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# Corrosion and adherence properties of cement clinker on porous periclase-spinel refractory aggregates with varying spinel content

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ABSTRACT

The corrosion and adherence properties of cement clinker on porous periclase-spinel refractory aggregates with varying spinel content were examined using a static crucible test and a sandwich test, respectively. The reaction characteristics of porous periclase-spinel aggregates and cement clinker and the effects of spinel content on the adherence property were investigated through scanning electron microscope (SEM), energy dispersive spectrometer (EDS), and FactSage® thermo-chemical software. It was observed that the spinel content and pore characteristics strongly affected the corrosion results and thus affected the adherence ability of cement clinker on porous periclase-spinel aggregates. With an increase in the spinel content, the amount of glass phase formed from the reaction of the refractory and cement clinker increases because the rate of the spinel dissolution into the cement clinker is higher than that of periclase. The glass phase acts as a bridge between the cement clinker and the aggregate to enhance the adherence property, which depends on the amount, area distribution and viscosity of the glass phase and its penetration in aggregates. When the spinel content is 15–40 wt%, the refractory aggregate not only has a high cement clinker resistance but also a high adherence property. Once the spinel content exceeds 50 wt%, the skeletal structure of the aggregate will be destroyed, which will lead to a substantial decline in the cement clinker resistance.

## 1. Introduction

To reduce the pollution of $Cr^{6+}$ from magnesia-chrome refractories, periclase-spinel refractories have become the most promising non-chrome substitute material used for the burning zone of cement rotary kiln in China due to their excellent properties and abundant resources [1–5]. The traditional periclase-spinel refractories consisting of dense aggregates and matrixes have high thermal conductivities, and result in the high temperature at the surface of the kiln shell and the energy waste. This affects the safe operation of the refractory because of the deformation of kiln shell at higher temperature. In order to solve the above issues, it is necessary to develop a type of lightweight periclase-spinel refractory with micro pores and low thermal conductivities. Comparing with the aggregate, the matrix is more vulnerable because of its higher porosity, lower strength and corrosion resistance in the traditional refractories. Therefore, it is an alternative approach to develop the expectant lightweight periclase-spinel refractories by substituting porous aggregates for the traditional dense ones [6].

The corrosion and adherence properties of cement clinker on porous aggregates play important roles in their application in fabricating refractories for the burning zone of cement rotary kiln. The corrosion and adherence properties of cement clinker on traditional dense basic refractories, such as MgO-$FeAl_2O_4$, MgO-CaO and MgO-$MgAl_2O_4$, have been previously studied [7–12]. Chen et al. [7] investigated the kiln coating formation mechanism of MgO-$FeAl_2O_4$ refractories, and found the network and “tree root” structures (consisting of $C_4AF$ and glass phases) were formed at the interface of the cement clinker and the refractories, and thus caused the brick possessed good kiln coating formation performance. Chen et al. [8] studied the effect of nano-sized $ZrO_2$ on the cement clinker resistance of MgO-CaO refractories and concluded that the liquid phase with high viscosity, which was generated from the reaction of $ZrO_2$ and the cement clinker, coated on the surface of the refractories and inhibited the further penetration of slag. Guo et al. [12] researched the reaction characteristics of magnesia-spinel refractories with cement clinker, and examined how the liquid in the cement clinker penetrated into the brick and decomposed the spinel through the formation of more liquid. This accelerated the sintering process and built the sustained coating on the surface of the brick. The second phases rather than the periclase in the basic refractories have higher reactivity with the cement clinker

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to form the glass phase or the low melting point phase, and the quantity and viscosity of the glass phase fiercely affect the corrosion and adherence properties of the cement clinker onto the refractories.

Once the magnesia aggregates in the periclase-spinel refractories are replaced by the porous periclase-spinel aggregates, the reaction behavior at the refractory/cement clinker interface will change because of the existence of the spinel phase and micro pores in the porous aggregates. However, the effects of the phase composition and pore characteristics on the corrosion and adherence properties of the cement clinker onto the porous periclase-spinel refractory aggregates have not been fully understood. In early work, the porous $MgO$-$Al_2O_3$ and $Al_2O_3$-$SiO_2$ aggregates prepared using an in-situ decomposition pore-forming technique have been corroded by slag, and the results showed that the slag resistance of the porous aggregates could be enhanced by changing their phase composition and pore characteristics [13–21]. In order to develop the suitable porous aggregate for the lightweight refractories used for the cement rotary kiln, the corrosion and adherence properties of the cement clinker on the porous periclase-spinel refractory aggregates with different spinel contents were conducted. The effects of the spinel content and the pore characteristics on the corrosion resistance and adherence property were investigated in the present work.

## 2. Experimental

In the present work, the porous periclase-spinel aggregates were gathered by crashing their corresponding porous ceramics. Owing to the dimensions of the crashed porous aggregates are too small to process into acquired samples, their corresponding ceramics are adopted as the research subjects. But this work focus on the properties of porous periclase-spinel aggregates and their possibilities of application in the refractories, the research subjects were called as porous refractory aggregates. Twelve porous periclase-spinel refractory aggregates with different spinel contents (0–100 wt%) were processed into the crucibles (50 mm in height and 50 mm in diameter, with a 23 mm diameter and 18 mm deep hole) for the static crucible test and the right trapezoidal block samples (with an angle of 45°, which can be observed in Fig. 1) for the sandwich test. 10 g of cement clinker were placed in the hole of the crucibles, 8 g cement clinker were placed in the middle of the two block samples, as shown in Fig. 1. The crucibles and blocks were heated at 1600 °C for 3 h in an electric chamber furnace, which was then turned off and cooled naturally to room temperature. The samples are denoted as $S_x$, where the subscript 'x' denotes the spinel content in the aggregates and are calculated by the semi-quantitative method based on the X-ray diffraction patterns (XRD, X'Pert Pro, Philips). The chemical compositions, spinel contents, apparent porosities and bulk densities of the porous periclase-spinel aggregates and the chemical compositions of the cement clinker are listed in Table 1.

The apparent porosities and bulk densities were measured based on Archimedes' principle using kerosene as the medium. After the corrosion test, the crucibles were cross-sectioned perpendicularly to the cement clinker/refractory interface. The actual corroded and penetrated areas in each crucible were measured by counting the number of pixels. Corrosion here is defined as regions of refractory that were replaced by low melting point phase. The corrosion index $I_C$ and penetration index $I_P$ were obtained by the following equation: $I_{C(P)} = S_{C(P)}/S_O$, where $S_O$ is the original sectional area of the crucible inner chamber, $S_C$ is the sectional area of corroded region and $S_P$ is the penetrated sectional area. The adherence strength was measured by the sandwich test as shown in Fig. 1. The adherence strength, δ, is obtained by the following equation: $\delta = X/(\cdot S)$, where X is the ultimate load to the sample, and S is the area of the interface between the sample and cement clinker. The microstructures and compositions of the polished samples were measured with a scanning electron microscope (SEM, JSM-6610, JEOL Company, Japan) with an energy dispersive spectrometer (EDS, QUANTAX200-30, BRUKER Company, Germany). The distributions of the pore size, the area percentages and distributions of the glass phase were statistically analyzed through an image analysis method [22]. The reaction of the refractories and cement clinker as well as the viscosities of the glass phase at 1600 °C were simulated by the Equilib and Viscosity modes of the FactSage® thermo-chemical software (version 6.2), respectively.

## 3. Results and discussion

### 3.1. Cement clinker resistance and adherence property

The corrosion and penetration indexes of the crucible samples after the corrosion tests are given in Fig. 2. When the spinel content of the samples are 85–100 wt%, the crucibles are severely deformed, as the sample S100 shown in Fig. 3. Both the corrosion and penetration indexes are high, which indicates that the cement clinker resistance of the aggregates is very low. When the spinel content decreases to 40–85 wt%, both the corrosion and penetration indexes show little change, and the shapes of the samples remain intact, as shown with sample S60 and S80 in Fig. 3. Whereas, when the content of the spinel is 10–40 wt %, the samples have low penetration and corrosion indexes, which indicates that these samples possess high cement clinker resistance.

The adherence strengths of the cement clinker on the porous periclase-spinel refractory aggregates are shown in Fig. 4. The adherence strengths of the cement clinker on samples S0 and S10 are too low to be measured. The adherence strength increases from 0.2MPa to 1.35 MPa when the spinel content increases from 15 to 50 wt%. A further increase in spinel content to 80 wt% sharply decrease the adherence strength to zero. When the spinel content is more than 85 wt %, the sandwich test failures and the adherence strength can not be measured because the samples are severely deformed.

The above results indicate that when the spinel content is in the range of 15–40 wt%, the aggregates possess higher cement clinker resistance and higher adherence strength. Additionally, it is interesting that with the increasing of the spinel content from 50 to 85 wt%, the penetration and corrosion indexes showed little change (Fig. 2). However, whether these samples have high cement clinker resistance or not will be discussed in the later section.

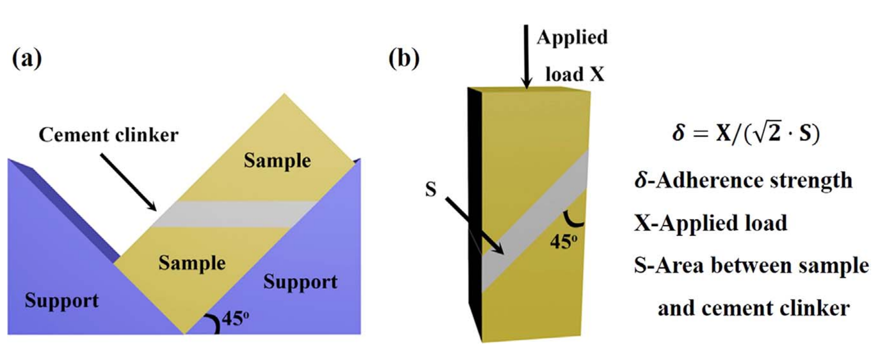


**Fig. 1.** Schematic diagram of the "sandwich test" for measuring adherence strength.