REFRAX®, IMPROVED SIC & WASTE-TO-ENERGY APPLICATION

Author: L. San-Miguel, Saint-Gobain Research Provence, 550 avenue Alphonse Jauffret, 84300 Cavaillon, France
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Context: Waste-to-Energy Markets and Stakes

Over the last decades, huge amounts of waste resulted in increasing public concerns; leading to the subsequent health and environmental impacts. At present, approximately 70% of Municipal Solid Waste (MSW), still ends up on landfills or uncontrolled dumpsites; which often contaminate surface water, ground water, or soil, and emit greenhouse gases [13]. Waste-to-Energy (WtE) facilities based on steam generating units (boilers) have proven to be a reliable option, solving not only the pressing waste disposal problems but also to meet simultaneously environmental, sustainability and compensate shortage of other energy sources.

Ten years ago, WtE in the UK represented less than 10% of the overall waste disposal against 90% for waste landfill. Hopefully, the situation is expected to turn around soon with, for the first time, a proportion of waste balanced between landfill and WtE alternatives [1]. Mid 2017, 52 WTE plants were operated in the UK with an overall capacity of 11.5 MT/year. Nearly 65% of the UK capacities are under 10 years of age.

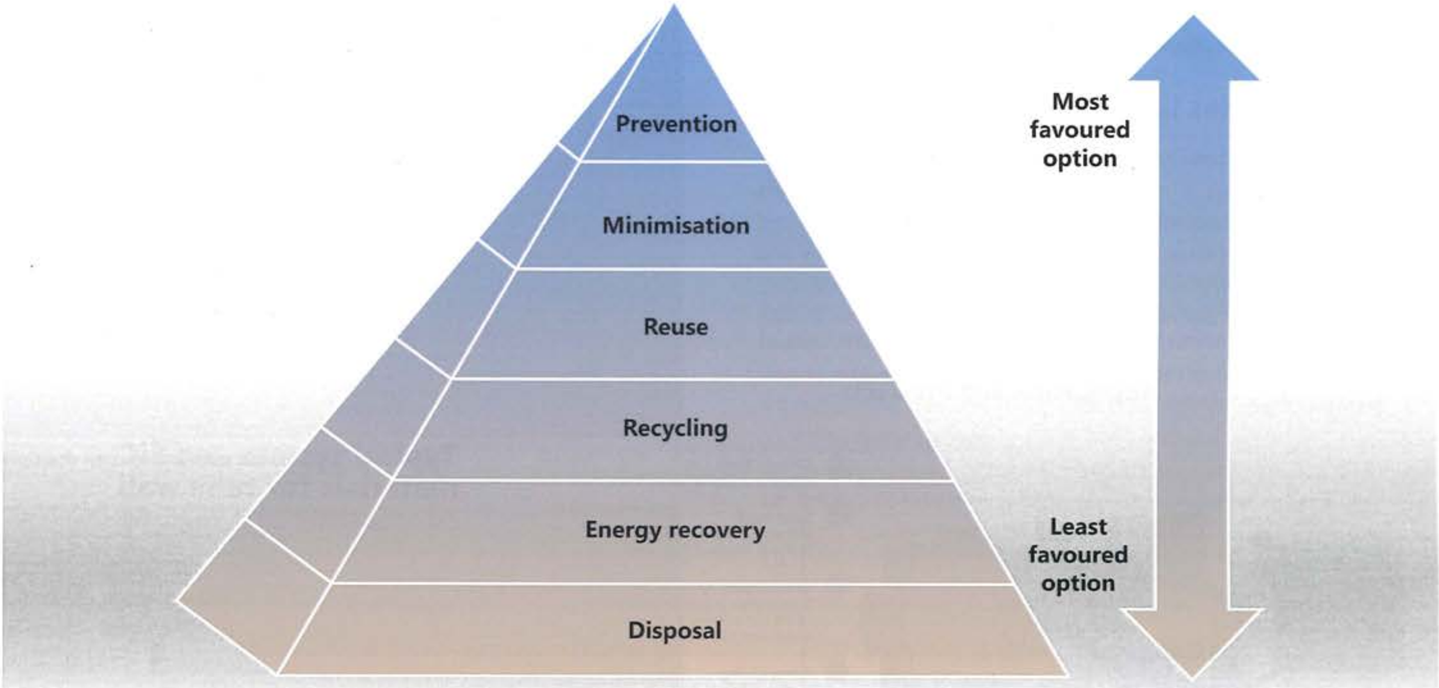
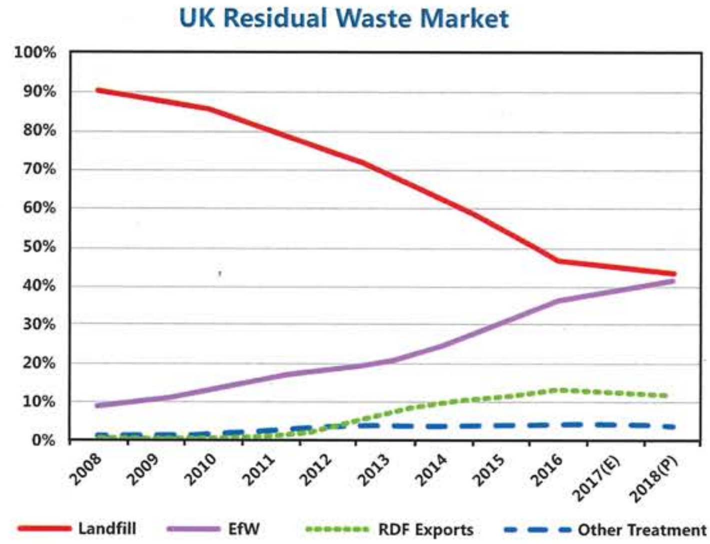
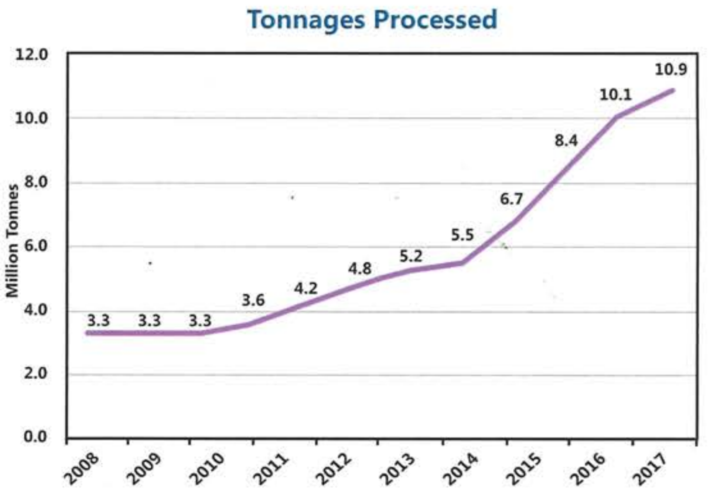


Figure 1: Waste hierarchy

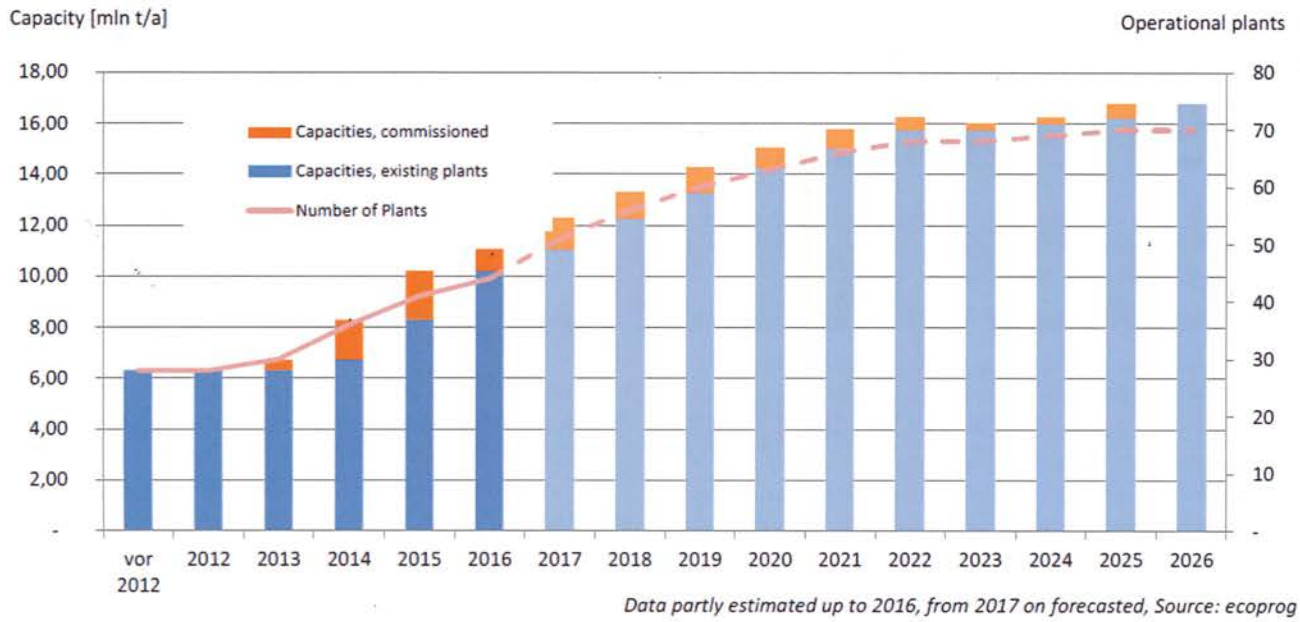


Graph 1: Evolution of the residual waste management segmentation in UK from 2008 to 2018 (E = Estimated, P = Provisional, EfW = Energy from Waste) [1]



Graph 2: Total tonnage of Waste accepted in WtE between 2006 to 2017 in UK

Source: Annual Performance Report either provided by operators or released under the Freedom of Information Act. [1]



Graph 3: Development of plants and capacities in the UK - *Source: Ecoprog*

Why refractories lining in WtE Plants

The current trend for more compact installation and the need for higher energy throughput result in more severe operating conditions; including severe temperature fluctuations, higher operating temperatures and higher variety of chemically aggressive substances. Consequently, safe and efficient operation of WtE boilers requires the use of high performance refractories to protect the metallic membranes from corrosion. In WtE plants, the combustion chamber is an essential part of the system. The chamber is formed with metallic tubes, arranged vertically and welded together in continuous section (a wall membrane). The water circulating in the tubes recovers part of the heat generated from the burning waste. The energy recovery in the form of steam and/or electricity is then used for the local communities in which the facilities operate. Considering the high temperatures generated in the burning of the waste and the corrosive nature of the flue-gas, refractories are generally applied over the metal boiler tubes to protect them from the harsh environment.

Application and Products

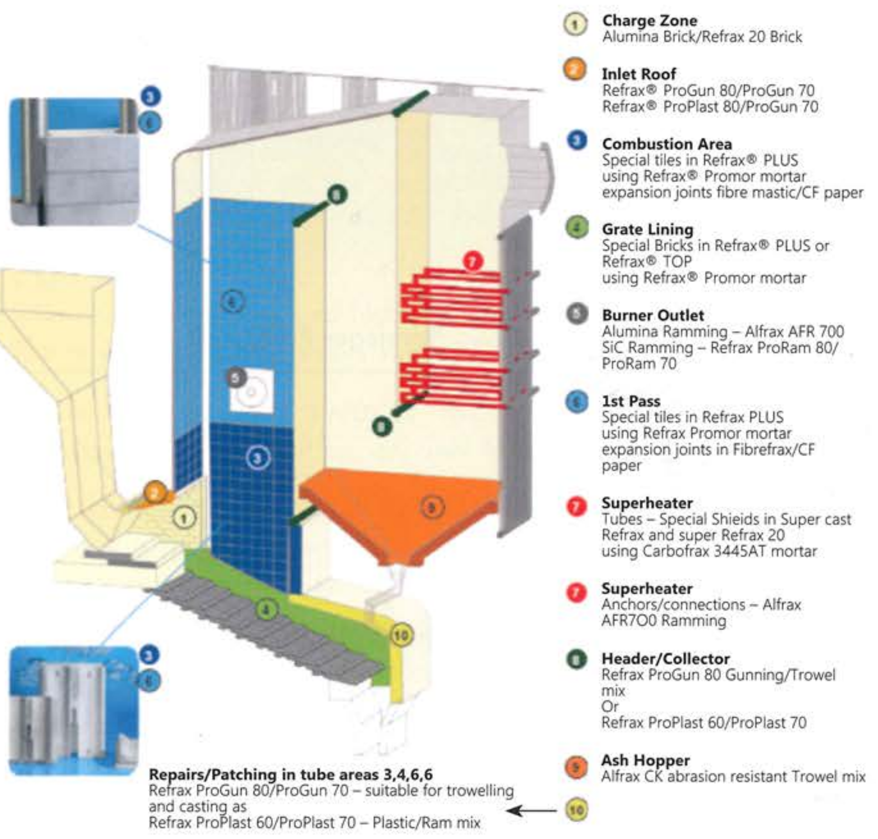


Figure 2: Refractory segmentation in WtE units - *Source: Saint-Gobain*

Typical system and SiC materials for tube wall protection

The current generation of Saint-Gobain advanced refractory protection consists of refractory tiles systems attached to the boiler tubes walls and backed by a self-flowing refractory castable or mortars. The backing castable has generally high silicon carbide content (60-80%) to increase the thermal conductivity, thus complementing the high conductivity of the tile system to ensure an efficient thermal transfer from the combustion chamber to the boiler tubes.

Besides being an excellent path for thermal transfer, the added advantage of the back-cast tile system is that in the event of damage or failure of the tile, the cement behind provides an additional tube wall protection until appropriate repairs. In addition to this safety function, the T-Clip Pro system installed with conductive castable results in lower tile temperatures (below 800°C) [2], [7] therefore limiting the corrosion mechanisms and ash accumulation on their surface. (Figure 4 and Figure 5).

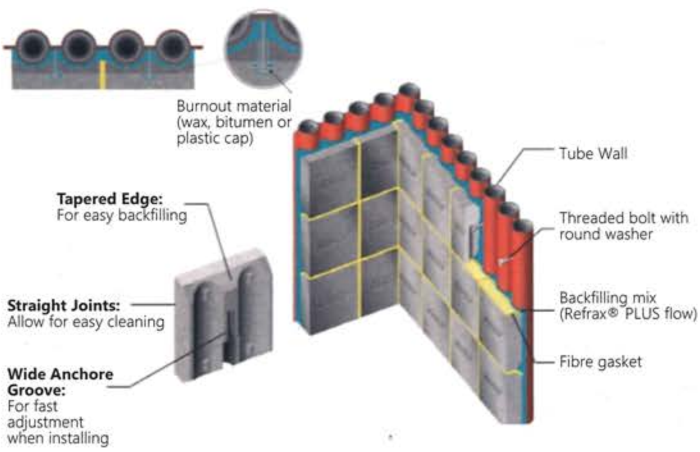


Figure 3: Typical tile design – Saint-Gobain T-Clip Pro

Figure 4: Refrax® PRO tiles with mortar - 8000 eoh [1]

Figure 5: Refrax® PRO tile without mortar - 8000 eoh

Refractories corrosion issue in WtE units

Flue gases and ashes produced under several forms during the process condensate and/or penetrate the refractories through the porosity and can cause reactions with its constituents. In most of the cases, these reactions lead to a significant volume expansion. Combined with thermal stresses caused by temperature fluctuations or thermal gradient; an excessive expansion of the refractory parts would lead to material failure, cracking or rupture under compressive forces generated by the contact between adjacent tiles (Figure 6).

Figure 6: Typical expansion issues in WtE units

In the case of SiC refractories, 3 main types of corrosive degradations have been reported widely in the literature [3], [4], [5], [6], [8]: 1) Passive oxidation, 2) Active oxidation 3) Deposit-induced corrosion by molten salts. Other mechanisms probably also exist, but are not yet well understood due to their complexity and sensitivity to random variation from incinerator to incinerator.

In oxidizing atmospheres, SiC and Si_3N_4 are known to form a protective scale of silica or silicon oxy-nitride. This process, called **passive oxidation**, corresponds to the following reactions:

[a] $SiC_{(s)} + 2O_{2(g)} \rightarrow SiO_{2(s)} + CO_{2(g)}$

[b] $Si_3N_{4(s)} + 3O_{2(g)} \rightarrow 3SiO_{2(s)} + 2N_{2(g)}$

[c] $2Si_3N_{4(s)} + 3/2O_{2(g)} \rightarrow 3\ Si_2N_2O_{(s)} + N_{2(g)}$

However, depending on the environment temperature, the silica formed can be found as amorphous or crystalline (cristoballite, quartz or tridymite) phases. The formation of silica inside the material microstructure can lead to non-negligible volume expansion of the refractory (Figure 7). As a consequence, tiles may touch each other and fail due to cracking or to anchoring system fatigue.

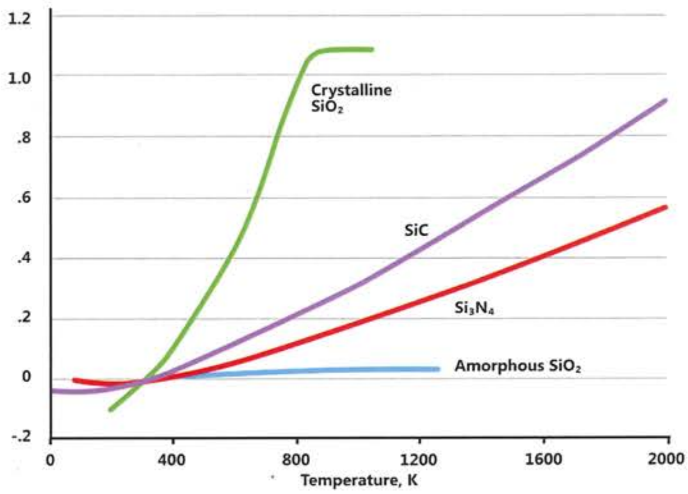


Figure 7: Thermal expansion of Silicon Carbide, amorphous SiO_2 and crystalline SiO_2 as a function of the temperature

In atmospheres with low oxygen partial pressure and possibly with high velocity gas flows, **active oxidation** may occur by forming volatile silicon components [5]. In this case, the material microstructure can be weakened via the following reactions:

[d] $SiC_{(s)} + 2H_2O_{(g)} \rightarrow SiO_{(g)} + CO_{(g)} + 2H_{2(g)}$

[e] $Si_3N_{4(s)} + 3H_2O_{(g)} \rightarrow 3SiO_{(g)} + 2N_{2(g)} + 3H_{2(g)}$

[1] *Eoh = equivalent operational hours*

Nevertheless, the incinerator environment cannot be characterized as simply oxidizing. In the presence of chemically aggressive compounds as molten slag and alkali-rich compounds in the process, other reactions may occur.

In contact with alkali-rich environment, studies have shown possible mechanisms of degradation of the protective silica layer (formed from the passive oxidation); leading to the formation of liquid silicate film or the formation of new phases. These liquid silicate films can move away and the protection of SiC or Si_3N_4 phases against oxidation is not insured anymore.

[f] $M_xCO_3 + x.SiO_{2(s)} \rightarrow M_xO.xSiO_{2(l)} + CO_{2(g)}$

[g] $M_xSO_{4(s)} + x.SiO_{2(s)} \rightarrow M_xO.xSiO_{2(l)} + SO_{3(g)}$

Another possible reaction concerns the modification of the protective layer oxidation into SiO_3^{-2} followed by the reaction with calcium cation from the dissolution of calcium sulphate at high temperature to form wollastonite ($CaSiO_3$)[4].

[h] $CaSO_4 \rightarrow SO_4^{-2} + Ca^{+2}$

[i] $SO_4^{-2} \rightarrow SO_2 + O^{-2}$

[j] $SiO_2 + O^{-2} \rightarrow SiO_3^{-2}$

[k]$SiO_3^{-2} + Ca^{+2} \rightarrow CaSiO_3$

The third type of reactions is linked to the condensation of the calcium sulphate or alkali compounds species into the porosity of the refractory leading to the formation of Cristobalite phase at lower temperature (below 700°C) in the matrix and around the SiC grains [9].

The temperature boundaries between all these mechanisms are only approximated and are dependent on the specific system. In practical cases, several mechanisms operate simultaneously. However, as general rule the kinetics of these reactions is strongly impacted by temperature, oxygen pressure, material microstructure and compositions and lead in the majority of the case to an undesirable volume expansion. Hence, the lower the volume expansion is, the better the material performance will be.

Therefore, it will be recommended to prefer refractory lining systems (i.e. material composition, microstructure and design) offering low permeability to corrosive gas, high resistance to oxidation and capable of generating a suitable thermal profile to limit the penetration of the corrosive gases and kinetics of damaging reactions at the surface of the refractory.

Advanced refractory materials for enhanced oxidation resistance

Typical SiC- based shaped refractories are composed of 3 main phases: SiC grains, with a well-defined and controlled particle size, a binding matrix and porosity. The choice of silicon carbide grogs is driven by their excellent resistance to oxidation, chemical stability, outstanding mechanical and thermo-mechanical properties and high thermal conductivity [9], [11]. On the other hand, the role of the binding phase in the final product is often underestimated. Additionally, it plays an important role in the corrosion resistance of the product, since corrosive slag, fumes and ashes penetrate into the tile through it. Hence, good corrosion resistance of the binding phase itself and low permeability are key properties when selecting a lining configuration to extend the lifetime not only of the refractory lining, but also of the metallic parts protected by it.

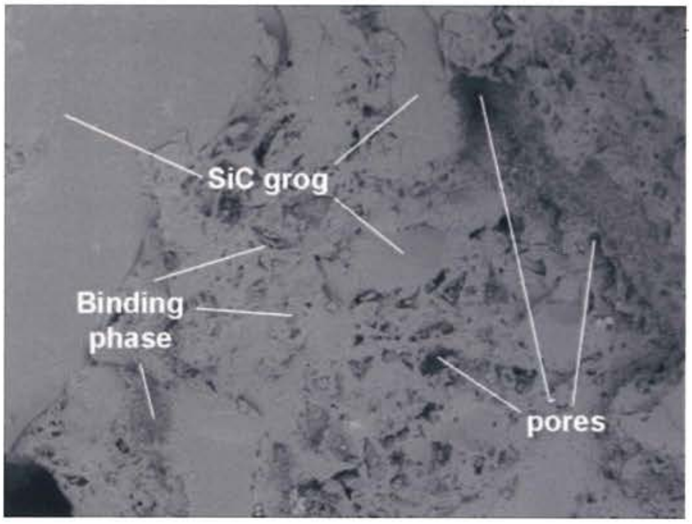


Figure 8: Type structure of SiC materials employed in waste-to-energy plants (Refrax®)

We can distinguish 2 main families of SiC carbide refractories for WtE applications.

- Oxide Bonded SiC denoted [O-SiC)]
- Silicon nitride bonded SiC denoted [N- SiC]

Saint-Gobain Performance Ceramics & Refractories develops, manufactures and sells high quality refractory products. Considering the well-known concern about oxidation of silicon carbide, our research on non-oxide ceramics composite matrix with enhanced resistance to oxidation was the main focus of the R&D team and evolved into the development of the **Refrax®** brand.

The table below outlines the average material properties of the different products supplied by Saint-Gobain in comparison to conventional proposed on the market.

Among the bonding phases known (silica, oxides...), the use of silicon nitride (Si_3N_4 or oxy-nitride) leads to good mechanical properties and chemical resistance in several corrosive/oxidative environments, in addition to high thermal conductivity, low thermal expansion and good abrasion resistance [10]. The specialities of the Refrax® product range lie in the special

	O-SiC 1	Refrax® PRO	Refrax® PLUS	Refrax® TOP
SiC content *[%]*	91	75	77	78
Binding phase	Cristobalite, Mullite	Si_3N_4, Si_2ON_2	Si_3N_4, Si_2ON_2	Si_3N_4, Si_2ON_2
Density *[g/cc]*	2.64	2.70	2.74	2.70
Porosity *[%]*	<16	<14	<13	<13
MOR *[MPa]*	48	62	60	52

Table 1: Basic Properties of SiC based shapes refractories

engineering of the refractory microstructure and of the bounding phases constituting the matrix.

Refrax® PRO (Figure 9) shows the first matrix improvement with the modification of the matrix towards the formation of Si_2ON_2 phase instead α-Si_3N_4. Si_2ON_2 phase is characterized by a large plate-like structure, with a lower reactive surface, thus enhancing the resistance to oxidation. This effect is increased with **Refrax® PLUS** with the addition of a specific additive that promotes the formation of both Si_2ON_2 and β-Si_3N_4.

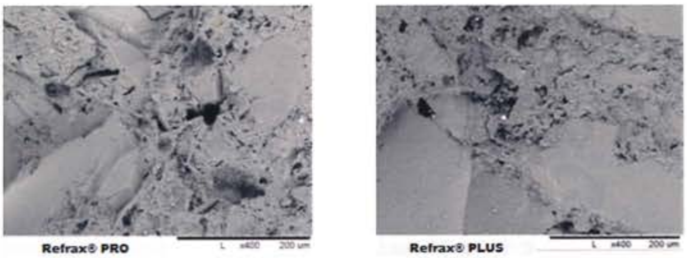


Figure 9: SEM microstructure Refrax® PRO (Left) and Refrax® PLUS (Right)

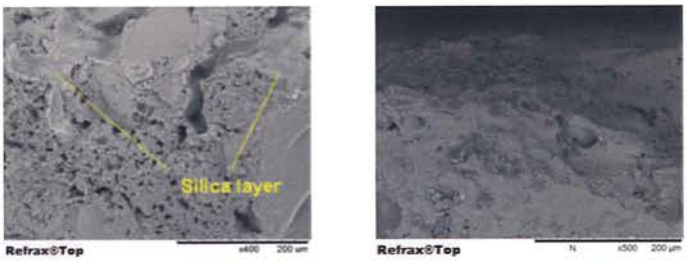
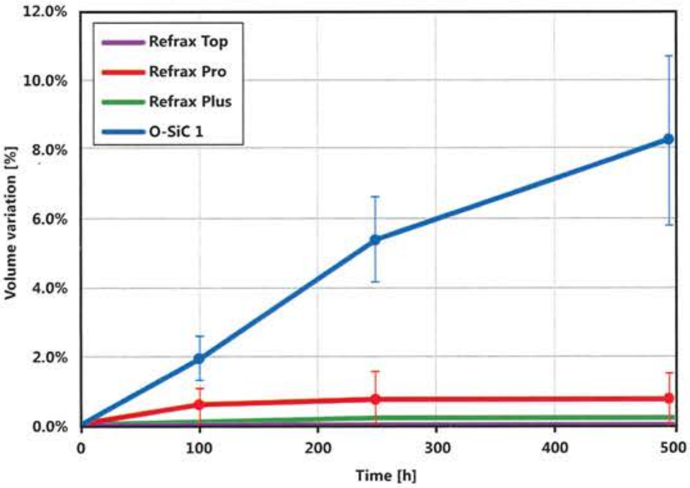


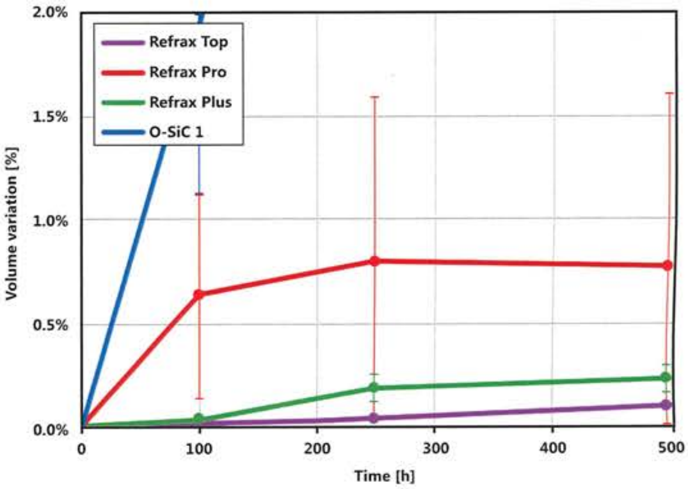
Figure 10: SEM microstructures Refrax® TOP (core) and Refrax® PLUS (glazed surface)

Concerning **Refrax® TOP**, thanks to its special additives and a second firing process, a glazed phase is generated at the surface, which closes the material porosity and acts as physical barrier to corrosive media. **Refrax® TOP** is preferred in areas where ash or slag adhesion is a problem or where high corrosion is apparent.

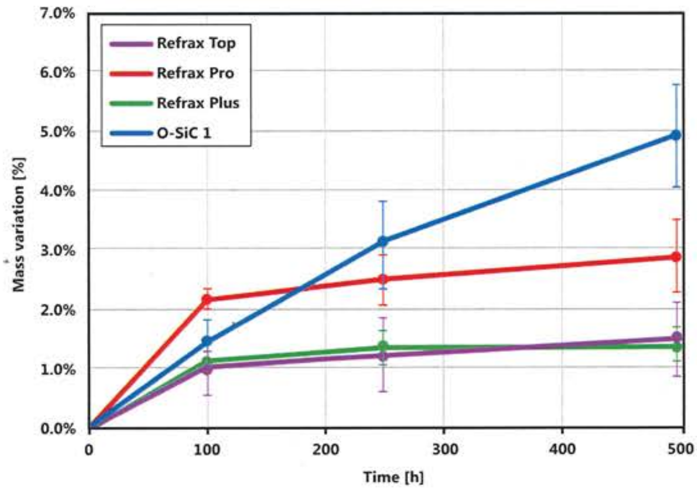
As highlighted, refractories have to be carefully designed to ensure a safe, reliable and efficient performance of the WtE unit. The resistance to high temperature oxidation, which is one of the main phenomena leading to material corrosion in incinerators, is the refractory's key property whatever



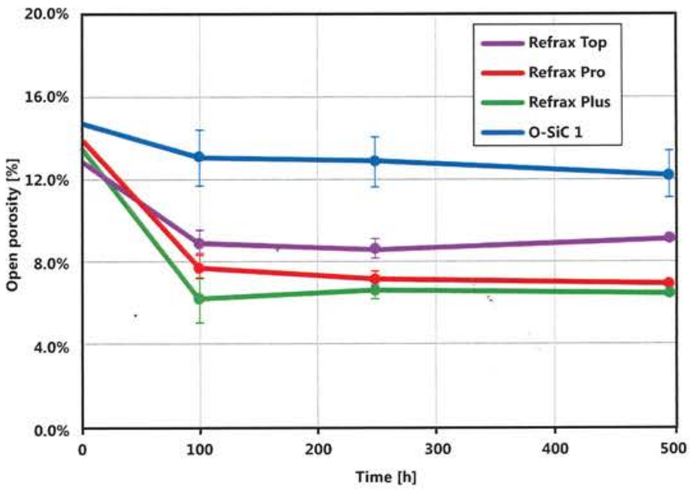
a) Comparison of the change in volume for the different SiC materials during steam oxidation tests



b) Comparison of the change in volume for the different SiC materials during steam oxidation tests (zoom)



c) Comparison of the mass variation for the different SiC materials during steam oxidation tests



d) Comparison of the open porosity evolution for the different SiC materials during steam oxidation tests

Graph 4: Comparison of the volume change, mass variation and open porosity evolution for the 4 different SiC products during steam oxidation tests- 1000°C

the position inside the combustion chamber. The current assessment of corrosion resistance of SiC refractory materials at high temperature follow well known standardized methods (steam oxidation).

Methods and results

Four SiC based shaped refractories where investigated in this study:

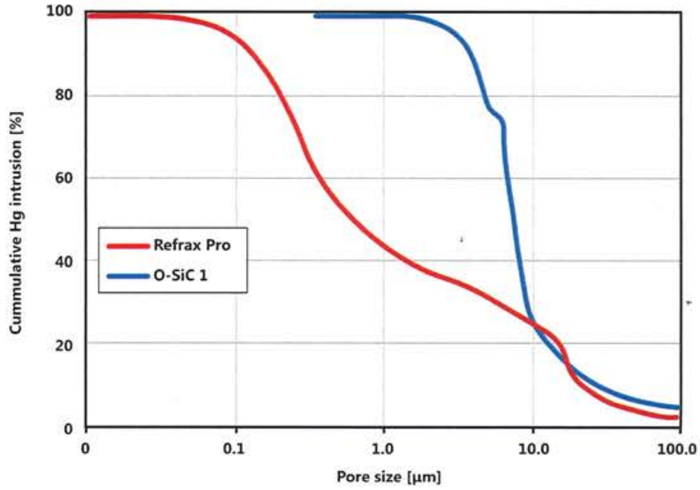
- Oxide-bonded SiC quality denoted (O-SiC 1) which is widely used in French and Italian WTE plants, among other location
- Nitride- bounded SiC quality 1 (**Refrax® PRO**, standard N-SiC from the Saint-Gobain's portfolio)
- Nitride-bounded SiC quality 2 (**Refrax® PLUS**, enhanced N-SiC from the Saint-Gobain's portfolio)
- Nitride- bounded SiC quality 3 (**Refrax® TOP**, enhanced N-SiC, double firing from the Saint-Gobain's portfolio)

ASTM C863-00 Standard Test Method for Evaluating Oxidation Resistance of Silicon Carbide Refractories at Elevated Temperatures was used to compare existing and new compositions for oxidation resistance. The ASTM C863-00 standard is an accelerated oxidation test conducted on test samples within a steam environment (steam rate of 32 kg/h/m^3) at temperatures in the range of interest (1000°C) for up to 500 hours. Test samples are withdrawn from the furnace at 100-hour intervals, 250 h and 500 h for testing. Measurements are made for changes in weight and volume.

Graph 4 depicts the evolution of measured volume expansion evolutions during the steam oxidation test. All the materials exhibit the well-known parabolic oxidation behaviour of SiC- based materials [8]. The kinetic of this behavior is considerably lowered in the case of silicon nitride bounded SiC quality (PRO, PLUS, TOP) due to the formation of a protective scale at the surface of the grains and over the Si_3N_4 matrix. Further material oxidation is slowed down by the diffusion of oxygen across this scale as described by a plateau observed after 200 hours.

Refrax® TOP and **Refrax® PLUS** exhibit the lowest mass gain and volume expansion with volume change less than 0.4% and 0.2% respectively for PLUS and TOP. In comparison, O-SiC exhibits a volume variation up to 8%, suggesting a significant dimensional instability for the tiles inside the boilers. The better performance of the Refrax® products cannot only be attributed to their chemical composition but also to the engineered microstructure of the nitride-bounded matrix. Indeed, the reactive nitration of the silicon during the firing process leads to the formation of a relative fine and hence low permeable matrix as shown in Graph 5 (pores distribution: N-SiC d50: <1 µm vs. O-SiC 1 d50 ~ 8 µm in the case).

This effect is further increased in the case of the **Refrax® TOP** in which a strong physical barrier is intentionally generated thanks to a second firing. The formation of this low permeable glazed structure is fully and carefully controlled during the process and achieved thanks to a specific treatment above the application temperature. The microstructure obtained



Graph 5: Pore size distribution measured by Hg intrusion for fresh materials- Comparison N-SiC (Refrax®) and O-SiC

that way, exhibits a very low permeability to the gas and slag penetration, a low oxygen diffusion and high intrinsic temperature stability and a high inertness to corrosive media.

Monolithic range

Indeed, Saint-Gobain not only have their own tile design system, T-Clip PRO, and the specialist material family we have discussed today (Refrax® PRO, PLUS & TOP) but also offer a range of complimentary monolithic materials again designed and aimed specifically at addressing the problems and issues encountered specifically in WtE facilities.

Concentrating on high quality raw materials, correct particle size, size distribution & optimum physical factors like applied density and porosity, we achieve the best results in real life site tests time after time. We develop products to achieve a desired change, e.g. longer life / higher conductivity/ resistance to oxidation conditions, not to copy existing market trends.

Conclusions

Due to the high thermal and complex operating conditions in incinerator boilers, high performance refractory material and systems are indispensable to protect the metal membrane from corrosive media. The most critical parameter in the choice of these materials is their resistance to oxidation.

N-SiC Refrax® range of products developed by Saint-Gobain has demonstrated performances superior to the ones of oxide bounded SiC refractories with outstanding stability in the steam oxidation test (volume change <0.4% after 500 hrs @ 1000°C). Consequently they are able to provide longer and more effective protection and limiting failure. This performance is achieved thanks to a special design of the binding phase, combining a low permeability, a finer porosity a high resistance to oxidation, and a specific morphology of the Si_2ON_2 and β-Si_3N_4 crystals.

The real challenge where we succeed is to design, manufacture and supply

	Castable	Gunning	Plastic	Ramming
= 60% SiC	Refrax® ProCast 60	Refrax® ProGun 60	Refrax® ProPlast 60	Refrax® ProRam 60
= 70% SiC	Refrax® ProCast 70	Refrax® ProGun 70	Refrax® ProPlast 70	Refrax® ProRam 70
= 80% SiC	Refrax® ProCast 80	Refrax® ProGun 80	Refrax® ProPlast 80	Refrax® ProRam 80

Figure 11: Saint-Gobain monolithic range