



## Short Communication

# Investigation of alkali induced corrosion of SiC filter candles at high temperature, in gasification environment

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## Abstract

The corrosion of silicon carbide filter candle material by alkali species (NaCl and NaOH) vapours was systematically investigated from 800 °C to 1400 °C in a gasification like atmosphere (He/H<sub>2</sub> (4 vol%)/H<sub>2</sub>O (4 vol% and 8 vol%)). Inline hot gas analysis was done by molecular beam mass spectrometry (MBMS). The results of the experiments verify proposed SiC corrosion mechanisms from the literature and propose advanced reaction mechanisms with regard to alkali metal species.

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## 1. Introduction

Cleaning the product gas from gasification and combustion systems is required to meet the environmental regulations and to prevent corrosion and erosion of turbine blades and other downstream components.<sup>1,2</sup> Already since the 1990s the usage of ceramic hot gas filters in advanced coal-fired power generation systems has been established.<sup>1,3</sup> Candle filters are barrier filters which are composed of porous ceramic material which is highly resistible against high temperature and which allows the hot gas to pass through but collect particles on the surface. Hot gas filter candles are highly efficient at gas cleaning from particulate matter in gasification systems. In these applications the ceramic filters operate at high temperature.<sup>4</sup> Hot gas filters need to operate reliably for more than 10,000 h, maintaining particulate removal efficiencies and high flow capacity. They should also possess durability and reliability against mechanical and thermal stresses.<sup>3</sup> In a gasification environment H<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O, N<sub>2</sub>, and CO<sub>2</sub> are formed. The composition of the gas and solid phases, which are released during gasification, depends on the process operating temperature, pressure, feed fuel, and operation atmosphere.<sup>5–7</sup> Sulfur is released as H<sub>2</sub>S

and COS, and chlorine is emitted as volatile HCl and alkali chlorides. Sodium is released as NaCl and NaOH as recently shown.<sup>5</sup> Alkali species are projected to remain in cooler parts of the system.<sup>4</sup> These aggressive process environments, containing steam, dust, gaseous sulfur and alkali,<sup>2</sup> cause microstructural changes in common hot gas filter materials, including oxide, non-oxide, and mixed-oxide ceramics.<sup>3</sup> Especially water vapour can cause remarkable corrosive effects to filter candle materials, like SiC. Silicon carbide (SiC) is a commonly used filter candle material because of its high temperature stability, its thermal shock resistance, its low thermal expansion, its high fracture toughness and its creep resistance at high temperatures.<sup>1,3,8</sup> Furthermore, SiC has a very high oxidation resistance in certain environments. However, for high temperature applications SiC material exhibits either active or passive oxidation depending on the oxygen content of the atmosphere.<sup>9</sup> A low oxygen partial pressure causes an active oxidation to [SiO] gas.<sup>10</sup> A higher oxygen partial pressure results in a passive oxidation, the formation of SiO<sub>2</sub>, that forms a thin layer on top of the SiC surface. This layer acts as a kind of protective surface. Because of the lower oxygen diffusion rate in this layer, the oxidation rate in dry oxygen is decreased to a parabolic progress.<sup>11–13</sup> On the contrary, the oxidation in water vapour containing atmospheres is a major disadvantage of SiC. The oxidation of SiC caused by wet oxygen or even pure water vapour is ten times higher than in dry oxygen.<sup>12,14</sup> Moreover, the oxidation rate increases with increasing water vapour content.<sup>15–17</sup> Additionally, it was shown

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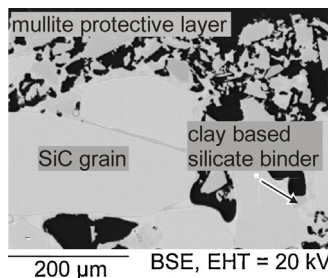


Fig. 1. SEM picture of the SiC-based filter candle in original state.

that water vapor containing atmospheres cause oxidation of the SiC grains and crystallization in the binder phase. The microstructural changes decrease the strength of filter markedly.<sup>11</sup> Further results indicate that most of strength degradation occurs by degradation of the binder phase from hot corrosive gas.<sup>18</sup> The presence of alkaline metals in atmosphere increases the oxidation rate of SiC significantly which is of major interest in alkali loaded gasification product gases. The alkali species seem to have an influence of the corrosion mechanism and the oxidation rate.<sup>12</sup> With alkali metals the oxidation rate is linear for all temperatures instead of the usual parabolic progress.<sup>9</sup> The reason for the increase in oxidation rate may be caused by the formation of an alkali silicate melt.<sup>11,19</sup> However, this has not been proven by online experiments so far.

## 2. Materials and methods

In this study the influence of alkali vapours on the corrosion mechanism of SiC filter candle materials produced by Pall Schumacher was investigated by sector field molecular beam mass spectrometry (SF-MBMS). Fig. 1 shows a SEM image of the original SiC-based filter candle. The filter candle was bonded with clay based silicate binder and covered with a mullite protective layer. The SiC candles have an overall porosity of 35% and a pore diameter of nearly 75 µm.

The corrosion experiments were carried out in an electrical heated tube furnace at temperatures between 800 °C and 1400 °C. The high temperature gaseous products were detected online by a molecular beam mass spectrometer (MBMS). The experimental setup is depicted in Fig. 2. The experiments were performed as packed bed studies using 1 cm<sup>3</sup> pieces of candle material. The setup mainly consists of a heated flow channel housed in a furnace with 5 independent heating zones. For the channel, a 25 mm in diameter, 850 mm long high density Al<sub>2</sub>O<sub>3</sub>-tube was used to minimize interaction of the tube walls with the vapour alkalis as well as other vapour species. The packed bed had a length of 60 mm and was inserted into the tube between two bounds of high temperature (up to 1800 °C resistance) Al<sub>2</sub>O<sub>3</sub>-foam with several holes (ø 1 mm) for enabling the gas stream to pass through. The desired concentration of gaseous alkali species was achieved by evaporating alkaline salts inside the tube. Therefore, the alkali source (NaCl or NaOH) was positioned upstream the bed to load the gas with a concentration of 500 ppm<sub>vol</sub> alkali metal specie of interest. The source boat consisted of a high density Al<sub>2</sub>O<sub>3</sub>-boat, surface area 10 cm<sup>2</sup>.

For all experiments a mixture of 3.5 l/min He/H<sub>2</sub> (4 vol%)/H<sub>2</sub>O (4 vol% and 8 vol%) was used. The gas stream was directed through nebulizers to provide the demanded moisture. Due to the five available heating zones of the furnace, all parts of the reactor tube could independently be kept at elevated temperatures related to the source as shown in the temperature profile in Fig. 2. This prevented alkalis from condensing on the tube walls downstream the source. The last heating zone was kept at a constant temperature of 1100 °C due to the expected heat transfer induced drop in temperature towards the flow channel exit. Additionally, the hydrogen in the gas stream led to a flame formed by the reaction of H<sub>2</sub> with O<sub>2</sub> deriving from the ambient air at the reactor outlet, which kept the tube walls at the flow channel exit at high temperature. For investigations on the gas stream composition leaving the bed, the flow channel reactor was coupled to the MBMS system. MBMS is a highly suitable method used for real time gas analysis of atmospheric and pressurized atmospheres up to 1800 °C. The detection limit is <10 ppb<sub>vol</sub>. Furthermore, the MBMS technique is ideally suited for determining both condensable and non condensable vapour species at the same time without changing the integrity of the hot gas. The integrity of the sampled gas is preserved during the free-jet expansion since chemical reactions are effectively quenched and condensation is prohibited. The nonequilibrium nature of the free-jet expansion and the subsequent formation of a molecular beam allows reactive and condensable species to remain in the gas phase at temperatures far below their condensation point for long periods of time in comparison to reaction rates.<sup>6</sup> The general setup for a MBMS system has been described in literature,<sup>6,20</sup> therefore only additional information concerning the MBMS used in this study is given. The MBMS consists of three differentially pumped chambers. Gases enter the first chamber through a 0.3 mm diameter orifice. Due to the pressure difference between the corundum reactor ( $p = 1.013$  bar) and the first chamber ( $p = 4 \times 10^{-2}$  mbar), the gases undergo a supersonic free jet expansion with strong cooling of the gas significantly below room temperature in microseconds. About 10 orifice diameters downstream from the orifice the expansion has attained free molecular flow. Interaction of the molecules of the product gas with residual gas molecules in the vacuum chambers is inhibited by the high vacuum of the chamber system and the big distance between the molecules in the so-called molecular beam. The core of the free jet expansion is extracted by a conical skimmer of 1 mm diameter and directed into the third chamber. There, a hot filament emits electrons with an electron energy of 50 eV and an emission of 1 mA. Every 10<sup>-4</sup> to 10<sup>-3</sup> molecule is ionized by electron impact. The ions are filtered in a magnetic sector field mass analyzer. After mass separation the ions were detected by an off-axis electron multiplier and the amplified signal is recorded by a computer and software package as a function of time and mass-to-charge ratio.

## 3. Results

Overview scans over the mass to charge range from 15 to 150 showed the main alkali metal species <sup>58</sup>NaCl<sup>+</sup>, <sup>39</sup>NaO<sup>+</sup> (fragment of NaOH due to high ionization energy as recently shown<sup>7</sup>)

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