THE DAMAGE MECHANISM OF SIC-MULLITE BRICKS IN CEMENT INDUSTRY

Zhou Yandun,Liu Xijun,Wang Juntao,Chen Songlin,Yuan Lin

Ruitai Materials Technology, Beijing,China

ABSTRACT

This essay will focus on SiC-mullite 1680 in the transition zone of 5000 t/d large dry-process cement rotary kiln and explore erosion mechanism by layers connected with Portland cement clink in the upper transitional zone. The brick(the thickness is 220mm) is divided into four parts equally, XRD and SEM is employed to analysis phases changes and relative variable in chemical composition of different depth of the SiC-mullite brick; and reaction products between cement clinker and the brick. The results reveal that potassium contained in alkali salt reacted with corundum and mullite phase to produce $KAlSi_2O_6$ and $KAlO_4$ of low melting point. Moreover, SiC contained in the reaction layer was oxidized seriously, and the difference of thermal conductivity in different depth of the brick lead to the formation of distortion strain. Therefore the impact of alkali salt and partly oxidation of SiC are the main causes for damage of SiC-mullite brick.

Keywords: SiC-mullite brick, alkali salt, XRD, oxidation

INTRODUCTION

Second Generation of Cement Kiln Furnace is proposed by China Building Materials Academy, one of the characteristics is harmless treatment and Resource Utilization of wastes, which points out that alternative energy should reach 40% under current situations. Now development tendency of cement industry is large-scale, diversified fuels and energy-saving, cement kilns of 2500t/d are forced to shut down by Chinese government, and cement kilns of 5000t/d or above are encouraged, therefore large-scale kilns has higher rotary speed(3.4r/min to 4r/min),higher burning temperature(maximum 1400℃) and mechanical stress. Moreover certain amount of potassium, sodium, chlorine, Sulphur and heavy metals contained in domestic wastes, after burning volatile materials are easily concentrated in inlet, decomposing furnace and preheating furnace, which exacerbate refractories 'erosion. Above factors will influence refractories' lifetime, performance[1].

SiC-Mullite Brick was developed by Chinese refractories experts in 1990s, and due to its high strength, abrasion-resistance, low thermal conductivity, now the brick is widely used in every areas of cement industry, expect burning zone. In order to improve their performance to meet basic requirement of cement industry, one piece of used brick is taken from cement kilns, layer-by-layer analysis is employed to find out damage mechanism.

SAMPLE PREPARTION

The research object is SiC-mullite system, chemical composition of these raw materials are displayed in Table1.The technique of this batch of the product is aggregates and fines , and 3.5% sulphite liquor. Bauxite is used as aggregates, the matrix contains homogeneous bauxite powders, clay, 90SiC fines. Meanwhile in-situ mullite reaction between alumina and silicon contributes to generation of mullite.

According to ratio, raw materials will be weighted, mixed and formed, the water addition amount is 4% for all samples, then drying process for 24 hours, then heated it up to 1430 degrees. Then these bricks are used in transition zone of cement rotary kiln(Hunan South Cement Group) of 5000t/d for about 6 months, then part of these bricks are dismantled. So in this essay different layers of SiC-mullite bricks are researched in order to find out damage mechanism of this bricks during operation.

One used SIC-mullite brick has been collected , and different layers of SiC-mullite brick was analyzed.

Tab1.Raw Materials' Chemical Composition

Raw Materials	Bauxite	Magnesia sand	α-Al_2O_3 micropowder
Al_2O_3	88	0.16	98.42
MgO	-	96.8	0.02
SiO_2	0.03	0.89	0.03
CaO	0.08	1.51	0.02
Na_2O	0.3	0.02	0.17
Fe_2O_3	2.0	0.57	0.03

Raw Materials	Spinel	ZrO_2	SiO_2 powder
Al_2O_3	77.02	0.81	1.32
MgO	22.44	0.02	1.18
SiO_2	0.07	0.96	92.94
CaO	0.23	0.1	0.42
Na_2O	0.1	0.15	-
Fe_2O_3	0.09	0.08	0.44
ZrO_2	-	97.36	-

RESULT AND DISCUSSION

Normally the main phase of SiC-mullite brick is mullite, corundum, glass phase, SiC and so on. While the main phase of cement clinker is alite($Ca_3Si_2O_7$), belite(Ca_2SiO_4), Aluminate ($Ca_3Al_2O_8$) and ferrite($Ca_4Al_2Fe_2O_{10}$), and chemical composition of cement clinker is shown in table 2. We separated the bricks for 4 layers, from hot face to cold face. Through spaces between matrix and aggregates molten clinker penetrated into bricks, then had chemical reaction with bricks and generated some new phase. Part A directly connected and reacted with cement clinker, so part A was seriously deteriorated; while part B, C and D displayed in order considering distance from clinkers or hot face. Table3 shows chemical composition of different parts reacted with clinker.

Tab2. Cement Clinker's Composition

Cement Clinker				
CaO	65.00	64.30	63.92	64.60
Fe_2O_3	3.49	3.66	3.42	3.55
SiO_2	21.26	20.92	20.79	21.04
Al_2O_3	4.74	4.69	4.87	4.93
MgO	2.84	2.86	2.74	2.78
SO_3	0.56	0.83	1.02	0.63
Na_2O	0.11	0.13	0.15	0.15
K_2O	0.63	1.14	1.71	0.98

We separated the bricks for 4 layers, from hot face to cold face. Through spaces between matrix and aggregates molten clinker penetrated into bricks, then had chemical reaction with bricks and generated some new phase. Part A directly connected and reacted with cement clinker, so part A was seriously deteriorated; while part B,C and D displayed in order considering distance from clinkers or hot face. Table 3 shows chemical composition of different parts reacted with clinker. The result shows some interesting finds. First, calcium oxide of part A is much higher than that of other layers. As the main chemical constitution of Silicate cement, abnormal high proportion of CaO represents clinkers easily penetrate the intern structure of bricks through open pores. While the content of SiO_2 of this layer is higher than other layers, the content of SiC of this layer is lower than other layers, which is due to the oxidation of SiC, $SiC + O_2 \rightarrow SiO_2 + CO_2$, increased silicon dioxide content. There is another point need special noticing is ferric oxide content, which is important factor influencing high temperature performance. Fe_2O_3 of the bricks primarily comes from iron oxide in bauxite, this content gradually increased from A to D, there is high possibility that Fe_2O_3 may react with some certain components to form iron oxide, even ferrite($Ca_4Al_2Fe_2O_{10}$). But mullite($3Al_2O_3$ $2SiO_2$) as main components resist chemical erosion and thermal shock, its relatively components cannot be gained from chemical examination, so XRD is employed to discover some other phases.

Tab3.Chemical composition of different layers

	A	B	C	D
SiO_2	20.18	18.57	15.43	15.45
Al_2O_3	61.23	66.20	65.97	67.64
Fe_2O_3	1.02	1.37	1.50	1.55
CaO	2.05	0.40	0.33	0.36
MgO	0.11	0.14	0.13	0.16
K_2O	5.66	2.24	1.71	1.50
Na_2O	0.16	0.12	0.22	0.10
SiC	3.62	6.46	8.07	8.17

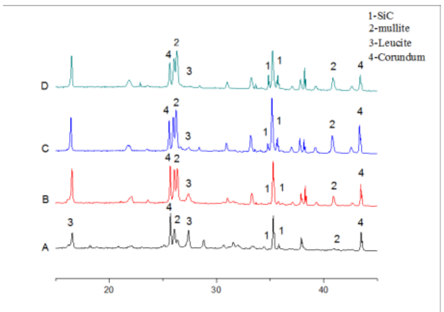


Fig.1: XRD of different layers

XRD patterns illustrate Peak intensity of SiC pattern increased significantly and intensity of SiO_2 decreased, conforming to chemical analysis in diagram3, oxidation of SiC is one factors for damage of SiC-mullite bricks.

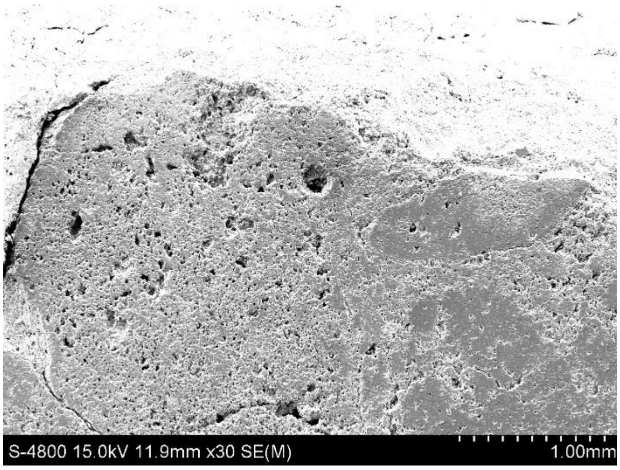
As for mullite phase, its intensity in part A is much lower than that in other three parts. It is generally believed that mullite has the characteristic of excellent resistance to chemical erosion and thermal shock, so only mullite in first layer reacted and abraded seriously, that can explainable this reduction.

And there are two new phases, leucite and potassium metaaluminate, existing only in the part A. There is high possibility that Potassium, sodium contained in alkali salt reacted with corundum and mullite phase to form alkali compounds of low melting points like feldspar.

Feldspar ,with the formulation of $KAlSi_3O_8$ and bulk density is about 2.54kg/cm3. K_2O in cement clinkers may reacted with matrix of SiC-mullite bricks to form feldspar of melting point of

1200°C. Now the firing temperature of transitional zone is about 1100°C, gas temperature can reach 1200 or above. Excessive temperature leads to deterioration in alkali salts formed [3].

Alkali vapor like K_2O, Na_2O, penetrated into bricks through open pores and had in-situ reaction with matrix to form other compounds with low density, like intermediate $K(AlSi_2O_6)$, $KAlO_2$ and so on. However, these new compounds cannot match former position taken by Al_2O_3, SiO_2, which leading to structural loose, especially in matrix parts in Fig2. Cement kiln is on the move, so every piece of brick experienced shear strength and stress-strain behavior, loose internal structure are easily destroyed during cement operation [2].



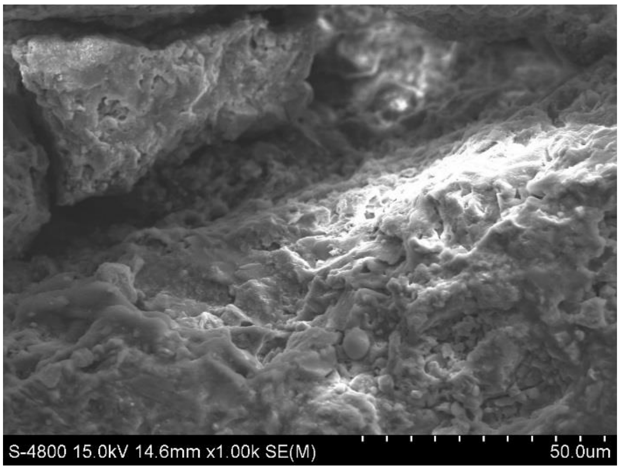


Fig.2: Micrograph of part A with 30x magnification.

CONCLUSION

Due to the prevalence of alternative energy in cement industry, it will be more and more important to realize damage mechanism of SiC-mullite brick. In this paper, two aspects are explored to find out the reason: 1. SiC in the first layer oxidized seriously, the gradient change of thermal conductivity in different layers leads to formation of distortion strain; 2. potassium contained in alkali salt reacted with corundum and mullite phase to produce $KAlSi_2O_6$ and $KAlO_4$ of low melting point, which severely influence alkali-resistance and thermal-shock resistance of this brick. So some methods should be taken to avoid this tendency:1. The additional amount of ZrO_2 can improve refractory materials' resistance to chemical erosion and thermal shock. 2. Open Pores is regarded as channel for alkali invasion and for thermal loss, so works can be done to transform pore size, distribution. Nano-sized pores can efficiently prevent cement clinker erosion and maintain lower thermal conductivity.

REFERENCES

1.Shan Yuxiang, Zhu Lingli. Rotary kiln of cement and corrosion of lining, Industrial Furnace. 2008;30(1):36-40.

2.Lu You, He Xianchao. Relationship between refractories' damage type and lining mechanical property, China Cement.2012;73-76.

3.Xie Congchao.Impact of alkali substances on refractories in rotary kiln, Refractories&Lime.2013;30(3):22-24.