Volatilization of Refractory Silica in Hydrogen Water Vapour Gas Streams

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The volatilization of silica (SiO_2) from refractory concrete in steam-hydrogen environments has been studied extensively and reaction thermodynamics are also well published. This research has shown that silica volatilization occurs over a wide range of temperatures and that at temperatures less than 980 °C the dominant species is $Si(OH)_4$ and at temperatures above approximately 1000 °C the dominant species formed is SiO. By using a reaction kinetics approach it is shown that the rate of silica volatilization can be reasonably well calculated from refractory used in industrial processes. Analysis of refractory samples from an ammonia transfer line shows that shows that the loss of silica occurs from the aggregate and not the matrix.

1 Introduction

Understanding the degradation of the refractory containing silica in hydrogen/steam gases at temperature is important when designing and selecting refractory linings for gasifiers or boilers particularly in low temperature processes such as ammonia plant transfer lines which operate in the temperature range of 700 °C to 950 °C.

The reduction of silica into SiO (g) not only accelerates refractory corrosion and strength loss but can also lead to downstream deposits of SiO_2 (s) on boiler tubes which results in fouling and decreases in plant throughput. However, the majority of literature published is on silica volatilization at high temperatures, greater than 1200 °C. For example, *Wright* and *Wolff* [1] have reported refractory degradation by silica volatilization occurs by CO and H_2 at temperatures >1349 °C and *Plibrico* states that the volatilization reaction in hydrogen occurs at temperatures >1140 °C. However, *Day* and *Gac* [2] have reported silica volatilization for refractory at 199 °C. Given that there are a number of processes that operate at temperatures <1000 °C understanding how refractories behave in low temperature hydrogen/steam environments is important for asset owners. Research [3] has

found that silica volatilization at temperatures less than 980 °C is dominated by the formation of $Si(OH)_4$.

The opportunity to study silica volatilization from industry occurred when a refractory lined transfer line in an ammonia plant had inadvertently been lined with a standard alumina silica refractory castable hotface. The transfer line had been in operation for several years. In ammonia plants the process gas is a composition of H_2, N_2, CO, CO_2, CH_4 and H_2O. Transfer lines operate at temperatures varying from 750 °C to 950 °C and at pressures of approximately 2026,5 Pa.

This paper investigates silica volatilization under various reducing conditions, temperature and pressures and shows that it is possible to estimate the rates for silica volatilization from refractories. Validation of the methodology was possible by using data from two industrial samples. Good agreement was achieved between measured and predicted results. Using this method it is possible to predict the volatilization of silica species (SiO or $Si(OH)_4$) from refractory under reducing conditions at various temperatures and pressures. It was further found that the silica lost from a refractory castable was from the aggregate and not the matrix which is in line with other research.
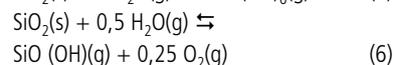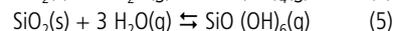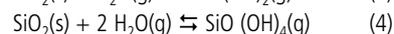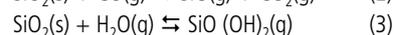
2 Literature review

The corrosion of silica based refractory by hydrogen and steam has been extensively studied over the past sixty years [4–9]. The attack of refractory brick by hydrogen gas was reported by Wright and Wolff [1] who in 1948 studied the effect of reducing gases on silica brick, alumino-silica brick and alumina brick. *Gardner* and *Buchanan* [10] report that refractory silicates such as zircon, mullite and forsterite are known to lose SiO_2 at high temperatures. It is reported by [1] that silica can be lost from the surface of a silica based refractory by vapourization, silica reduction, carbon and carbon monoxide reduction and hydrogen reduction.

The volatilization of silica, SiO_2, in hydrogen is described by the following reaction:

$$SiO_2(s) + H_2(g) \leftrightarrows SiO(g) + H_2O(g) \qquad (1)$$

In addition to the above reaction, SiO_2 can also react with water vapour and CO according to the following reactions,

$$SiO_2(s) + CO(g) \leftrightarrows SiO(g) + CO_2(g) \qquad (2)$$
$$SiO_2(s) + H_2O(g) \leftrightarrows SiO(OH)_2(g) \qquad (3)$$
$$SiO_2(s) + 2\,H_2O(g) \leftrightarrows SiO(OH)_4(g) \qquad (4)$$
$$SiO_2(s) + 3\,H_2O(g) \leftrightarrows SiO(OH)_6(g) \qquad (5)$$
$$SiO_2(s) + 0,5\,H_2O(g) \leftrightarrows$$
$$SiO(OH)(g) + 0,25\,O_2(g) \qquad (6)$$

The majority of the published literature on silica volatilization in hydrogen or steam environment has been at high temperatures

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(>1000 °C) and little published at temperatures <1000 °C. In contrast, Day and Gac [2] tested three types of refractory (1. dense high alumina: 94 % Al_2O_3, 2. dense medium alumina: 45 % Al_2O_3 and 3. lightweight insulation: 34 % Al_2O_3) at 199 °C. Their results (after 18 d) show the medium alumina and insulating castables lost weight in both steam/N_2 and steam/CO while the high alumina sample gained weight. Their results also showed a volume increase for each sample varying from (1) 2,81 %, (2) 0,17 % and (3) 1,14 % in steam/CO. The increase in weight was attributed to the formation of $CaCO_3$, $Ca(HCO_2)_2$ and boehmite and the loss of weight was due to the dissolution of SiO_2 and CaO.

Misra [11] discusses the stability of silica and mullite ceramics in hydrogen and hydrogen/steam environments. In this case a silica ceramic in H_2 was shown to have a constant SiO ($P_{[SiO]}$) partial pressure as the total pressure increased but the partial pressure of silane (SiH_4), which is favoured at low temperatures, is low but slowly increases. At a temperature of 900 °C the data shows that the partial pressure of $P_{[SiO]} < P_{[SiH4]}$. In H_2-steam environments it is reported that the partial pressure $P_{[SiO]}$ was relatively constant as the total pressure increased and was greater than $P_{[SiH4]}$ partial pressure. Similarly, *Jacobsen et al.* [3] has shown that silica hydroxides or oxy-hydroxides (3 to 6) will form with increasing stream pressure.

Crowley [4] published the results for nine different refractory bricks, from 95 % silica brick to 90 % alumina brick (SiO_2 = 8 %), exposed to hydrogen vapour over a temperature range of 740 °C to 300 °C. It was found that the volatilization rate increased linearly with percentage of SiO_2 in the refractory. It was also found that the volatilization flux rate when plotted against temperature was not constant in pure hydrogen over the temperature range. It was concluded that the reaction thermodymanics of SiO_2 volatilization (1) at temperatures less than 970 °C did not agree with the experimental results.

Crowley [5] also found that the silica volatilization rate increased linearly for silica bearing refractory in wet hydrogen gas and the mass loss of SiO_2 increased with velocity and pressure in both hydrogen and steam environments [12].

Robinson and *Smialek* [13] and *Opila et al.* [14–16] have studied the volatilization of silica (SiO_2) from the surface of oxidized SiC ceramic. They found that the volatilization of silica varied with pressure and velocity and that silica hydrates formed in the presence of steam at low temperatures.

Crowley [5] further reported that the silica content in a refractory sample taken from a secondary reformer had twice the amount of SiO_2 12 mm below the surface compared to the surface.

Johnson and *Crowley* [17] reported that in the 1960's gasifiers lined with 60 % Al_2O_3/35 % SiO_2 brick performed acceptably. Though at about the same time it was reported that SiO_2 refractory in hydrogen reformer refractory lost weight and strength above 925 °C. Consequently, refractory used in hydrogen environments moved to high alumina (>95 %) and low silica (<5 %) contents. In 2005 two grades of low cement castable refractory with, 20 and 30 % SiO_2 respectively, were tested in a gasifier. The samples were placed into the gasifier manway with a gaseous environment (mol/mol) of 45 % H_2, 35 % CO, 13 % H_2O, 6 % CO_2, 0,5 % CH_4 and 0,3 % N_2. The process gas temperature was 1315 °C. After six months of operation the samples were removed and analysed and it was found that the SiO_2 content in the 0–6 mm layer at the hotface was approximately 5,15 % lower than the SiO_2 in the 6–12 mm layer from the hotface. The mass flux rate calculated from the published data for the 30 % SiO_2 and 20 % SiO_2 castables were 0,0207 and 0,0184 mg/cm²/h, respectively. It was concluded that low cement castable refractory can successfully replace high alumina brick in gasifiers.

Robbins and *Mauer* [18] studied the reactions and transformations in two castable refractories, a high purity $CaO-Al_2O_3$ with tabula alumina aggregate and a $CaO-Al_2O_3$-SiO_2 with calcined kaolinite aggregate. The cured castable generally consists of calcium aluminates (CA's) and CA hydrates. The specimens were exposed to steam, steam/CO_2 and a simulated gasifier environment ($CO:CO_2:H_2:H_2O$) with pressures up to 7 MPa and temperatures up to 1000 °C. In both the laboratory and pilot plant studies it was found that the dominant reaction was cristobalite with free α-A, A_3S_2 and the calcium aluminate binder (CA, CA_2) to form the bonding phase CAS_2 (anorthite). The pilot plant studies also found that specimens show a loss of SiO_2 from the calcined kaolin aggregate (reaction rims) and some of the silica reacts to form CAS_2. At ~900 °C it was found that some silica react with free α-A to form A_3S_2, and some is lost from the refractory.

Herbell et al. [19] tested mullite at 1050 °C and 1250 °C for 500 h in dry hydrogen. It was found that the grain-boundary glass phase is firstly removed from the surface followed by the mullite silica. A reduction in room temperature strength for both test temperatures was found and attributed to severe corrosion and actual removal of the glassy grain boundaries.
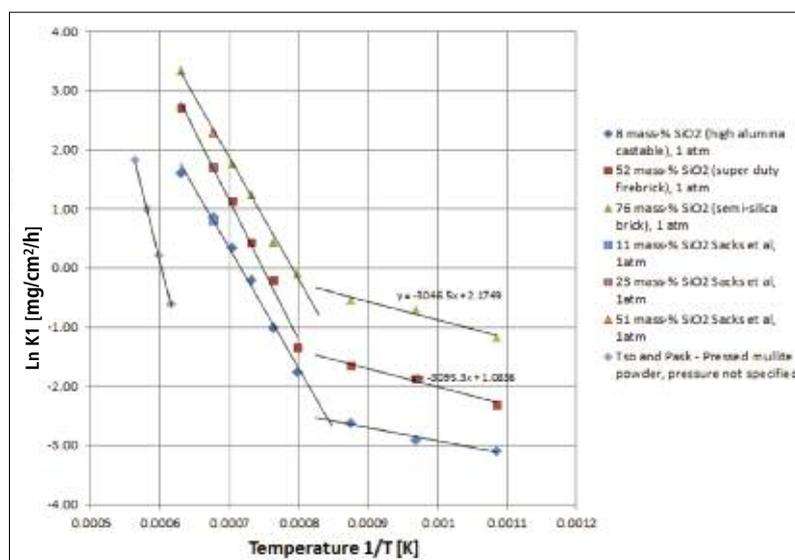

Fig. 1 Volatilization of refractory silica in hydrogen

3 Reaction thermodynamics

Reaction kinetics' is a useful method used to study chemical reaction mechanisms. The reaction rate constant is defined as $k1 = Ae^{-Ea/RT}$ and the activation energy can be determined by plotting of $\ln k_1$ vs $1/T$, *Arrhenius* plot. Thus a variation in E_a will indicate a different reaction occurs.

Fig. 1 is the Arrhenius plot for the data published by Crowley [5] for three different refractory bricks with increasing silica exposed to H_2 at 101,3 Pa (1 atm). The data, presented in Tab. 1, show two different activation energies for the low and high temperature regions, with a transition temperature of approximately 980 °C. This transition point is slightly higher than that published by *Fox et al.* [18] who found that $Si(OH)_4$ (g) formation was expected from the reaction of SiO_2 in H_2 below 827 °C and above 827 °C the formation of $SiO_{(g)}$ was favoured.

The mean low temperature region E_a was 23 kJ/mol and the mean high temperature region E_a was 178 kJ/mol. The data also shows the activation energy for the high silica (95 %) refractory was 377 kJ/mol.

Tso and *Pask* [21] concluded that the presence of CaO lowers the activation energy. However, given there are a number of possible reactions [15] it is possible that the variation in activation energy is due to these reactions.

The activation energy for other silica bearing materials in hydrogen is given in Tab. 2. Comparison of the 95 % silica refractory [4] with the silica ceramics listed in Tab. 2 shows there is good agreement between the published values. Thus it is concluded that very high silica refractory in hydrogen behaves like pure silica or alumina-silica ceramics at temperature greater than approximately 1000 °C.

The volatilization flux at one atmosphere and 1200 °C for different refractory materials in hydrogen was calculated and the results presented in Tab. 3. The data shows good agreement for the different refractories at 1200 °C in hydrogen at one atmosphere with an increased volatilization flux as the silica content increases.

In practice pure hydrogen environments rarely occur in industrial processes but understanding hydrogen/steam environments may be a good proxy for industrial process gases. To evaluate this, the published data for a steam/H_2 environment is used to determine the activation energy and volatilization

rate for three refractory materials. The mass flux rate was calculated and plotted against the reciprocal of temperature [1/K] and the results are plotted in Fig. 2. Results include data from Crowley from 740 °C to 1200 °C and 607,8 Pa [12], *Robinson* and *Smialek* from 1230 °C to 1450 °C and 638,2 Pa pressure [13] and *Cheng* and *Cutler* from 790 °C to 1300 °C and 638,2 Pa pressure [22] as indicated.

Given that there was a distinct reaction transition temperature for silica in hydrogen the volatilization rate over a wide temperature range (740 to 1200 °C) was evaluated for H_2/steam. If there is a dominant reaction at

approximately 1000 °C (as shown in Fig. 1) then this should be detected.

The data published by *Cheng* and *Cutler* [22] shows that the volatilization rate of silica in steam does not deviate at low temperatures indicating a constant reaction type. This seems to be supported by *Jacobsen et al.* [3] who concluded that at low temperatures (<1200 °C) $Si(OH)_4$ was the dominant species and at high temperatures (>1400 °C) a mixture of $Si(OH)_{4(g)}$ and $Si(OH)_{2(g)}$ was formed for silica vaporization in steam.

The activation energy (E_a) calculated from the regression lines for the three refractory
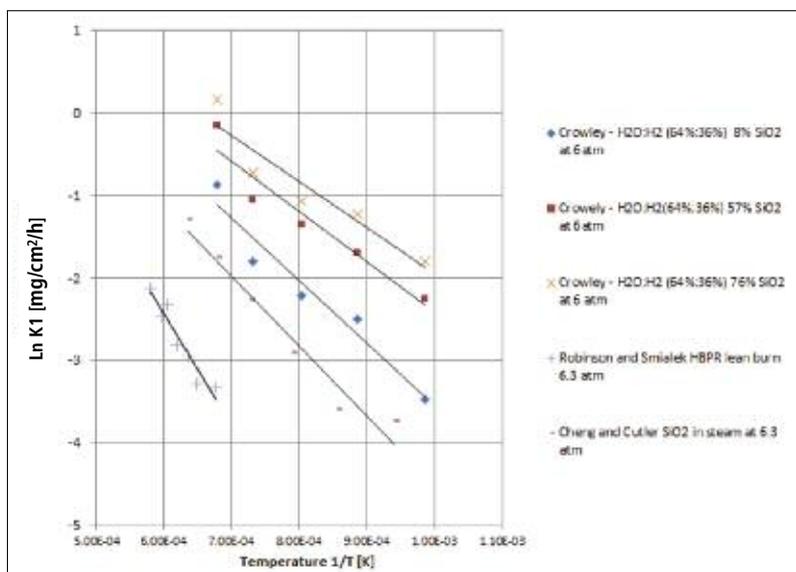
Tab. 1 Activation energy for refractory in H_2 at 101,3 Pa [5]

Activation Energy [kJ/mol]	8 % SiO₂ Refractory	57 % SiO₂ Refractory	76 % SiO₂ Refractory	95 % SiO₂ Refractory
Lower temperature (650 °C to 980 °C)	18	26	25	–
High temperature (980 °C to 1315°C) calculated separately	168	195	171	377 (temp. range 1260–1370 °C)

Tab. 2 Activation energy and mass flux rate for refractory in H_2

Author	Material	Activation Energy [kJ/mol]
Gardner [6] Total pressure not specified, temp. range 1400–1630 °C	silica in dry H_2	356
Gardner and Buchanan [10] Total pressure not specified, temp. range 1360–1630 °C	zircon ($ZrSiO_4$) in dry hydrogen	343
Misra [11]	SiO_2 in H_2 at 100 kPa	343
Tso and Pask [21] In H_2 total pressure not specified, temp. range 1300–1500 °C	silica	347
	alumina-silicate	358
	cold pressed mullite powder (73 % Al_2O_3 mass/mass); a glassy phase was reported at the grain boundary	389
	calcium alumino-silicate	284

Tab. 3 Silica volatilization mass flux rate for refractory in H_2

Author	Material	Mass Flux Rate (SiO_2) [mg/cm²/h]
Sacks et al. [9] Total pressure 1 atm (101,3 Pa), 1200 °C	11 % commercial alumina silica refractory	2,22
Sacks et al. [9] Total pressure 1 atm (101,3 Pa), 1200 °C	23 % commercial alumina silica refractory	5,47
Sacks et al. [9] Total pressure 1 atm (101,3 Pa), 1200 °C	51 % commercial alumina silica refractory	6,67
Crowley [5] pressure 1 atm (101,3 Pa), 1200 °C	8 % silica refractory brick	2,38
Crowley [5] pressure 1 atm (101,3 Pa), 1200 °C	57 % silica refractory brick	5,49
Crowley [5] pressure 1 atm (101,3 Pa), 1200 °C	76 % silica refractory brick	10,06

Fig. 2 Arrhenius plot for various refractory in steam/hydrogen

Tab. 4 Activation energy for refractory in steam/H$_2$ (64 % : 36 %) at 607,8 Pa [12]

Activation Energy [kJ/mol]	8 % SiO$_2$ Refractory Brick	57 % SiO$_2$ Refractory Brick	76 % SiO$_2$ Refractory Brick
Temperature range 740–1200 °C	62,8	50,9	46,4

Tab. 5 Silica volatilization mass flux rate for silica and refractory in H$_2$ + steam

Author	Material	Mass Flux Rate (SiO$_2$) [mg/cm²/h]
Crowley [12] Total pressure 6 atm (607,8 Pa), 1200 °C (H$_2$/steam)	8 % silica refractory brick	0,42
Crowley [12] Total pressure 6 atm (607,8 Pa), 1200 °C (H$_2$/steam)	57 % silica refractory brick	0,86
Crowley [12] Total pressure 6 atm (607,8 Pa), 1200 °C (H$_2$/steam)	76 % silica refractory brick	1,17
Cheng and Cutler [22] Total pressure 6 atm (607,8 Pa), 1200 °C (steam)	pressed cristobalite powder	0,163
Robinson and Smialek [13] Total pressure 6,3 atm (638,2 Pa), 1200 °C steam (12,3 % steam, 2,1% O$_2$)	silica from SiC ceramic	0,022

bricks and the results are given in Tab. 4. These compare to 87 kJ/mol [22] and 111 kJ/mol at 607,8 Pa and 12 kJ/mol at 1013 Pa [13] and *Opila* and *Hann* [14] who calculated the activation energy under lean burn (O$_2$/steam) conditions at 3±75 kJ/mol. It is concluded that there is reasonable agreement between the refractory brick activation energy and that published by the previous authors.

The mean activation energy for the three refractory materials was 53 kJ/mol and the standard deviation was 8,5.

When the volatilization flux for the different materials is compared (Tab. 3 and Tab. 5) it can be seen that steam suppresses the volatilization rate and increases the activation energy when compared to refractory in hydrogen. Given the similarity in the activation energy for the steam and steam/hydrogen and literature supporting the formation of Si(OH)$_4$ [14] in H$_2$O/O$_2$ (50 % : 50 %) it seems reasonable to conclude that silica hydrates are the predominant species formed in steam/H$_2$ environments and SiO$_{(g)}$ is a minor component.

The literature [18] also shows that silica vapour will react with CA cements in refractory castables to form CAS$_2$, which could reduce the available gaseous silica in the process gas.

4 Analysis of refractory in hydrogen, steam and CO

The opportunity to validate the theoretical results was carried out by analyzing a refractory lined transfer line in an ammonia plant. The duct was lined with two layers of refractory, an insulation layer approximately 100 mm thick and a hot face layer approxi-

Fig. 3 Transfer line showing hot face and insulation layers

Fig. 4 Transfer line showing condition of hot face refractory surface
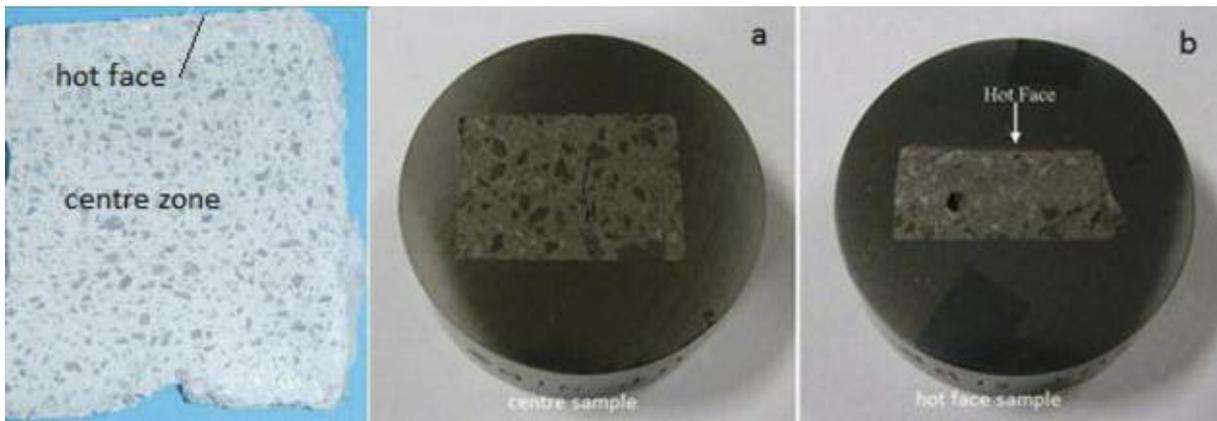
Fig. 5 Hot face refractory specimen and epoxy mounted samples

mately 75 mm thick but the exact initial composition of the refractory material used is not known. Though it was believed to be a conventional alumina-silica castable.

The line had been in service for greater than 10 years and exposed to H_2, H_2O and CO gases at high pressure. The condition of the refractory lining is shown in Fig. 3 and Fig. 4. Visually the hot face appeared in good condition with no sign of erosion or corrosion though there were some typical cracks and spalling of the hot face.

To evaluate the effect of hydrogen and steam on silica refractory a sample of the hot face was sent for SEM analysis and Energy Dispersive Spectroscopy (EDS) analysis. The original sample and the mounted samples for SEM analysis are shown in Fig. 5. A specimen near the centre of the sample was cut, mounted, and polished (Fig. 5a). Another specimen near the hot face was also cut, mounted, and polished (Fig. 5b).

Fig. 6 shows the SEM image of the centre specimen and EDS analysis areas marked as centre 2 and 3 and the EDS spectrum. The areas labelled centre 2 is a piece of aggregate and centre 3 is the matrix. The EDS results show the aggregate is an alumina-silicate with a small amount of calcium and the matrix is a mixture of alumina, silica and calcium. The SEM images of the aggregates indicate the aggregate particles have a relatively uniform appearance but some fissures could be seen. Elemental mapping of the SEM view area ($\times$ 100) show the aggregate is dotted with sodium and sulphur.
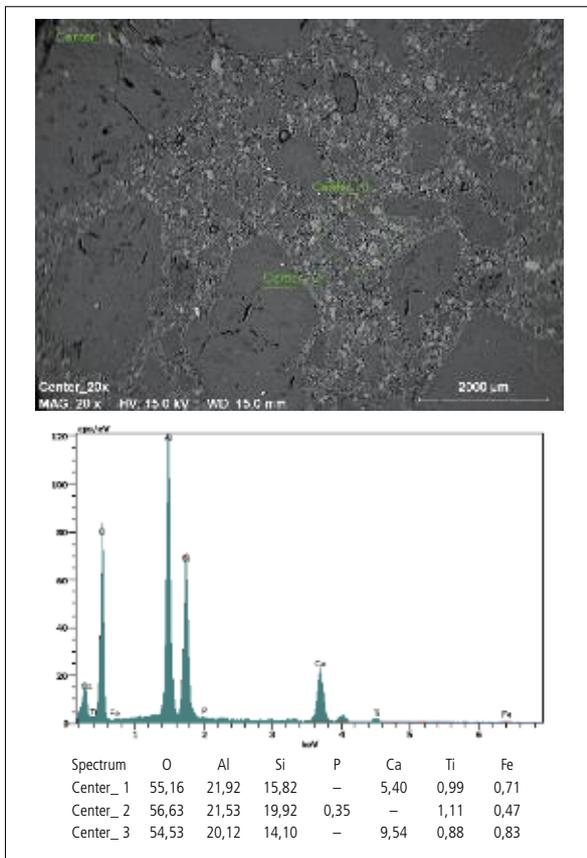

Spectrum	O	Al	Si	P	Ca	Ti	Fe
Center_ 1	55,16	21,92	15,82	–	5,40	0,99	0,71
Center_ 2	56,63	21,53	19,92	0,35	–	1,11	0,47
Center_ 3	54,53	20,12	14,10	–	9,54	0,88	0,83

Fig. 6 SEM image of centre specimen showing EDS points and spectrum

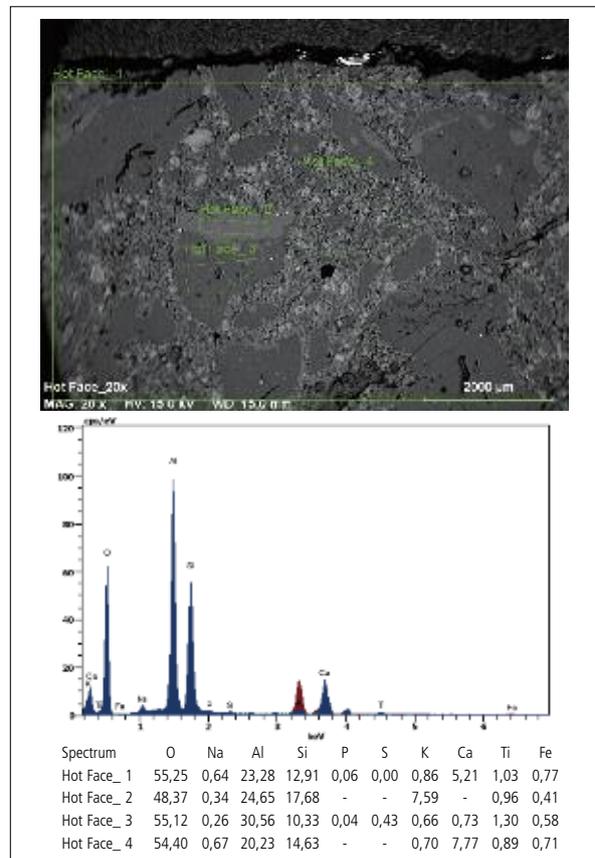| Spectrum	O	Na	Al	Si	P	S	K	Ca	Ti	Fe
Hot Face_ 1	55,25	0,64	23,28	12,91	0,06	0,00	0,86	5,21	1,03	0,77
Hot Face_ 2	48,37	0,34	24,65	17,68	-	-	7,59	-	0,96	0,41
Hot Face_ 3	55,12	0,26	30,56	10,33	0,04	0,43	0,66	0,73	1,30	0,58
Hot Face_ 4	54,40	0,67	20,23	14,63	-	-	0,70	7,77	0,89	0,71

Fig. 7 SEM image of hot face specimen showing EDS points

Tab. 6 Chemical analysis results for specimen [mass-%]

Spectrum x 100	Al_2O_3	SiO_2	P_2O_5	CaO	Ti_2O	Fe_2O_3	K_2O	Na_2O	SO_3
Hot face 1 overall	43,99	27,62	0,14	7,29	1,72	1,10	1,04	0,86	–
Center 1 overall	41,42	33,84	–	7,56	1,65	1,02	–	–	nm
Hot face 2 Aggregate edge	46,58	37,82	–	1,34	1,60	0,59	9,14	0,46	–
Hot face 3 Aggregate	57,74	22,10	0,09	1,02	2,17	0,83	0,80	0,35	1,07
Centre 2 aggregate	40,68	42,61	0,80	–	1,85	0,67	–	–	nm
Hot face 4 matrix	38,22	31,30	–	10,87	1,48	1,02	0,84	0,90	–
Centre 3 matrix	38,02	30,16	–	13,35	1,47	1,19	–	–	nm
Centre ×500 small aggregate	59,78	24,32	–	1,96	1,32	0,64	0,36	0,39	2,70

nm = not measured

Tab. 7 Combustion fuels used by Opila et al. [13]

Test	Combustion Fuel	Pressure	Velocity	Gas Composition [mol-%]
1	Synthetic lean fuel	1 atm (101,3 Pa)	$4,4 \times 10^{-3}$ m/s	50 % O_2, 50 % H_2O
2	Synthetic rich fuel	1 atm (101,3 Pa)	$4,4 \times 10^{-3}$ m/s	7,2 % CO_2, 10,0 % H_2O, 9,9 % CO, 4,5 % H_2, 68,4 % N_2
3	HPBR lean fuel	6,3 atm (638,2 Pa)	20 m/s	12,3 % H_2O, 74,6 % N_2, 11 % CO_2, 2,1 % O_2
4	HPBR rich fuel	6,3 atm (638,2 Pa)	20 m/s	3,6 % CO_2, 9,8 % H_2O, 16,2 % CO, 10,3 % H_2, 60,1 % N_2

HPBR = high pressure burner rig

Fig. 7 shows the SEM, EDS spectrum and elemental analysis of the hot face. The SEM images of the hot face aggregate were noticeably different to the centre specimen with zones of high potassium detected in some aggregates. The chemical oxide results for "area 2" (part of aggregate) had a potassium oxide content of 9,14 % while "area 3" (aggregate) and "area 4" (matrix) has a potassium oxide content of 0,80 and 0,84 %, respectively.

Elemental mapping of the SEM view area shows the aggregate is dotted with sulphur and large areas of sodium were detected near the hot face surface in the matrix. The titanium is predominantly restricted to the matrix.

The chemical analysis results (oxide basis) for each SEM "area" are given in Tab. 6. The bulk average chemical results show the hot face has a lower silica content compared to the centre. The silica (SiO_2) content of the hot face is 6,22 % lower. The SiO_2 volatilization flux was calculated using the internal planar

surface area and approximate operating time. The flux was 0,0041 mg/cm²/h.

The chemical results show the matrix is composed of calcium-alumina-silica mixture with small amounts of interdispersed titanium, iron and sulphur. The chemical results for the hot face and centre matrix are very similar with the silica (SiO_2) varying from 30,16 % to 31,30 %. The EDS analysis shows the chemical content for the aggregate particles vary significantly. The alumina content for the "centre" aggregate was approximately 42,6 % (Al_2O_3) and the hot face aggregate silica varied from 22 % to 38 % (SiO_2).

It is concluded that the loss of silica due to the process gas is confined to the upper zone of the hot face layer and then only to the aggregates within that zone. This is in line with results reported by Robbins and Mauer [18].

The EDS results indicate that calcium does not lower the activation energy as suggested by Tso and Pask. If calcium was acting as a catalyst then a significantly lower silica content of the matrix would be expected.

5 Predicting volatilization rates under industry conditions

While the literature for laboratory samples shows good agreement for the volatilization rate of silica from refractory materials in hydrogen or steam/hydrogen many industrial processes like hydrogen reformers or gasifiers have process gases which consist of hydrogen, steam and carbon monoxide. To get an understanding how a refractory material behaves in an industrial process it was decided to use the laboratory data and correlate that to actual site samples.

The study of silica volatilization from SiC under combustion conditions by *Robinson* and *Smialek* [13] and *Opila et al.* [15] as defined in Tab. 7 offers the opportunity to predict volatilization rates under various process conditions.

The volatilization rate for SiO_2 from SiC under HBPR (fuel rich) combustion conditions are plotted in Fig. 8. The volatilization results from Crowley [12] over the temperature range of 740–1100 °C, is plotted for reference.

Opila et al. [15] have shown that the flux of volatile silicon species, J, in laminar flow under combustion conditions is proportional to the gas velocity, total pressure and the partial pressure of volatile species as follows
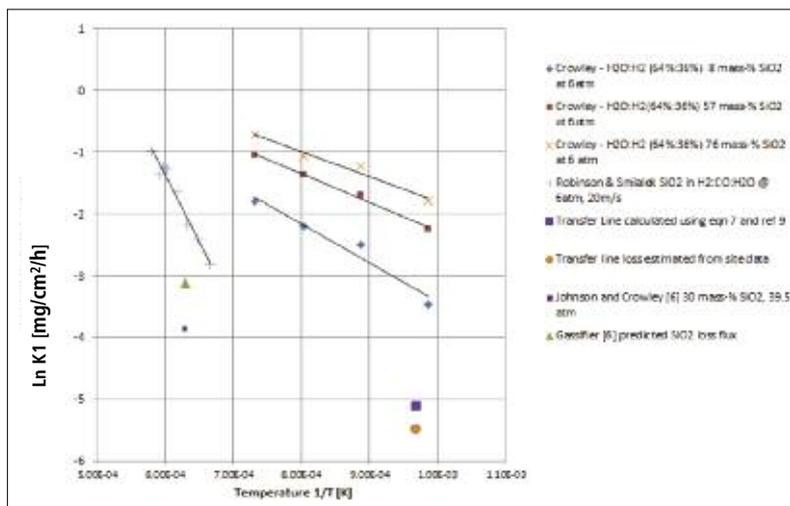

Fig. 8 Arrhenius plot for various refractory materials under different gaseous conditions

$$J \propto \frac{v^{1/2}}{p^{1/2}} \sum P_{volatile} \qquad (7)$$

This relationship is used to predict the volatilization rate for the reactions 1, 2 and 4 for two industrial samples – a piece of hot face refractory from a transfer line and a piece of refractory from a gasifier [13].

Given that these two processes have relatively high steam partical pressure it can be expected that reaction 4 will dominate. This reaction shows that the partial pressure of silica hydroxide is proportional to the square of the steam pressure, i.e. $P_{Si(OH)4} = K_e (P_{H2O})^2$ which means a small change in the steam partial pressure can make a large change in the formation of $Si(OH)_4$.

The first step was to calculate the silica volatilization flux from the transfer line assuming an average silica content of 34 %, a flat surface area and an estimated service life of 12 years. The loss of silica was measured (Tab. 6) at 6,4 % giving a calculated flux rate of 0,0041 mg/cm²/h. The volatilization flux for the gasifier [13] was similarly calculated giving a volatilization flux of 0,0184 mg/cm²/h.

Using the relationship (7) and the Opila et al. [15] data for silica volatilization as the beginning reference the volatilization rate was calculated for the refractory castable used in the gasifier [13] at 1315 °C and 39,5 atm (4001 Pa) and the transfer line at 760 °C and 23 atm (2330 Pa). The predicted volatilization rate for the gasifier was 0,0442 mg/cm²/h and the predicted volatilization rate for the transfer line was 0,00603 mg/cm²/h. While the predicted

volatilization flux tends to over predict the calculated result the values are generally in good agreement. The results are plotted in Fig. 8 for comparison.

It was not possible to correlate the Crowley data flux using the above methodology and it was thought that this may be due to the very small specimen size used.

6 Conclusion

It is concluded that silica volatilization occurs over a wide range of temperatures and that at temperatures less than 980 °C the dominant species is $Si(OH)_4$ and at temperatures above approximately 1000 °C the dominant species formed is SiO. The SEM analysis of a refractory taken from an ammonia plant transfer line, shows that the loss of silica occurs from the aggregate and not the matrix, which is in line with results published by Robbins and Mauer [18].

The literature also shows that refractory castables with CA cements will react with silica vapour to form CAS_2.

The literature shows that the activation energy for different ceramics and high silica content refractory in hydrogen is relatively constant at high temperatures but refractory materials with low silica content has a much lower activation energy. At low temperatures the activation energy for refractory is much lower. At low temperatures this is due to the formation of silica hydrate. The method as proposed by Opila et al. [15] to calculation of the silica volatilization flux for industrial refractory under various reducing conditions, temperatures and pressures was evaluated. Validation of the methodology was possible

by using data from two industrial samples and good agreementwas achieved between measured and predicted results.

Using this method it is possible to predict the volatilization of silica species (SiO or Si(OH)$_4$) from refractory under reducing conditions at various temperatures and pressures. The research also found that silica volatilized at low temperatures, <~1000 °C, is predominantly Si(OH)$_4$ and in this form the coating of boiler tubes is unlikely.

It was further found that the silica lost from a refractory castable was from the aggregate and not the matrix, which is in line with other research.

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