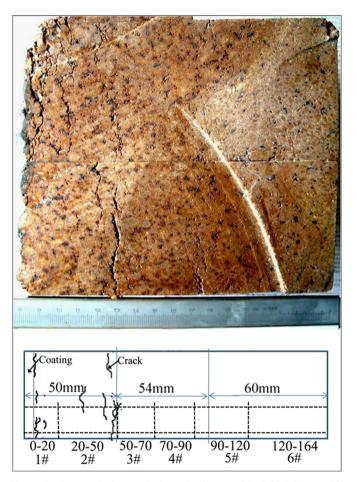


Fig. 1. Section morphology and schematic diagram of the PCS bricks used in cement rotary kiln.

Table 1 The chemical composition of the cement clinker and coal ash (wt%).

Material	MgO	Al_2O_3	SiO ₂	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	S	Coal ash content
Cement clinker	2.56	5.98	20.37	3.42	65.00	0.50	0.14	0.15	/
Coal ash ^a	1.51	27.08	47.94	7.67	11.04	0.95	0.72	3.08	15–17

^aMass of coal: 113 kg/t.

Ca₂[SiO₄] (C₂S), calcium aluminate C₃Al₂O₆ (C₃A), and calcium alumina-ferrite phase Ca₂AlFeO₅ (C₄AF) using X-ray diffraction (XRD). The chemical composition and properties of the original brick are provided in Table 2. The XRD pattern of the original brick is shown in Fig. 2. Composite spinel MgFe_{0.2}Al_{1.8}O₄ (CSp), magnesio-ferrite MgFe₂O₄ (MF), and merwinite Ca₃Mg[SiO₄]₂ (C₃MS₂) were the major secondary phases detected in the original brick. This brick is referred to as the periclase–composite spinel (PCS) brick [31].

2.2. Sample preparation and analysis

The length of the original brick was 220 mm, and after 10 months service it was 164 mm. The length of the brick was divided into six zones from the hot face to the cold side (Fig. 1), which were numbered 1 through 6, respectively. A significant number of cracks was observed in zones 1 and 2, as shown in Fig. 1.

The bulk density and apparent porosity of samples from the six zones of the brick were measured by Archimedes principle using kerosene as the medium.

Phase analysis was performed using X-ray diffraction and Cu Kα radiation with a scanning speed of 2 degrees per minute (X'pert PRO MPD, Philips, Eindhoven, Netherlands). The relative content of identified phases was calculated by the semi-quantitative analysis in HighScore works on basis of the RIR (=Reference Intensity Ratio) values [32]. The microstructure of the samples was obtained using scanning electron microscopy with EDS (SEM, Quanta 400, FEI Company, USA).

3. Results and discussion

3.1. Apparent porosity and bulk density of a PCS brick

The apparent porosity and bulk density of samples from different zones of the used brick are shown in Fig. 3. For comparison, the apparent porosity and bulk density of the original brick (OB) are provided in Fig. 3. The bulk density and apparent porosity of the used brick are greater and less than the bulk density and apparent porosity of the original brick, respectively. This suggests that sintering occurs and the pores are completely filled during the service of the brick. The sample from zone 3 had the highest bulk density and the lowest apparent porosity. Many cracks were observed in zones 1 and 2, and the apparent porosity of the samples increased and the bulk density of the samples decreased from zone 3 to zone 1. From zone 3 to zone 6, the apparent porosity of the samples increased and the bulk density decreased.

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