

Corrosion of Cement-Bonded Refractory Castables due to Hydrogen-Containing Atmosphere

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Abstract

This study examined the influence of a hydrogen-containing atmosphere on cement-bonded refractory castables. Two series of tests were conducted using different materials, a fireclay and a high-alumina castable with SiC. Each test series consisted of three samples exposed in a tube furnace at temperatures of 1 100 °C and 1 500 °C for 24 and 72 hours. The temperature of 1 100 °C represents the upper temperature limit of a direct reduction plant, while 1 500 °C should provoke corrosion. An optical examination revealed a change in colour, due to the formation of oxygen vacancies. At 1 100 °C, there were only minor changes, with no significant loss of mass or change in porosity. At 1 500 °C a greater loss of mass was observed, particularly at the gas inlet, and an increase in porosity was determined. The chemical composition of the high-alumina material undergoes a transformation, with the loss of SiO₂, SiC, and alkalis. Depending on the temperature and holding time, non-oxide agglomerates of iron and phosphorus, form on the surface. Similarly, agglomeration occurs in the castable with a high alumina content and SiC. In contrast to the other test series these agglomerates do not consist of iron and phosphorus, but of iron and silicon.

Keywords: Hydrogen, refractories, corrosion, high temperature.

I. Introduction

Climate change is a major challenge for humanity, with rising temperatures, natural disasters, and threats to ecosystems requiring urgent action. In order to mitigate climate change, it is crucial to reduce the consumption of fossil resources, as these contribute significantly to the emission of greenhouse gases such as CO₂¹. Various agreements, such as the Paris Climate Agreement, have been adopted to combat climate change and limit global warming to 2 °C. However, the latest IPCC report of 2023² forewarns that current measures are not sufficient to achieve this goal. It is therefore necessary to further reduce greenhouse gas emissions from industry. In 2018, the iron and steel industry in Germany produced 58.4 million tonnes of CO₂, accounting for 30 % of the emissions from the country's industrial sector³. To reduce these emissions, replacing fossil fuels with hydrogen is a potential solution.

However, the effect of hydrogen-rich atmospheres on refractory materials remains insufficiently understood. Hydrogen combustion produces water vapour and establishes highly reducing conditions, which can significantly alter the chemical and structural stability of refractory linings. Although several studies have investigated the behaviour of individual oxide components (e.g. SiO₂, Al₂O₃, MgO, ZrO₂) in hydrogen-containing environments, their findings point to substantial degradation

risks. One of the best-known reactions is the reduction of solid silica to gaseous silicon monoxide⁴. This reaction leads to mass loss, increased porosity, and microstructural instability due to the volatilization of SiO. Crowley (1967) demonstrated that silica bricks with a SiO₂ content of 95 % experienced up to 70 % mass loss at 1 400 °C in hydrogen atmospheres⁵. He further showed that the mass loss increases with SiO₂ content, and that the onset of SiO formation occurs between 870 and 970 °C. Notably, the presence of water vapour or high-pressure conditions was found to suppress this reduction to some extent.

Aluminium oxide (Al₂O₃), in contrast to silica, is considered highly stable under reducing conditions. According to Misra⁶, the main gaseous reaction products that may form at elevated temperatures are Al(g) and Al₂O(g). Among these, Al(g) is thermodynamically favoured due to its lower equilibrium partial pressure. Consequently, volatilization of Al₂O₃ is typically negligible under industrial conditions, reinforcing its role as a chemically stable refractory component.

A commonly employed refractory phase that combines both silica and alumina is mullite (3Al₂O₃·2SiO₂). Owing to its high thermal stability, mechanical strength, and corrosion resistance⁷, mullite is widely used in high-temperature applications such as melting and reduction furnaces. However, its behaviour in hydrogen-rich atmospheres is governed by the relative stabilities of its constituent oxides. As previously discussed, SiO₂ is susceptible to reduction and volatilization, making it the critical component

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determining mullite's long-term stability in such environments.

Cement-bonded refractory castables are commonly used as furnace linings due to their ease of application and robust performance at elevated temperatures. With the growing interest in hydrogen-fuelled high-temperature processes, it is becoming essential to understand how such reducing atmospheres affect not only traditional phases like mullite, silica, and alumina, but also calcium-containing compounds derived from the cement matrix such as anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Therefore, the aim of this study is to investigate the impact of hydrogen-containing atmospheres on the microstructural stability of low-cement refractory castables. Two material systems – a fireclay-based and a high-alumina castable with SiC – are exposed to different temperatures under controlled reducing conditions. The resulting changes in phase composition, porosity, and surface morphology are analysed in order to assess their suitability for hydrogen-based industrial applications.

II. Material and Methods

Two commercially available low-cement refractory castables were selected for this study. The first, referred to as F-Clay, is a fireclay-based castable consisting primarily of Al_2O_3 and SiO_2 , with an alumina content of 51 wt%. The second material, designated Al-SiC, is a high-alumina castable that contains 81.5 wt% Al_2O_3 and 8.5 wt% SiC. The detailed chemical compositions of both materials are presented in Table 1 and Table 3.

Both castables were processed by means of vibration casting. After shaping, the specimens were dried at 110 °C until constant mass and subsequently sintered at 1 300 °C. The original blocks were cut to smaller test dimensions. For F-Clay, specimens measuring 100 × 25 × 25 mm³ were used. For Al-SiC, two formats were prepared: 100 × 25 × 25 mm³ and 25 × 25 × 25 mm³.

Corrosion testing was carried out in a horizontal alumina tube furnace (inner diameter 55 mm, tube purity > 99.5 %). Samples were exposed to a reducing gas atmo-

sphere consisting of 90 vol% argon and 10 vol% hydrogen.

The gas mixture had a nominal purity of 99.95 %; however, trace impurities such as oxygen, water vapour, and nitrogen could not be entirely excluded. These minor contaminants may influence redox equilibria and local corrosion processes, particularly under high-temperature conditions and extended exposure durations. The chosen gas composition and thermal parameters were based on the experimental setup used by Leber *et al.*⁸, enabling direct comparison with previously published data and ensuring compatibility with established methodologies.

Two test temperatures were selected: 1 100 °C, representing the upper operating limit of hydrogen-based direct reduction processes, and 1 500 °C, to accelerate degradation mechanisms. Each temperature was applied with two holding times: 24 and 72 hours. The heating rate was set to 4 K/min, and the gas flow was controlled at 25 l/h using rotameters. In each test, three samples were placed in the furnace tube to account for spatial variation (gas inlet, centre, and outlet). Reference samples were also treated under the same thermal conditions in ambient air to distinguish purely thermal effects from atmosphere-induced changes.

Open porosity was measured according to DIN EN 993–1. Microstructural characterization was conducted using a Zeiss GeminiSEM 500 scanning electron microscope. Chemical composition was determined by means of X-ray fluorescence spectroscopy (XRF) using a PANalytical PW2404 instrument. In selected samples, elemental distributions were further investigated using energy-dispersive X-ray spectroscopy (EDS). The X-ray diffraction (XRD) for the mineral phase measurement was performed with a Bruker (USA) D8 Advance.

To complement the experimental findings, thermodynamic equilibrium calculations were performed using the Equilib module of the FactSage software (version 8.2). These simulations provided theoretical insight into phase stability, reduction reactions, and volatilization behaviour under the specific experimental conditions.

Table 1: Chemical composition of the F-Clay after the different tests using XRF.

wt%	Sintered	Trial 1	Trial 2	Trial 3	Trial 4
Parameter	-	1 100 °C/24 h	1 100 °C/72 h	1 500 °C/24 h	1 500 °C 72 h
SiO ₂	43.7	44.3	43.6	44.4	44.0
Al ₂ O ₃	51.2	50.6	51.5	50.9	51.2
Fe ₂ O ₃	0.7	0.7	0.7	0.7	0.6
TiO ₂	1.2	1.3	1.3	1.3	1.3
CaO	2.1	1.9	2.0	2.0	2.0
P ₂ O ₅	0.4	0.2	0.3	0.1	0.0
Others	0.7	1.0	0.6	0.6	0.9
LOI (1 050 °C)	0.03	-0.09	-0.16	-0.16	-0.14

III. Results

(1) Refractory castable F-Clay

After exposure to the hydrogen-containing atmosphere, all F-Clay samples exhibited a distinct blackening, increasing with temperature and exposure duration (Fig. 1). Before the tests, the material had a light beige colour. This change did not occur in reference samples fired in air, suggesting a reduction-driven process.

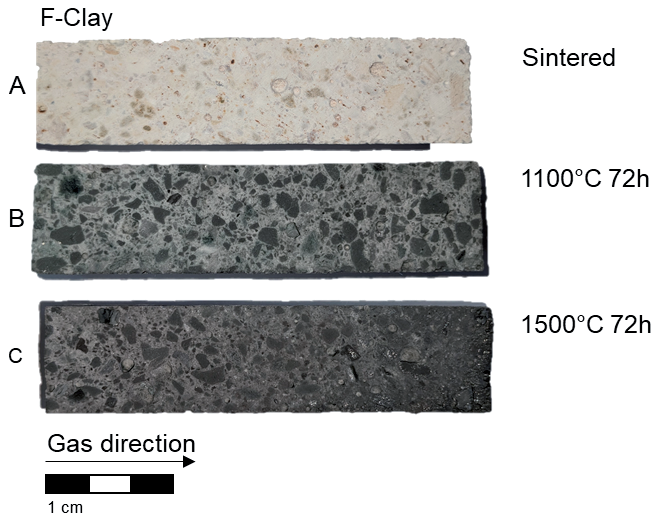
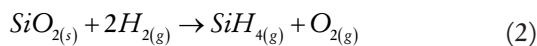
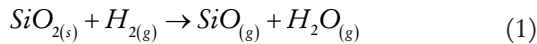
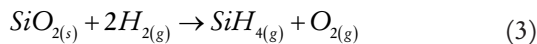


Fig. 1: Optical comparison of samples of the F-Clay after sintering (A), 1100 °C/72 h (B), 1500 °C/72 h (C).

The discoloration is attributed to the formation of oxygen vacancies⁹ primarily due to the reduction of SiO₂ and mullite in the matrix. The following gas-solid reactions are relevant^{10, 4}:



The mullite contained in the material is reduced according to the following equation¹¹:



As with the reduction of pure SiO₂, gaseous SiO is produced. The assumption that the colour change is due to the formation of oxygen vacancies is supported by the fact that, in a further test, the samples were again exposed to an atmosphere containing hydrogen in a furnace. This time, however, in air. This exposure caused the oxygen vacancies to be replenished and the samples returned to their original colour.

Measuring mass balance was used to express the reduction process. A loss of mass always indicates that certain components of the sample have volatilized and been removed from the sample with the exhaust gas. For example, elements such as phosphorus, sodium, potassium and the SiO described above tend to volatilize in the systems considered in this work due to the increased vapour pressure.

Fig. 2 illustrates the mass change across conditions. At 1100 °C, mass loss was minor (<0.2 %). At 1500 °C, a clear gradient was observed along the tube. Samples closer to the gas inlet lost up to 1 % of mass after 72 h, whereas outlet specimens showed lower loss or even slight gain due

to re-deposition of volatile SiO. XRF analysis (Table 1) showed stable bulk composition at 1100 °C. At 1500 °C, changes remained within the method's detection limits. However, the loss on ignition (LOI) values became negative (up to −0.16 wt%), indicating the formation of non-oxide phases or reduction of oxides.

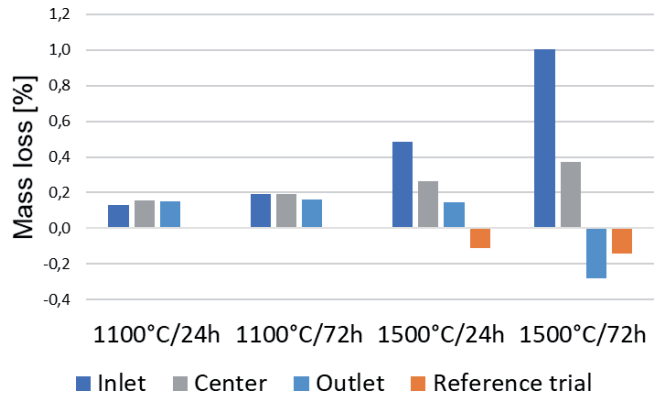


Fig. 2: Overview of the change in the mass of the F-Clay in the various tests.

It can be assumed that this phase was generated by the reducing atmosphere. In the 1500 °C tests, almost all the samples indicated a greater loss of weight than in the 1100 °C tests. In the test at 1500 °C and a holding time of 24 hours, the mass loss of the sample at the gas inlet is the highest at just under 0.5 %. This is followed by the sample in the centre of the tube with just under 0.3 %. With a mass loss of approximately 0.1 %, the sample at the gas outlet is approximately at the level of the tests at 1100 °C. At a holding time of 72 h and 1500 °C, the samples show some differences. The mass loss at the gas inlet increased significantly to over 1 %, while the loss at the centre increased only slightly. There is only a 0.3 % increase in the weight of the sample at the gas outlet. This can be explained by the fact that, as already mentioned, reduced products from the first two samples are carried with the gas flow and finally deposited on the sample at the gas outlet. It is therefore noticeable that there are clear differences in mass loss between the three samples. The greatest mass loss is always experienced by the sample at the gas inlet. The H₂/Ar mixture flows through the furnace tube so that it is saturated at the end of the tube and no longer carries sufficient reactants. As with the 1100 °C experiments, this greater mass loss cannot be demonstrated by a shift in chemical composition.

Open porosity remained unchanged at 1100 °C (Fig. 3). SEM images (Fig. 4) confirmed a stable microstructure. In contrast, exposure at 1500 °C caused significant structural change. Here the porosity decreases by up to 15 %. In the reference test, the porosity decreased by more than 25 %. While additional sintering in air increased density, the reducing atmosphere counteracted this effect via volatilization, yielding increased porosity. However, the graph in Fig. 3 shows that the evaporation of the volatile elements in the main tests counteracts this phenomenon as the increase in porosity is less. However, the graph in Fig. 3 shows that the evaporation of the volatile elements in the main tests counteracts this phenomenon as the increase in porosity is lower.

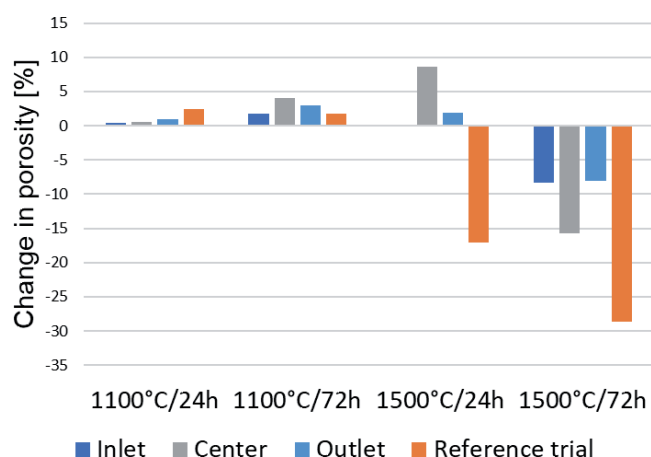


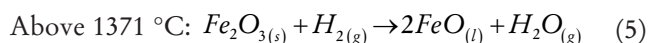
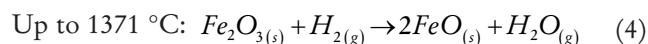
Fig. 3: Overview of the change in the open porosity of the F-Clay in the various tests.

SEM-EDS revealed spherical agglomerates rich in Fe and P (Fig. 5), which increased in size and frequency at 1 500 °C. The observed spherical structure is due to a minimized surface energy by this shape and a state of lowest interfacial tension is established. This type of agglomerate has also been described in previous studies ⁸.

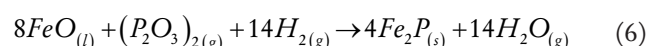
Due to the high diffusion capacity and the comparatively high porosity of refractory products, hydrogen penetrates into the samples and can thus reduce impurities such as iron, phosphorus or titanium oxide within the sample. Iron is reduced by the hydrogen from a temperature of ap-

prox. 550 °C which has already been described in Chen's work ¹². According to FactSage, the resulting FeO has a melting point of 1 371 °C. This means that the reaction takes place depending on the temperature. The reaction with the phosphorus then takes place.

The reactions proceed as follows:



Since the test temperature is 1 500 °C, the agglomerates visible in the SEM images in Fig. 5 are formed according to Equations 5 and 6.



The different agglomerate sizes can be explained by the fact that diffusion is a thermally activated process. Diffusion causes the reduced particles to disperse. However, agglomeration occurs due to their affinity for each other in the reduced state. At higher temperatures, more energy is available, which increases the thermodynamic force for reduction. This means that the probability of reduction occurring increases. The rate of reduction also increases. A higher concentration of hydrogen gas increases the hydrogen partial pressure. This leads to an accelerated reduction rate as a greater number of hydrogen molecules strike the surface of the sample. It also shifts the equilibrium towards H_2 . The reduced compounds have a higher mobility which

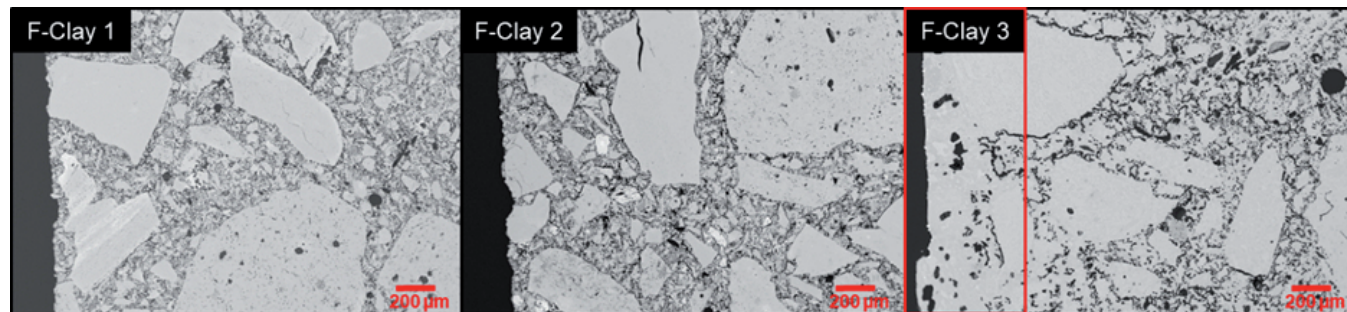


Fig. 4: Overview of the microstructure of the F-Clay after sintering (F-Clay 1), 1 100 °C/72h (F-Clay 2) and 1 500 °C/72 h (F-Clay 3).

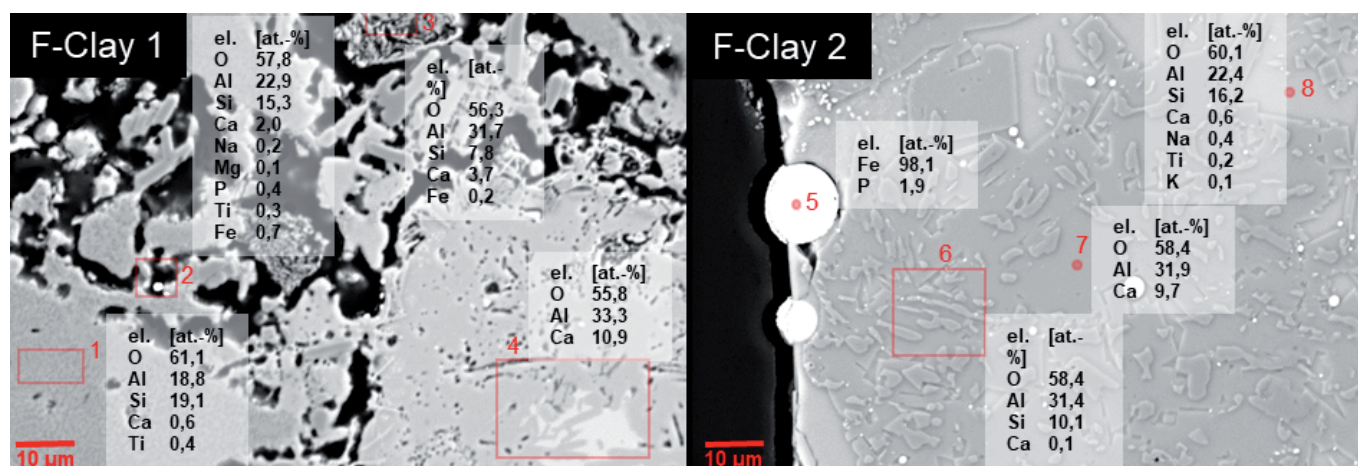


Fig. 5: SEM-micrograph and EDS measurements of the interface sample to gaseous F-Clay: sintered (F-Clay 1), 1 500 °C/72 h (F-Clay 2).

then follows the concentration gradient to the sample/gas interface. This movement is driven by a concentration gradient and can be described by Fick's first law of diffusion:

$$J = -D \frac{dC}{dx} \quad (7)$$

where J is the diffusion flux (amount of substance per unit area per unit time), D is the diffusion coefficient (which increases with temperature), C is the concentration of the diffusing species, and x is the position. The negative sign indicates that diffusion occurs in the direction of decreasing concentration.

In addition, the surfaces have a higher surface energy, which favours the attachment of reduced compounds. This is also the reason why an increased concentration of agglomerates can be observed at the grain/pore and grain/matrix interfaces in image 3 of Fig. 4 and in Fig. 6. In samples exposed at 1 500 °C, a glassy phase was observed near the hot face (Fig. 5, point 8), confirmed by Na and K enrichment in EDS. Alkalis likely lowered the melting point and facilitated liquid phase formation. Fig. 6 shows silicon-rich regions along the surface, attributed to SiO transport and re-condensation at the edge of this sample as a consequence of a temperature gradient. This also explains the increase in weight of this sample.

In the fireclay-based material, mullite remained the dominant crystalline phase across all test conditions, showing strong and consistent peak intensities, indicating its relative thermal and chemical stability even under reducing conditions (Table 2). Cristobalite was also present in the sintered state and at 1 100 °C, but its intensity slightly decreased with increasing temperature and exposure time, suggesting partial decomposition or volatilization. Anorthite was detected in the sintered and 1 100 °C samples, but was no longer visible at 1 500 °C, indicating either decomposition or transformation into an amorphous or liquid phase, consistent with the SEM observations of a glassy surface layer. Interestingly, a weak signal for tridymite appeared in the longest 1 500 °C exposure (Trial 4), suggesting a potential reformation pathway for silica under prolonged thermal load.

Thermodynamic calculations (Fig. 7) support these findings. It is clear that no change can be recognized in the various phases at 1 100 °C. However, according to the calculation, reactions of the material with the hydrogen containing atmosphere occur from a temperature of 1 300 °C. It can be seen that the masses of both SiO₂ and mullite decrease from this temperature. This is mainly due to the reduction of solid SiO₂ to gaseous SiO. At the same time, the formation of a glassy phase and a decrease in the amount of anorthite present in the sample can be observed.

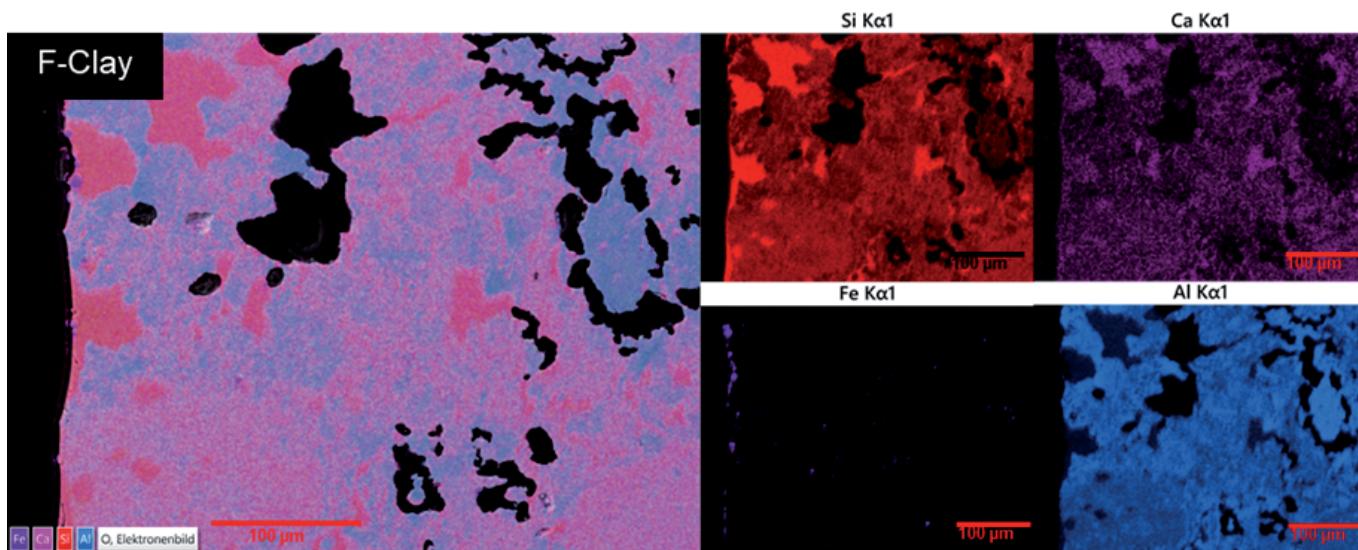


Fig. 6: EDS mapping and element distribution of the edge region of the sample of the F-Clay after 1 500 °C for 72 h.

Table 2: Mineral phase composition of the F-Clay castable (main phase [+++], secondary phase [++], third phase [+], traces [-]).

	Sintered	Trial 1	Trial 2	Trial 3	Trial 4
Parameter		1 100 °C/24 h	1 100 °C/72 h	1 500 °C/24 h	1 500 °C/72 h
Mullite	+++	+++	+++	+++	+++
Cristobalite	++	++	++	+	+
Anorthite	++	++	++		
Corundum	++	++	++	+	+
Tridymite			-	+	

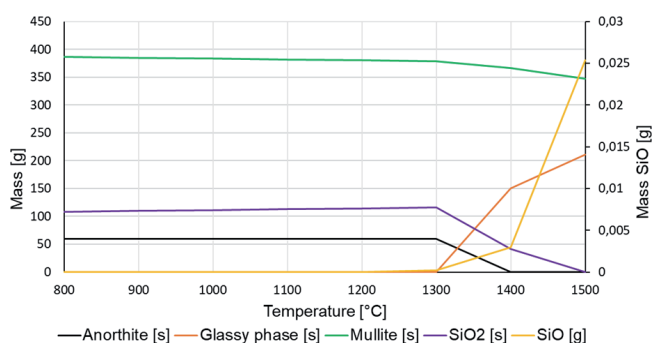


Fig. 7: Thermodynamic calculation for F-Clay between 800 °C and 1500 °C.

(2) Refractory castable Al-SiC

The second material under examination is a high-alumina castable with an addition of SiC. As with the F-Clay, the Al-SiC underwent a colour change due to the formation of oxygen vacancies (Fig. 8).

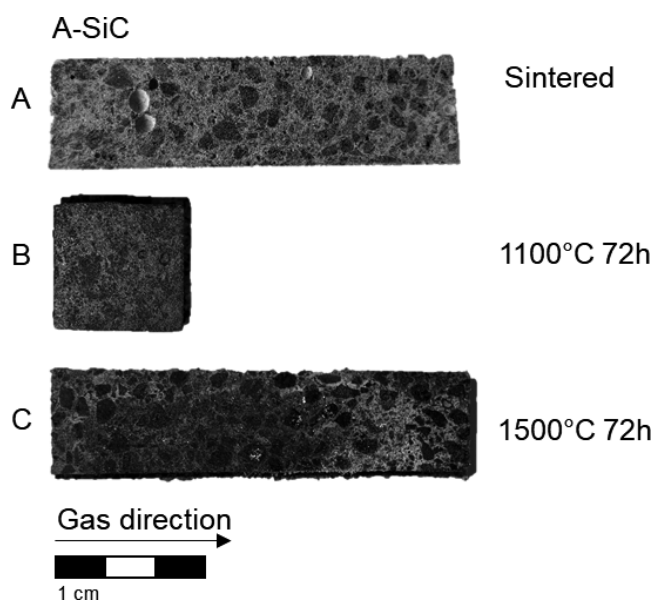


Fig. 8: Optical comparison of the samples of Al-SiC after sintering (A), 1100 °C/72 h (B), 1500 °C/72 h (C).

Mass loss analysis (Fig. 9) showed a significant effect of temperature: while negligible at 1100 °C, mass loss in-

creased sharply at 1500 °C up to 123 g/cm² at the gas inlet after 72 h.

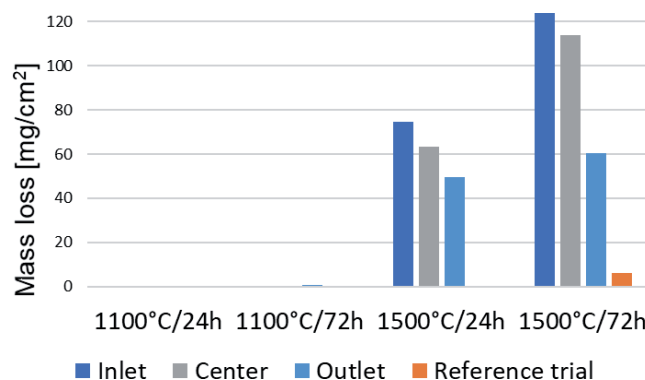
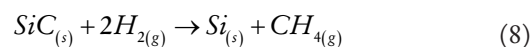


Fig. 9: Overview of the change in the mass of Al-SiC in the various tests.

It is evident that there is a correlation between mass loss and location within the furnace, with the samples located at the outlet exhibiting the lowest mass loss at 60 g/cm². This mass change can be attributed to two reactions in particular. As described for the first material, the SiO₂ in the sample is reduced to SiO and then evaporates. The SiC also reacts with the hydrogen in the atmosphere to form silicon and methane according to Equation 6. Notable contributions include those of Jacobsen *et al.*¹³, Misra⁶ and Herbell¹⁴.



This reaction, accounts for the measured decrease in SiC content (Table 4) from 12.25 wt% to 9.58 wt% after 1500 °C. SiO₂ also decreased from 7.94 wt% to 4.01 wt%. XRF data (Table 3) showed significant silicon depletion, while Al content increased due to relative enrichment.

A comparison of the EDS mappings in Fig. 13 shows that both a reduction of silica and a reaction of silicon carbide have taken place. Further analysis (Section 3.2) will demonstrate the reduction and removal of additional elements, including aluminium, iron, magnesium, potassium, sodium and phosphorus, as a consequence of the gas flow, resulting in a loss in mass.

Table 3: Chemical composition of the Al-SiC after the different tests using XRF.

wt%	Sintered	Trial 1	Trial 2	Trial 3	Trial 4
Parameter	-	1100 °C/24 h	1100 °C/72 h	1500 °C/24 h	1500 °C/72 h
Si	7.7	7.4	7.7	5.5	5.0
Al	41.6	41.8	41.6	43.4	44.9
Fe	0.1	0.1	0.1	0.4	0.1
Ti	1.3	1.3	1.2	1.9	1.3
Ca	1.4	1.3	1.4	1.5	1.2
Others	47.9	48.1	48.0	47.3	47.5
LOI (1050 °C)	-0.39	-0.48	-0.43	-0.82	-0.63

The porosity evolution observed in this series of tests clearly highlights the influence of hydrogen on the microstructure of the Al-SiC material (Fig. 10). At 1 100 °C, no significant changes were detected in mass, chemical composition, or open porosity, indicating that the material remains stable under these conditions. In contrast, at 1 500 °C, a substantial increase in open porosity exceeding 50 % in some cases was recorded. This porosity growth is attributed to the volatilization of reactive phases, as confirmed by the concurrent mass loss and compositional changes. The formation of gaseous species, primarily through the reduction of SiO₂ and the reaction of SiC with hydrogen, leads to the removal of solid components and the generation of additional pore volume. Reference samples treated in air exhibited densification due to post-sintering effects at 1 500 °C, which typically reduce porosity. However, this effect was counteracted in the hydrogen-exposed specimens, suggesting that the reducing atmosphere inhibits re-densification and promotes material degradation.

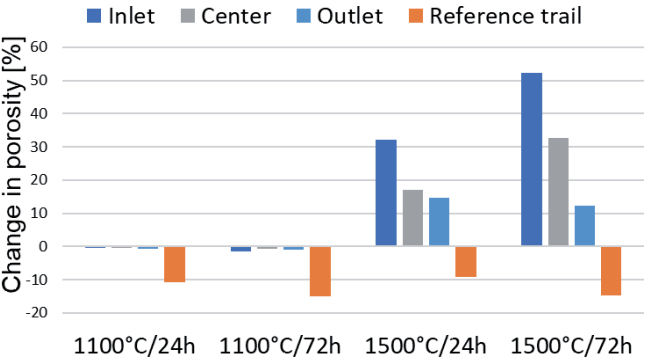


Fig. 10: Overview of the change in the open porosity of Al-SiC in the various tests.

The microstructural analysis supports this interpretation. SEM images (Fig. 11) show that while samples treated at 1 100 °C (micrograph 2) remain largely unchanged, those exposed to 1 500 °C in a reducing atmosphere (micrograph 3) exhibit pronounced surface attack and increased porosity. The enlarged pore structures and the lack of matrix densification further indicate that hydrogen plays a critical role in altering sintering behaviour. Moreover, a solid-state reaction between SiC and metal oxides is likely to have occurred under these conditions. This assumption is supported by earlier attempts to conduct reference tests in a nominally inert argon atmosphere, which unexpectedly led to sample reduction, implying that even trace impurities in the gas can facilitate redox reactions at high temperatures.

Table 4: Overview of the amount of carbon, SiC and SiO₂ in the various trials.

wt%	Sintered	Trial 2	Trial 4
Parameter	-	1 100 °C/72 h	1 500 °C/72 h
C	3.67	3.56	2.87
SiC	12.25	11.89	9.58
SiO ₂	7.94	8.27	4.01

Finally, as in the fireclay-based material, agglomerates were observed at the specimen edges. In this case, however, EDS analysis (Fig. 12, area 4) revealed that these consist primarily of silicon, iron, and titanium distinct from the iron-phosphorus agglomerates found in F-Clay. These

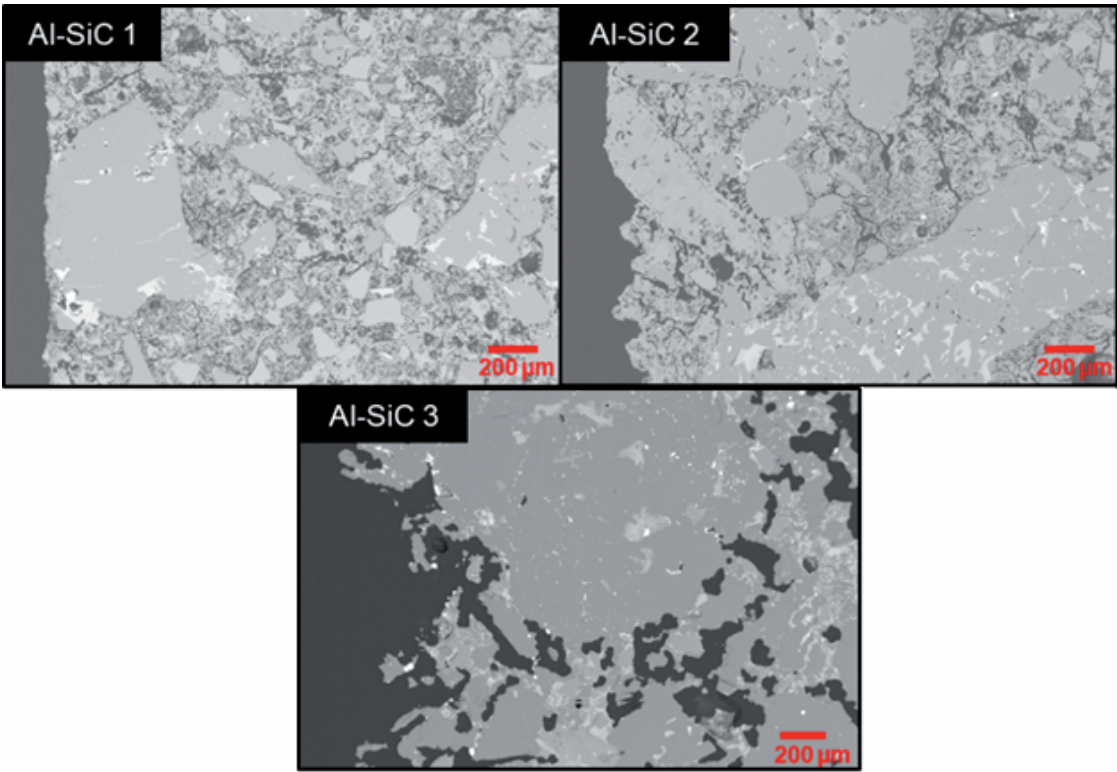


Fig. 11: Overview of the microstructure of Al-SiC after sintering (Al-SiC 1), 1 100 °C/72 h (Al-SiC 2) and 1 500 °C/72 h (Al-SiC 3).

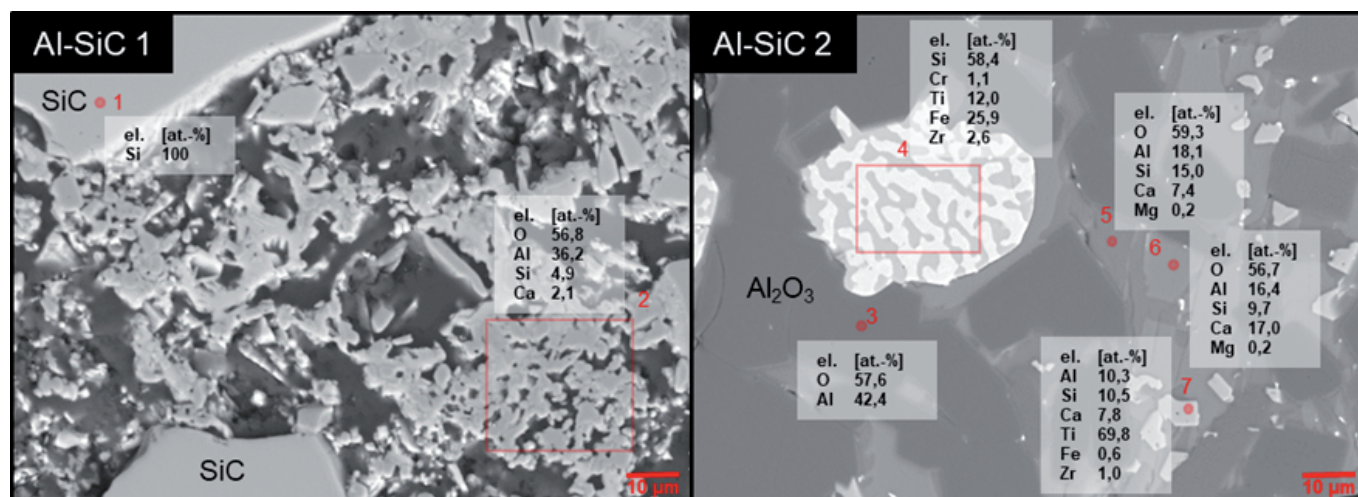


Fig. 12: SEM-micrograph and EDS measurements of the interface sample to gaseous Al-SiC: sintered (Al-SiC 1), 1 500 °C/72 h (Al-SiC 2).

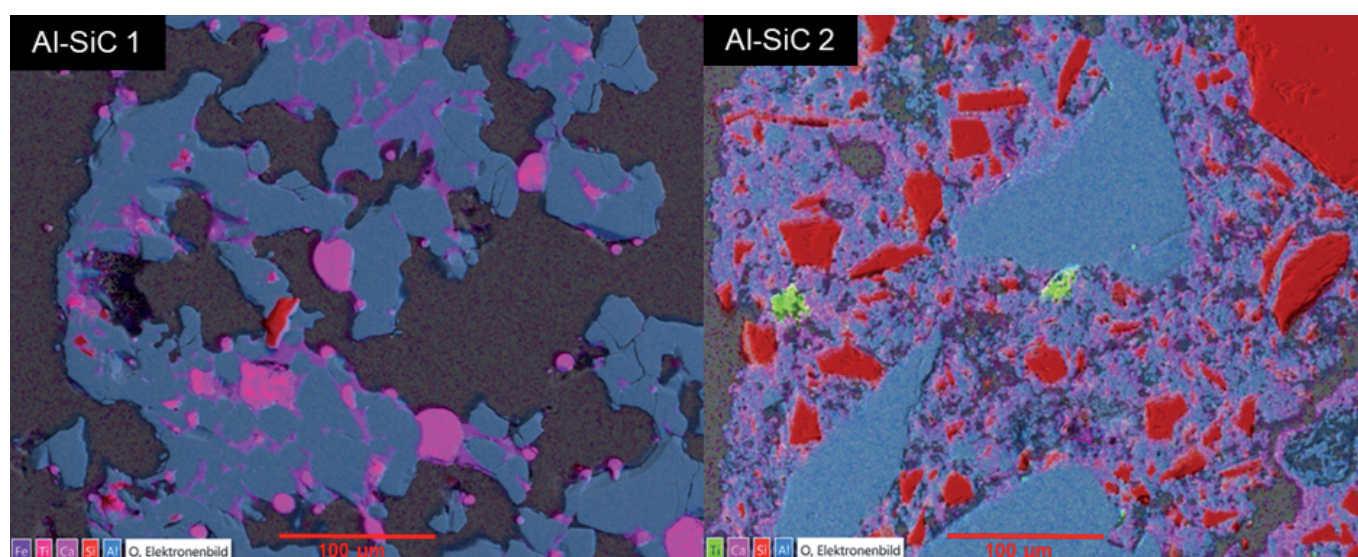


Fig. 13: Comparison of EDS mapping of the edge region of the sample after 1 500 °C for 72 h (Al-SiC 1) and a reference test (Al-SiC-2).

findings further emphasize the compositional and structural transformations induced by hydrogen exposure at elevated temperatures.

The EDS mappings shown in Fig. 13 illustrate pronounced changes in both microstructure and porosity resulting from hydrogen exposure. Image 1 of the figure represents a specimen exposed to 1 500 °C in a hydrogen-containing atmosphere. A significant increase in porosity is clearly visible, particularly near the surface, indicating extensive material degradation due to the reducing environment. Surface attack is further evidenced by the formation of agglomerates composed predominantly of iron, silicon, and titanium. These are distributed along the surface and in intergranular regions. Calcium is present between the grains in the form of anorthite, which appears unaffected in its distribution. The red-coloured regions in the elemental maps correspond to silicon carbide grains, identifiable by the absence of oxygen in these areas. A comparative analysis of the two mappings (hydrogen-exposed vs. reference) reveals a substantial loss of SiC grains after exposure. In the reference sample, the SiC grains re-

main uniformly embedded within the matrix. In contrast, in the aged sample, these grains have largely disappeared, confirming the reaction between SiC and hydrogen as described earlier. The elemental silicon released during this reaction appears to contribute to the formation of the surface agglomerates observed on the left-hand side of the hydrogen exposed sample. This spatial redistribution of silicon supports the proposed degradation mechanism involving SiC decomposition and reprecipitation under reducing conditions.

In the high-alumina castable with SiC, corundum remained highly stable across all conditions (Table 5), with strong peaks even after 72 h at 1 500 °C. Mullite was only weakly present in the sintered sample and disappeared entirely after thermal exposure, suggesting its transformation or decomposition under hydrogen. Moissanite (SiC) was detectable in all conditions, but only with weak peak intensity, which did not change significantly over the course of testing. This suggests a gradual rather than complete degradation, possibly limited to the surface. Anorthite showed moderate intensity at 1 100 °C but weakened

Table 5: Mineral phase composition of the Al-SiC castable (main phase [+++], secondary phase [++], third phase [+]).

	Sintered	Trial 1	Trial 2	Trial 3	Trial 4
Parameter		1 100 °C/24 h	1 100 °C/72 h	1 500 °C/24 h	1 500 °C/72 h
Corundum	+++	+++	+++	+++	+++
Mullite	+				
Moissanite	+	+	+	+	+
Anorthite	++	++	++	+	+
Hibonite				+	

at 1 500 °C, mirroring the behaviour observed in F-Clay. In Trial 4, a new phase (hibonite) was detected, possibly formed as a secondary reaction product from aluminium, calcium components under reducing and high-temperature conditions.

Thermodynamic calculations for the Al-SiC material (Fig. 14) provide insight into the temperature-dependent stability and reactivity of its components. The simulation results are consistent with the experimental observations. At 1 100 °C, no significant mass changes are predicted for the major phases; both corundum (Al₂O₃) and silicon carbide (SiC) remain thermodynamically stable under these conditions. Chemical reactions become thermodynamically favourable above approximately 1 300 °C. At this point, mullite begins to decompose in the presence of hydrogen, as described in Equation 3, leading to the formation of corundum and volatile SiO. The reduction of SiC by hydrogen becomes significant at around 1 400 °C, resulting in the formation of elemental silicon and methane, as shown in Equation 6. The progressive increase in reaction extent with temperature is reflected in the positive slope of the calculated phase mass curves. Unlike the behaviour observed in the fireclay castable, the amount of anorthite in Al-SiC remains constant throughout the temperature range studied. This suggests that SiC may play a stabilizing role in the matrix, possibly by consuming reactive silica or buffering the chemical environment, thereby preventing anorthite decomposition.

(3) Consequences of the reduction in exhaust gas streams

Two noteworthy phenomena were observed during the high-temperature testing of the Al-SiC material, both related to the transport and redeposition of volatile species.

In the initial test at 1 500 °C with a holding time of 72 h, a fracture of the alumina furnace tube occurred during cooling. The rupture took place at the position of a lightweight refractory plug (Fig. 15, image 1). The plug's bore was completely clogged with a dense deposit (images 2 and 3), and a continuous layer had formed between the plug and the tube wall. XRF analysis (Table 6) indicated a high silicon content in the deposit, absent in the original plug material. This suggests that volatile SiO, formed by reduction of SiO₂ or SiC, was transported by the gas flow and re-oxidized upon cooling, forming cristobalite or tridymite. The resulting SiO₂ layer caused thermal stress due to its differing expansion behaviour from the alumina tube, ultimately leading to mechanical failure. In later tests, the sam-

ple geometry was reduced to limit material loss through volatilization.

Table 6: Chemical composition of the raw material of the plug, clogged plug and membrane using XRF.

wt%	Lightweight refractory brick	Plug	Membrane
SiO ₂	0.8	5.1	84.5
Al ₂ O ₃	98.8	94.2	1.7
Fe ₂ O ₃	0.1	0.1	0.2
MgO	0.0	0.0	3.1
K ₂ O	0.1	0.2	1.6
Na ₂ O	0.1	0.3	2.7
P ₂ O ₅	0.0	0.0	2.1
ZnO	0.0	0.0	3.6
Others	0.1	0.1	0.5
LOI (1 050 °C)	-0.06	-0.3	-17.23

A second effect was observed near the outlet of the furnace tube: a thin, circular “membrane” formed where the tube meets ambient air (Fig. 16). As it was not present before the test, it is assumed to originate from volatilized material. XRF analysis (Table 6) confirmed the presence of silicon, aluminium, iron, magnesium, potassium, sodium, phosphorus and zinc. This indicates that even components with low vapour pressures were partially volatilized

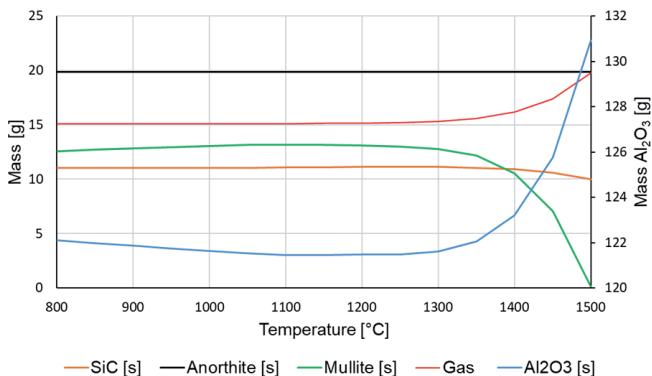


Fig. 14: Thermodynamic calculation for Al-SiC between 800 °C and 1 500 °C.

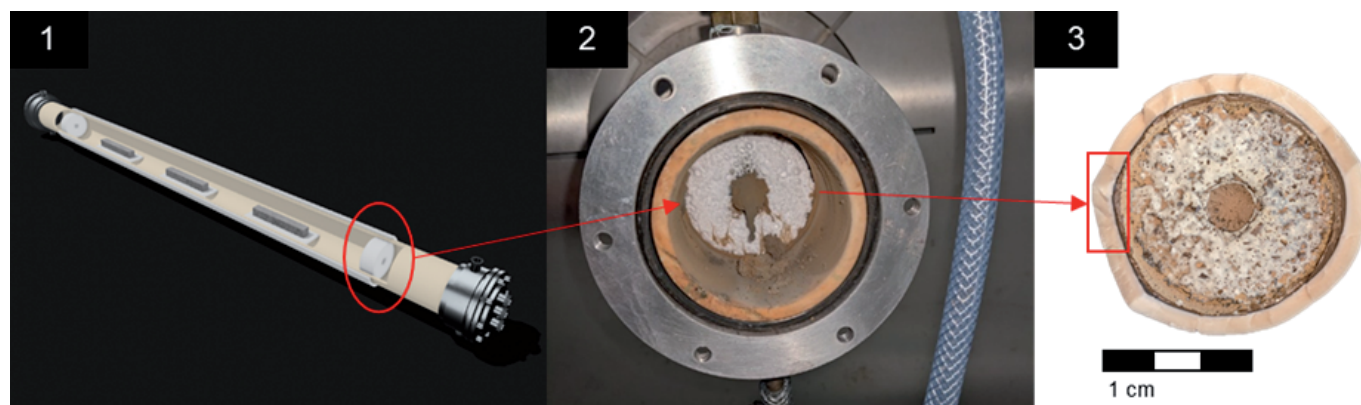


Fig. 15: Schematic representation of the samples and the plug in the pipe (1), clogged plug in the pipe (2), fracture edge of the broken tube (3).

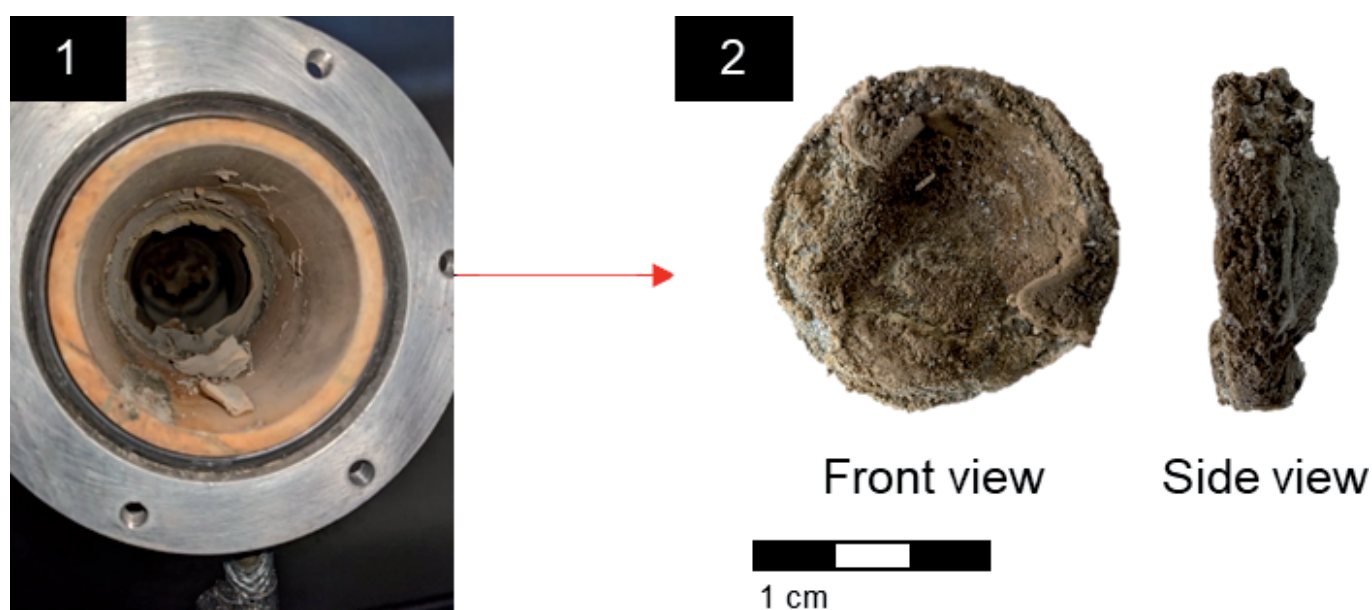


Fig. 16: Position of the membrane formed in the tube (1), front and side view of the membrane (2).

and redeposited. The detection of aluminium is particularly noteworthy, as Al_2O_3 is typically considered stable in hydrogen-rich environments. However, previous work by Dooley *et al.*¹⁵ has shown that volatilization of alumina is possible under specific conditions.

These observations highlight the potential for material transport and condensation in cooler furnace regions. In industrial applications, such effects could impair refractory longevity and contaminate downstream components, underscoring the need for careful system design for operation under hydrogen-based atmospheres.

IV. Conclusions

The experimental findings demonstrate that the behaviour of cement-bonded refractory castables in hydrogen-containing atmospheres is strongly dependent on both temperature and material composition. While no significant changes were observed at 1 100 °C, exposure at 1 500 °C induced measurable degradation effects, including mass loss, increased porosity, surface reactions, and the formation of volatile species.

The fireclay-based material (F-Clay) showed only minor structural changes, even at 1 500 °C. Although mass loss and localized microstructural effects were observed, the overall integrity of the material remained largely intact. The formation of spherical agglomerates containing iron and phosphorus suggests selective reduction and migration of trace elements, consistent with known reduction behaviour of Fe_2O_3 and P_2O_5 in hydrogen atmospheres. These effects were localized and did not compromise the matrix significantly.

In contrast, the high-alumina castable with SiC (Al-SiC) exhibited pronounced degradation at 1 500 °C. The reduction of SiC and SiO_2 led to increased open porosity, depletion of silicon content, and the formation of silicon-rich agglomerates. These changes were supported by XRF, SEM/EDS, and thermodynamic calculations. The observed loss of SiC, in particular, confirmed the expected gas-solid reaction between SiC and hydrogen, forming elemental silicon and methane.

Thermodynamic modelling further substantiated these results, predicting the onset of relevant reactions above 1 300–1 400 °C. While corundum and SiC remained stable

at 1 100 °C, elevated temperatures promoted the reduction of mullite and SiO₂, and in the case of Al-SiC, the decomposition of SiC. Notably, anorthite in Al-SiC remained stable, possibly due to the buffering effect of SiC or the absence of reactive silica in sufficient quantities.

The observed transport of volatile species, including silicon and aluminium, further emphasizes the complexity of material behaviour in hydrogen-rich atmospheres. The formation of condensates in cooler regions of the furnace, including dense SiO₂ layers and multi-element membranes, poses practical concerns. These effects could damage furnace components and downstream systems in industrial settings.

Taken together, the results indicate that refractory degradation in hydrogen environments is not solely a function of bulk chemistry, but also of the interplay between reduction thermodynamics, vapour phase transport, and microstructural accessibility. While the F-Clay composition exhibited relative resistance under the given conditions, the Al-SiC castable despite its high alumina content suffered more extensive damage due to the reactivity of its SiC component.

Future work should therefore include mechanical strength testing (e.g. CCS, CMOR) to evaluate the structural consequences of the chemical changes observed. Additionally, further studies on gas-phase transport mechanisms and atmosphere composition particularly under real exhaust gas conditions would provide valuable insight for industrial applications.

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