Refractory Linings in Waste-to-energy Plants – New Developments for Improved Oxidation Resistance

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In waste-to-energy plants, the combustion chamber, i.e. the boiler is an essential part of the system. Due to the relatively high temperatures, the acidic slags, ashes and flue gases, the burning of waste produces a highly corrosive atmosphere. Under these extreme operating conditions, high performance refractory materials are essential to provide a high level of safety and efficiency. The objective of this report is to give an overview of the new, improved Saint-Gobain materials for the waste-to-energy market.

1 Introduction

In waste-to-energy plants, the combustion chamber, i.e. the boiler is an essential part of the system. It is lined with tubes, arranged vertically and welded together in continuous sections. Water, circulating through the tubes absorbs the heat generated from the burning of waste, producing steam. This steam then can be used for both heating and the generation of electricity. Due to the relatively high temperatures, the acidic slags, ashes and flue gases, the burning of waste produces a highly corrosive atmosphere. Under these extreme operating conditions, high performance refractory materials are essential to provide a high level of safety and efficiency. The requirements are diverse: maximum protection of the tube walls against corrosion and erosion, i.e. superior oxidation and abrasion resistance, optimal thermal conductivity and excellent mechanical resistance. *Saint-Gobain Ceramic Materials* is the largest producer of ceramic tube wall protection systems. Its product portfolio comprises, next to the well-known silicon carbide (SiC) tiles in different qualities, a whole range of monolithic, refractory masses and mortars. In the last years, Saint-Gobain's strong dedication to R & D in this field has mainly been focused on the improvement of the oxidation resistance of refractory tiles made out of nitride bonded silicon carbide (NSiC). SiC is, in fact, preferentially used as a basis material for tube wall protection systems, due to its superior oxidation resistance, chemical stability and its outstanding mechanical and thermo-mechanical properties. Besides, SiC offers high heat conductivity, allowing an efficient energy recovery at the tube wall. The primary goal in the development department was to find the best technical and commercial solution in respect to lifespan and low maintenance for customers. The objective of this report is to give an overview of the new, improved Saint-Gobain materials for the waste-to-energy market.

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2 Oxidation of SiC materials in incinerator boilers

Oxidation of SiC materials in incinerator boilers is the most critical high temperature reaction, and its consequences. The burning of waste generates the most diverse corrosive media, e. g. different salts and aggressive water vapour (Fig. 1). Flue gases, ashes and condensates in several forms penetrate the refractory materials due to their porosity and can cause reactions with its different phases. These chemical reactions can generate new crystalline and vitreous phases that can lead to a change in volume and can negatively influence the material properties to the point of dissociation and disruption. The early oxidation of the refractory materials is the most critical high temperature reaction. Indeed, it can lead to corrosion and subsequently to the dissociation of the materials. The reaction rate and nature is affected by the gas pressure, by the temperature and the material's microstructure, i.e. its configuration. In

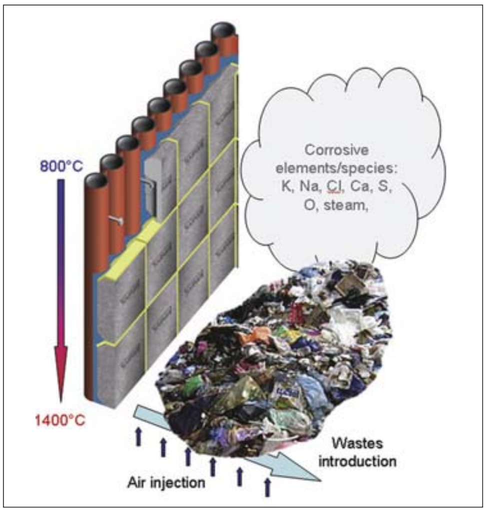

Fig. 1 Oxidation process in the incinerator boiler

Figs. 2 and 3 **Consequences of the volume expansion of SiC materials in the incineration boiler**

the lower parts of the combustion chamber, where the concentration of hazardous substances is relatively high, a stronger inclination to corrosion can be identified.

In the case of nitride bonded SiC materials, oxygen reacts with the nitrides and the SiC, forming crystalline (e.g. cristobalite) and vitreous silica. These reactions lead to a volume expansion which can cause the failure of the refractory parts. For instance, the volume expansion of the tiles can be such that adjoining tiles may come into contact with each other. The compressive stresses induced can cause, in the case of a further volume increase, the detachment of the tiles from the tube wall (Figs. 2 and 3).

At this point, it is important to highlight the role of the backfilling mix for tube wall protection systems. Due to their high corrosion resistance, backfilling mixes, e.g. Refrax® PROflow or Refrax® PLUSflow, defer the diffusion of hazardous substances. In fact, in case of the detachment of the tiles from the tube wall, they constitute a further protective layer both for the tube wall and the anchoring elements. Consequently the boiler's durability is markedly improved.

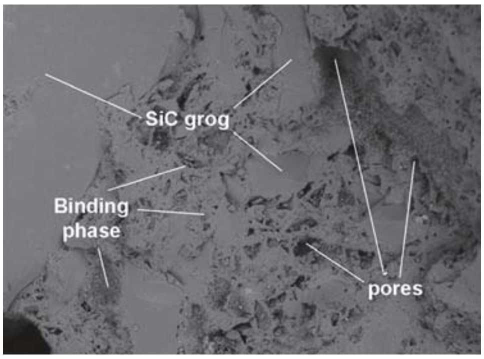

Fig. 4 **Typical structure of SiC materials employed in waste-to-energy plants (Refrax® BASIC)**

3 Typical structure of SiC materials for tube wall protection systems in waste-to-energy plants

The binding phase is the key element for the improvement of the oxidation resistance of refractory materials. Fig. 4 shows the typical structure of a NSiC refractory material. Three phases can be distinguished:

- SiC grains with a well defined and controlled grain size distribution
- Pores
- The binding phase.

A first important parameter to improve the oxidation resistance is the purity of the SiC material. For the production of SiC tiles, Saint-Gobain uses exclusively high-purity SiC qualities, which are also produced within the Saint-Gobain Group. According to the current state of knowledge, it is not possible to influence the quality of SiC in any other way than through the purity of its grains. The porosity of SiC-based refractory materials causes contrary properties. The thermo-mechanical properties are often increased thus the material becomes more robust regarding temperature changes.

On the other hand it promotes the diffusion of corrosive gases and liquids. Perfectly dense SiC-based materials are available, however, due to their brittleness and for price reasons, they have not proven to be successful in practice. For the sake of completeness it should be noted that silicon infiltrated SiC materials (Silit® SKD) have been used in certain areas. Further tests and new developments remain to be seen. The binding phase has a great influence both on the mechanical properties and on the heat conductivity of the material.In addition to this, it plays an important role regarding the stability of the material microstructure, since it is a pathway for the penetration of corrosive slags, flue gases and ashes. Therefore, high corrosion resistance as well as low permeability are essential properties of the binding phase for the durability of both the refractory materials and the metal parts they protect.

Consequently, it seems logical to give the further development of the binding phase top priority. Along with the choice of high purity SiC grains and a well-balanced porosity, the binding phase is the best component for further development.

4 Advanced refractory materials for enhanced oxidation resistance

Saint-Gobain Ceramic Materials develops, manufactures and distributes high-quality refractory products. In addition to sintered and unsintered shaped components, like tiles and bricks, made out principally of SiC, Al_2O_3, also monolithic masses on the basis of SiC, SiO_2 and Al_2O_3 are provided. The focus in this article will be on silicon carbide (SiC) products, since, as already mentioned, SiC has proved to be the best material for tube wall protection systems in incinerator boilers.

Tab. 1 shows the main properties of Saint-Gobain nitride bonded SiC materials. The binding phase of Refrax® BASIC is mainly composed of α-Si_3N_4. Its filigree, needle-like morphology leads to a relatively large surface, as shown in Fig. 5. Refrax® PRO marks the first step of the binding phase improvement, in comparison to Refrax® BASIC. It features a higher content of Si_2ON_2. This is characterized by a flaky structure that has a smaller surface, which results in a lower reactivity, thus enhancing the resistance to oxidation. Refrax® PRO is, at present, in use in many plants and sets the standard of performance for quality nitrided SiC. A further improvement in oxidation resistance has been achieved by using the materials Refrax® PLUS and Refrax® TOP. In the case of Refrax® PLUS, a special dopant is added to enhance the build up of Si_2ON_2 and β-Si_3N_4. The morphology, shown in Fig. 6, is responsible for a better oxidation resistance of the material. Refrax® PLUS has been tested successfully in plants over the past years and has shown a real improvement in lifespan and durability. Field trials are described later in this article. As far as Refrax® TOP is concerned, its basic structure can be compared to that of Refrax® BASIC. However, thanks to its special material composition and a double firing process, a glazed phase is generated, which fills in part of the porosity. The result is a material with a lower permeability to corrosive media. Refractory materials have to be composed and produced very carefully in order to secure reliable and efficient functioning within waste-to-energy plants. Depending on their position within the boiler, the refractory products have to withstand high thermal and mechanical stress as well as being resistant to the highly corrosive atmosphere. The resistance to high temperature corrosion, the most critical factor with respect to the lifespan within the incinerator plant, is not affected by the position in the boiler.

Tab. 1 Properties of the Refrax® materials that are used in waste-to-energy facilities

		Refrax® BASIC	Refrax® PRO	Refrax® PLUS	Refrax® TOP
SiC [mass-%]		78	75	77	78
$Si_3N_4 + Si_2ON_2$ [mass-%]		19	22	22	17
Cold crushing strength [MPa]		> 140	> 140	> 140	> 140
Density [g/cm³]		2,65	2,70	2,74	2,70
Porosity [%]		< 16	< 14	< 13	< 13
Conductivity [W/m·K]	400 °C	27,5	26,3	22,0	33,0
	800 °C	20,1	17,4	18,0	21,0
	1000 °C	18,5	16,9	16,0	18,0
Linear thermal expansion [%]	400 °C	$1{,}0 \cdot 10^{-3}$	$1{,}8 \cdot 10^{-3}$	$0{,}6 \cdot 10^{-3}$	$1{,}0 \cdot 10^{-3}$
	600 °C	$1{,}8 \cdot 10^{-3}$	$2{,}7 \cdot 10^{-3}$	$2{,}4 \cdot 10^{-3}$	$1{,}5 \cdot 10^{-3}$
	800 °C	$2{,}7 \cdot 10^{-3}$	$3{,}7 \cdot 10^{-3}$	$3{,}2 \cdot 10^{-3}$	$2{,}5 \cdot 10^{-3}$
	1000 °C	$4{,}0 \cdot 10^{-3}$	$4{,}6 \cdot 10^{-3}$	$4{,}6 \cdot 10^{-3}$	$3{,}7 \cdot 10^{-3}$

5 Steam oxidation test and SEM analysis

Steam oxidation test and SEM analysis are reliable instruments to measure the oxidation resistance. The change in material vol-

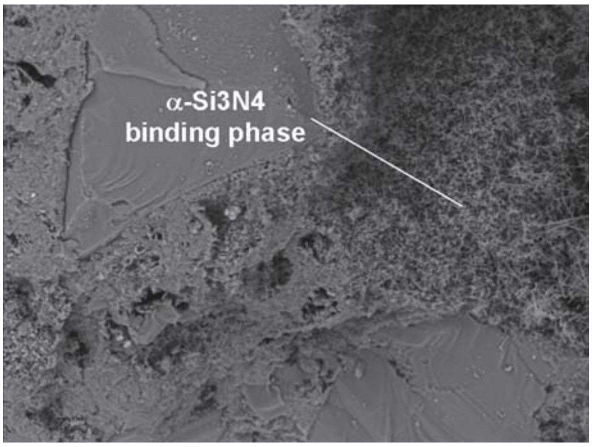

Fig. 5 α-Si_3N_4 binding morphology of Refrax® BASIC

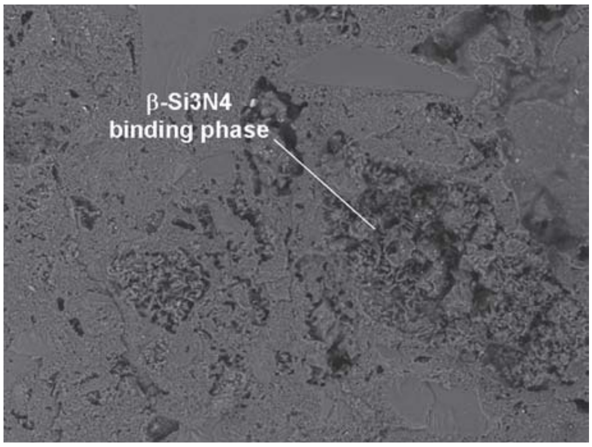

Fig. 6 β-Si_3N_4 and Si_2ON_2 binding morphology of Refrax® PLUS

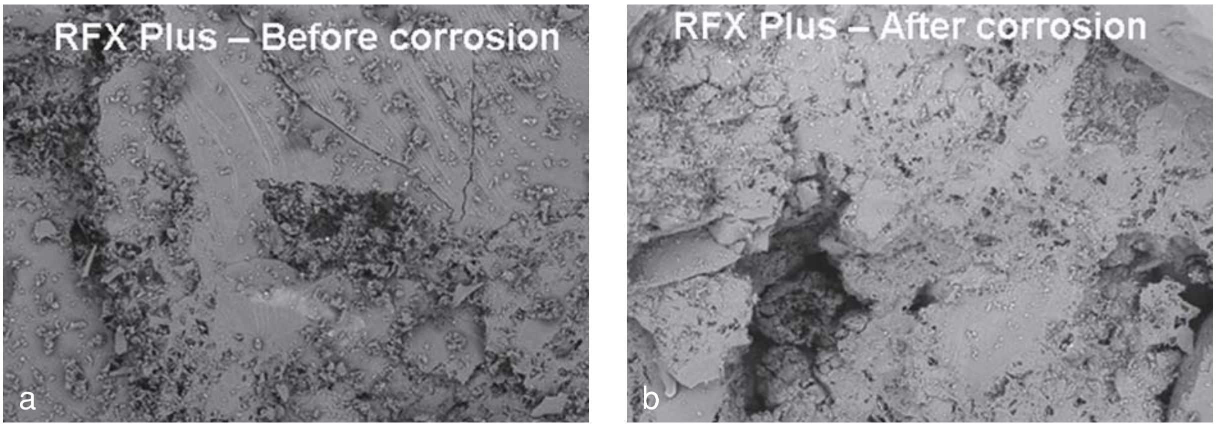

Fig. 8 a,b SEM analysis of Refrax® PLUS before and after the oxidation test

ume is the essential parameter to be monitored when examining the oxidation resistance of refractory materials. If the change in volume is too large it can lead to the spalling of the refractory component or to compressive loading between the adjacent tiles in the tube wall protection system. That means, that in the case of a volume expansion, the performance of the refractory components declines. Consequently, it is necessary to insure lower volume expansion of the materials and components.

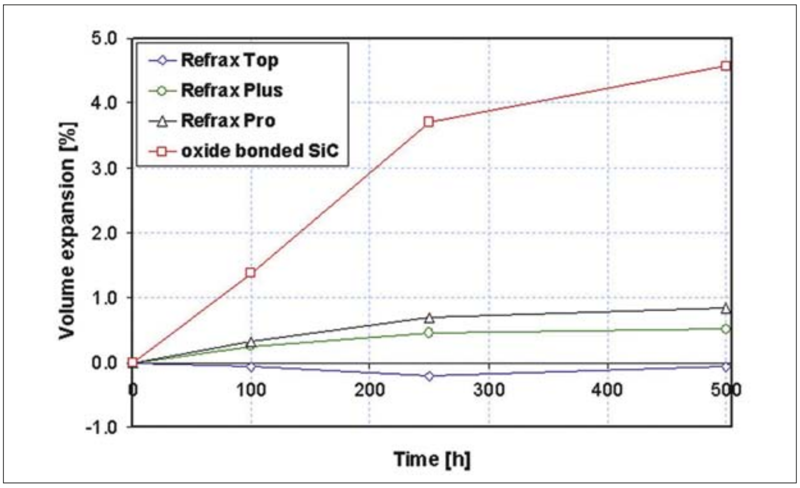

Fig. 7 Comparison of the change in volume for the different SiC materials during the oxidation test

To determine the oxidation resistance of refractory materials, the steam oxidation test is normally used.

The tests here described were carried out at the the company's R&D centre in Cavaillon (*Saint-Gobain CREE*, France). In a special kiln, Refrax® PRO, Refrax® PLUS, Refrax® TOP and oxide bonded SiC samples (65 x 25 x 25 m^3) were exposed to a temperature of 1000 °C for 500 h. The kiln was saturated with steam (rate of 32 kg/h·m^3). Weight, volume, thickness and porosity of the samples were monitored after 100, 250 and 500 h. Fig. 7 shows the change in volume of the different material qualities during the oxidation test. As expected, the NSiC qualities show a significantly lower change in volume in comparison to the oxide bonded SiC material. Moreover, a lower volume expansion can be observed for the new qualities Refrax® PLUS and Refrax® TOP. The outstanding steam oxidation resistance was confirmed by SEM observations. They clearly show that the mi-

Figs. 9 and 10 Refrax® PLUS belly bricks after 6000 h of operation

Fig. 11 Test panel: lining with T-Clip PRO tile system after 4000 h of operation

crostructure of Refrax® PLUS before and after the oxidation test does not undergo any particular change (Fig. 8). Except for a light oxidation of very fine particles, all phases remained almost unchanged, even though they were exposed to aggressive conditions of 1000 °C for more then 500 h.

6 Field trial results for Refrax® materials

Field trial results for the newly developed Refrax® materials are shown in two successful examples.

6.1 Refrax® PLUS belly bricks in a waste-to-energy plant

Belly bricks made out of several qualities were installed in the boiler of a waste-to-energy facility. After 6000 h of operation a strong wear of the refractory components as well as a cracking through the tube wall could be observed.

The recorded temperatures were as high as 1500 °C. Due to the initiating corrosion of the tube wall, the refractory linings had to be partly or completely renewed.

The test panel consisted of 5 m² of Refrax® PLUS belly bricks and was installed above the combustion chamber. After 6000 h of operation, a reduced wear of the refractory parts could be observed. Besides, no cracking at all was observed (Figs. 9 and 10).

6.2 Refrax® TOP T-Clip PRO tile systems in a biomass facility

In a biomass facility the conversion to fuel substitutes led to critical problems in the brick lining, i. e. the monolithic refractory cement. Some of the increased heat values lead to strong wear and increased slag on the brick lining. The use of water lances placed a further strain on the cement.

The test site, a combination of Saint-Gobain T-Clip PRO systems with the material Refrax® TOP, was placed directly beside the water lance equipment. After approximately 4000 h of operation, the test panel was in perfect condition. It could be observed how the dense surface of the Refrax® TOP tiles optimally enhanced the slag outflow. Furthermore, cleaning with water lances showed no negative impact on the test tiles (Fig. 11).

7 Conclusion

Due to the high thermal and complex chemical operating conditions in incinerator boilers, high performance refractory materials and systems are indispensable to protect the metal tube walls from corrosive media. The most critical parameter in the choice of these materials is their resistance to oxidation. Due to its superior oxidation resistance, chemical stability and the outstanding mechanical and thermo-mechanical properties, SiC is the first choice when choosing material for tube wall protection systems.

Focusing on the modification of its binding phase, Saint-Gobain has developed a range of nitride bonded SiC materials that show a real improvement in lining durability, contributing to provide the highest level of efficiency and safety for the management of waste-to-energy facilities.