

University of Groningen

Impact of silica deposition on the performance of gas-fired domestic appliances caused by the combustion of siloxanes in the fuel

Gersen, Sander; Visser, Pieter; van Essen, Martijn; Brown, Martin; Lewis, Andy; Levinsky, Howard

Published in:
Renewable Energy

DOI:
[10.1016/J.renene.2018.07.143](https://doi.org/10.1016/J.renene.2018.07.143)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gersen, S., Visser, P., van Essen, M., Brown, M., Lewis, A., & Levinsky, H. (2019). Impact of silica deposition on the performance of gas-fired domestic appliances caused by the combustion of siloxanes in the fuel. *Renewable Energy*, 132, 575-586. <https://doi.org/10.1016/J.renene.2018.07.143>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



Impact of silica deposition on the performance of gas-fired domestic appliances caused by the combustion of siloxanes in the fuel

Sander Gersen ^{a,*}, Pieter Visser ^a, Martijn van Essen ^a, Martin Brown ^b, Andy Lewis ^c, Howard Levinsky ^{a,d}

^a DNV GL, Nederland B.V., P.O. Box 2029, 9704 CA Groningen, the Netherlands

^b DNV GL Holywell Park, Ashby Road, Loughborough, LE11 3GR, UK

^c Cadent Gas Ltd, Ashbrook Court, Coventry, CV7 8PE, UK

^d Laboratory for High Temperature Energy Conversion Processes, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

ARTICLE INFO

Article history:

Received 27 September 2017

Received in revised form

19 July 2018

Accepted 30 July 2018

Available online 31 July 2018

Keywords:

Biogas

Siloxane

Silica

Deposition

Appliances

ABSTRACT

The effects of silica deposition resulting from the combustion of siloxane-containing biomethane on the performance of seven domestic appliances have been studied. The results show that silica deposition increases the flow resistance across the heat exchangers, which consequently reduces the air intake from the surroundings. For the flow-through hot water heater studied, the reduction in air intake in the appliance results in a substantial increase in the CO emission with time, ultimately resulting in a safety risk for the end user. For the fully premixed boilers examined, the increased flow resistance reduces the thermal input, and thus the thermal output, of the appliance. The extent of the reduction in thermal input is seen to depend strongly upon the concentration silicon in the fuel, and the configuration and material of the heat exchanger. For the boilers studied, the ion current measured by the flame safety device decreases with time because silica deposits on the probe used to measure the current in the flame; this ultimately results in boiler failure. Based on the results, extrapolation methods are proposed that can be used to assess the impact of low silicon concentrations in biomethane on appliance performance and safety with time.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The global drive towards sustainability has resulted in an increasing trend towards the use of biogas. An effective way to transport biogas to end users, both residential and industrial, is to inject the biogas into the existing natural gas grid after upgrading it to meet the natural gas specification, so-called biomethane. Depending on the point of injection of biomethane in the gas grid, end users who are located downstream of these points can receive up to 100% biomethane, especially in the summer when gas consumption is low.

Biogases from fermentation processes, for example from dairy waste, wastewater treatment or landfill, contain mainly CO₂ and CH₄. However, depending on the source, biogas can contain varying quantities of trace contaminant species, such as halogenated compounds, sulfur compounds and volatile organic compounds,

including compounds like siloxanes, which are organosilicon compounds [1–3].

Siloxanes and other silicon-containing compounds that are found in many types of biogas deserve special attention. These compounds are present in many consumer products, such as detergents and shampoos, and ultimately can end up in the biogas produced. Volatile siloxanes present in the fermenting waste products can be present in the resulting biogas. The siloxane concentration found in biogases varies strongly depending on the biogas production/process conditions and the properties of the siloxanes present in the biomass. The largest concentrations of siloxanes, up to 400 mg/m³, are found in fermentation gases from landfill and wastewater treatment [2]. Siloxanes have either linear (L) or cyclic (D) structures. Different types of siloxanes have been reported from landfill gases [3]. The literature further discusses several techniques to remove siloxanes from biogas [2, 4–6].

Upon combustion, siloxanes are converted to silicon dioxide particles (silica, SiO₂) [7–26], which deposit in combustion equipment such as engines, turbines and boilers [20–23]. In gas

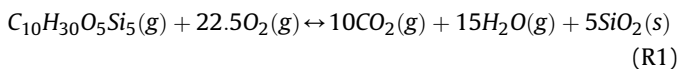
* Corresponding author. Energieweg 17, 9704 CA Groningen, the Netherlands.
E-mail address: sander.gersen@dnvgl.com (S. Gersen).

appliances for heating and hot water production, silica particles may deposit on various surfaces like the heat exchanger and can cause deterioration in equipment performance [22,23]. Since domestic appliances tend to have compact heat exchangers, which can be relatively easily blocked, these appliances may be particularly susceptible to clogging by silica formation. Progressive clogging of heat exchangers leads to increased flow resistance in an appliance, which can result in a decreased thermal output and/or increased carbon monoxide (CO) emissions. For these reasons, domestic appliances can be considered among the most sensitive applications for silica clogging caused by siloxanes in biomethane. From the perspective of the end user, this deterioration is unwanted since no significant deterioration in performance should occur during the lifetime of the equipment when normally used with natural gas as a fuel. Moreover, any silica particles formed that are not deposited in combustion equipment are instead expelled into the air. Since combustion-generated silica particles smaller than 100 nm have been reported in the literature [see, for example, 7–11, 18], the particles exhausted could contribute to the environmental burden of ultrafine particles and potential health issues [22,23].

Given the growing trend towards the injection of biomethane into the natural gas grid, the development of a well-founded specification for the maximum amount of siloxanes in biomethane is necessary to guarantee appliance performance. Technical information needed to develop these specifications for domestic appliances is currently lacking. The goal of this study is to determine a hierarchy of impacts of the silicon content in biomethane on the performance of commonly used domestic appliances, varying from “nuisance” effects to the potential impairment of safe operation. Moreover, this study provides insight to the extent to which the impact of silica deposition on appliance performance can depend on appliance design, such as the configuration and material of heat exchanger present and on the performance of flame safety devices [20–23]. To maximize the generality of the results while avoiding large scale testing the results obtained are used to develop methods based on extrapolation that can be used to assess the impact of low silicon concentrations in biomethane on appliance performance over long periods of time, i.e., approaching the 15–20 year lifetime of domestic appliances. These results can in turn be used to estimate maximum siloxane concentrations in biomethane that maintain appliance performance.

2. Silica particle formation in siloxane-containing flames

In this study, siloxane-containing biomethane is simulated by doping different quantities of siloxanes in natural gas. The siloxane decamethylcyclopentasiloxane ($C_{10}H_{30}O_5Si_5$, often simply referred to as D5) is used in the experiments. As an illustration, the overall oxidation reaction of D5 is shown below (R1).



It should be noted that reaction R1 is an overall representation of a chain of chemical reactions [12,17], similar to those occurring in hydrocarbon oxidation. Equilibrium calculations indicate that silicon-containing combustion products are mainly present as gaseous silicon oxide, SiO and silica, SiO₂, both in gaseous and condensed phases depending on the temperature. As an example, the calculated equilibrium fraction of silicon oxides present in the gas phase for a methane/air mixture doped with D5 with an equivalence ratio of $\phi = 0.7$ (typical for modern lean-premixed central heating boilers) is calculated as a function of temperature and D5 concentration and presented in Fig. 1. In these calculations,

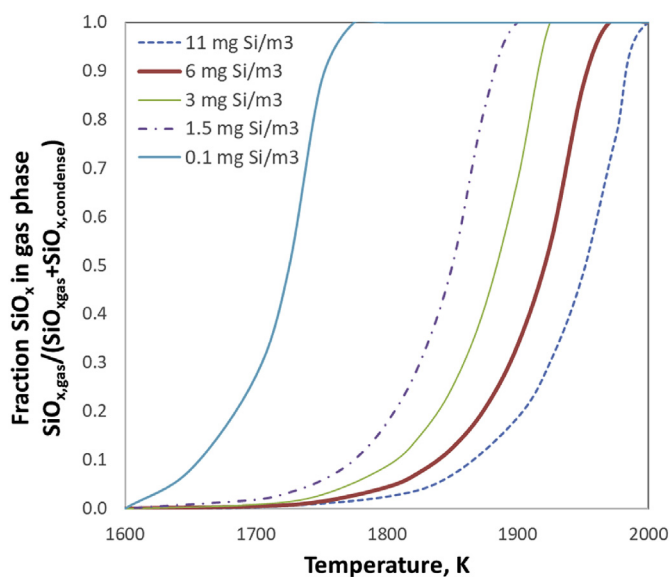


Fig. 1. Equilibrium fraction of gas-phase silicon oxides (SiO_x) for different silicon content in the fuel, as a function of temperature at an equivalence ratio of $\phi = 0.8$.

the siloxane concentration is given in mg Si/m³n in the fuel. The fraction of silicon oxides in the gas phase is calculated as the sum of the mole fractions of SiO and SiO₂ (together denoted as SiO_x) in the gas phase divided by the total fraction of SiO_x in the gas and condensed phases. Since different siloxanes can have both different numbers of silicon atoms and different molar masses, two different siloxanes at equal mole fraction can yield different masses of silica when burned. Expressing siloxane concentration as mg Si/m³ of fuel, as opposed to mole/volume fraction (in ppm) or mg siloxane/m³ fuel, provides an unambiguous measure of the potential to form silica during combustion. Fig. 1 shows that the fraction of silicon oxides in the gas phase depends strongly upon the temperature and concentration of silicon present in the combustion products. Therefore, we expect these parameters to affect the deposition processes of silica in domestic appliances, and their subsequent impact on appliance performance, when using silicon-containing fuel.

While the thermodynamic calculations accurately describe the final state of a system, which includes chemically reacting components, it is possible to observe deviation from the equilibrium when the characteristic times of the chemical reactions driving the system to equilibrium are of the same order as, or larger than, the characteristic residence times in a combustion chamber. In the reaction zone of the flame, siloxanes are quickly converted to gas-phase SiO and SiO₂ creating a supersaturated vapor, which proceeds to condense, forming nanoparticles or nanoclusters [e.g. 7–11, 18]. At high temperatures, the nanoclusters will continue to grow into larger clusters by taking up free SiO₂(g) molecules. These clusters, which are small particles with a diameter in the order of a few nanometers, become larger through collisions between SiO₂ particles. Depending on the temperature, the morphology of these new particles can be either spherical (clusters) or tightly attached fractal-like structures (“aggregates”) [8–11,26]. Further downstream the temperature decreases due to heat losses, particularly during heat exchange in the appliance, resulting in the condensation of more SiO₂ from the gas phase and continued particle and aggregate growth, as well as the formation of agglomerates of aggregates. All these forms of condensed silica will deposit, particularly via thermophoresis [22], in the appliance, for example the heat exchanger [22].

Table 1
Domestic appliances studied.

Appliance number and type	Combustion	Ionization safety device	Type of heat exchanger	Nominal Thermal Input, kW
1. Flow-through hot water heater	Partially premixed	No	Aluminium finned heat exchanger	10.0
2. Partially premixed boiler	Partially premixed	Yes	Aluminium finned heat exchanger	26.6
3. Partially premixed boiler	Partially premixed	Yes	Cast iron heat exchanger	11.7
4. Fully premixed boiler	Fully premixed	Yes	Aluminium lamella heat exchanger	18.3
5. Fully premixed boiler	Fully premixed	Yes	Welded Aluminium heat exchanger	25.2
6. Fully premixed boiler	Fully premixed	Yes	Aluminium block with stainless steel outer water jacket	24
7. Fully premixed boiler	Fully premixed	Yes	Stainless steel concentric coil heat exchangers	20

3. Appliances selection

For the experiments reported in this study, seven common domestic appliances were used, listed in Table 1.¹ The combustion principle of the burner, nominal thermal input, the configuration and material of the heat exchanger present in the appliance are also listed in Table 1.

When considering the effects of silica deposition in the appliances presented in Table 1, it will be convenient to distinguish between appliance types, which can be divided into two groups: fully premixed boilers (appliances 4–7), and partially premixed appliances, such as boilers and flow-through hot water heaters (appliances 1–3). In modern fully premixed domestic boilers, natural gas and excess air are mixed before exiting the burner. These boilers have zero-pressure regulators that keep the fuel/air ratio constant during heat load modulation. Additionally, these boilers often have a flame safety device, consisting of one or more ionization probes, positioned close to the burner surface. The probe monitors the presence of the flame by measuring the ion current through the flame. When a flame is present, a current is measured, while the current is zero when there is no flame. When the current has fallen below a certain limit value, the boiler shuts itself off (de facto, shuts off the gas supply to prevent accumulation of explosive mixture). Clogging of the heat exchanger by silica deposition leads to increased flow resistance in the appliance, which decreases the flow of air to the appliance, and results in decreased thermal input through the operation of the zero-pressure regulator. Silica deposition on the ionization probe(s) can impair the operation of the flame safety device.

Partially premixed appliances, in which only part of the air necessary for complete combustion is mixed with the fuel prior to exiting the burner, do not have a control system that keeps the natural gas/air ratio constant. As a result, a reduction of air flow to the appliance due to silica deposition in the heat exchanger will reduce the amount of oxygen in the appliance necessary for complete combustion, ultimately increasing the CO emissions from these appliances. In appliances 2 and 3, a fan is installed in the exhaust that creates underpressure in the appliance, drawing a flow of air from the surroundings to the flame to complete the combustion; in appliance 1 (the hot water heater), natural convection draws the required excess air into the appliance.

As described below, these seven appliances were used to characterize the response of a wide range of appliance types to burning silicon-containing fuel and identify critical performance aspects impacted by silica deposition for more detailed study. Based on the initial analysis, the four appliances deemed most sensitive were studied further.

4. Experimental protocol for studying silica deposition in appliances

In Fig. 2, a schematic diagram of the gas handling system used in the experiments is presented. The appliances studied are intended for use with so-called high-calorific gas in the EU (with a range of Wobbe Index² 45.7–54.7 MJ/m³ [28]). For the purposes of these experiments, we bring the local natural gas into this range through the addition of propane. During the measurements, the Wobbe Index is kept constant at 48.4 MJ/m³ by controlling the natural gas/propane ratio; this ensures normal functioning of the appliances in terms of thermal input and exhaust gas emissions. All gas flows are measured using Bronkhorst EL-FLOW mass flow meters. Using a dedicated gas bubbling system, we added a controlled amount of siloxane D5 to the natural gas stream. The concentration of siloxanes in the natural gas flow leaving the gas bubblers were determined gravimetrically, i.e., by weighing the gas bubblers before and after the experiment.

The siloxane concentration³ used in the initial experiments with the eight appliances shown in Table 1 was 11.2 mg Si/m³. For the more detailed study of the four ‘sensitive’ appliances, three different concentrations were used: 6.3, 2.8 and 1.5 mg Si/m³. At every concentration, each individual appliance was replaced by a new, identical appliance to avoid cumulative effects.

To determine the impact of silica deposition, the appliance performance was monitored. The oxygen and CO fractions in the flue gases was measured periodically during the experiments using a flue gas analyzer (Testo 300 M-I with a precision of better than 20 ppm for CO for fractions lower than 400 ppm and 0.2 vol% for oxygen). Further, the ionization current of the flame safety device, the temperature of the flue gas, the fuel gas flow and temperature, and the cool water flow were monitored periodically. The heat input to the boiler was derived from measured flow, temperature and composition of the fuel gas. After the experiments, samples of the material deposited in the appliances were analyzed using energy dispersive X-ray spectroscopy (EDX).

For the initial experiments at 11.2 mg Si/m³, all appliances were operated at full thermal input (maximum rated power). The central heating boilers were operated at flow/return temperatures of 70 °C/50 °C, commonly used settings. These relatively high water temperatures are expected to provide worst case conditions for silica deposition, as at lower water temperatures more condensation occurs (at least in condensing boilers) and larger fractions of the silica would stick to the surface of the heat exchanger will be washed out of the appliance. A start/stop procedure was used for

¹ While all of the appliances are approved for use across the EU, the appliance selection was based on their use in the UK. While the results observed are generally applicable, where local appliance preferences are important for considering the implications of the results, this will be discussed below.

² Here, the Wobbe Index (the higher heating value divided by the square root of the relative density) is expressed in MJ/m³ at reference conditions 15 °C/15 °C, i.e., the reference temperatures for both the heating value and the volume are 15 °C [27].

³ The reported concentrations are averages; the variations in concentration during the measurements was generally within 5%. In addition, the volume of the siloxane concentration is expressed in m³ at 0 °C.

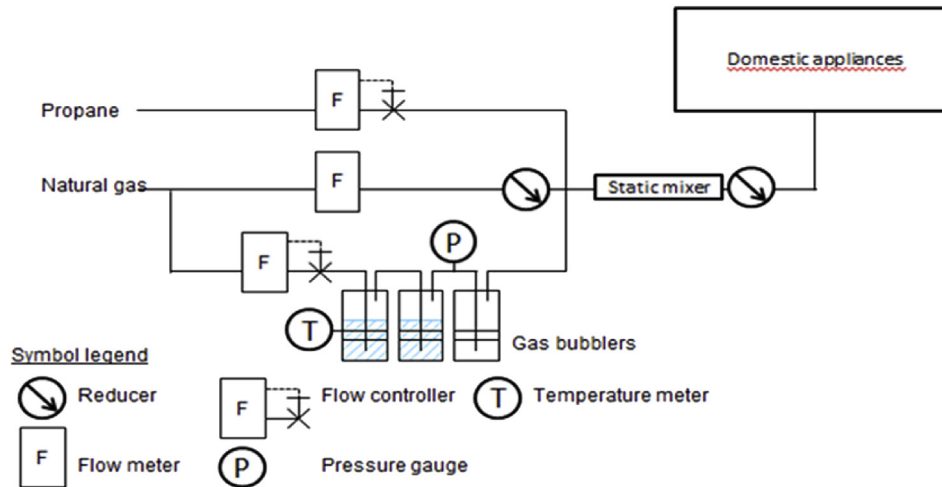


Fig. 2. Gas handling system for the domestic boilers and the flow-through hot water heater.

the hot water heater (Appliance 1 in Table 1): the appliance switches itself off automatically after 10 min running at maximum power. After 10 min of cooling down (no combustion) the appliance switches itself back on. For the other appliances, we used the following operating procedure; the appliances are switched off twice a day to cool down for about 15 min and once a day the boilers modulate over the full power range, from minimum to maximum load. Before starting the experiments with siloxane doping, a reference measurement was performed for each appliance by using the natural gas mixture with a Wobbe Index of 48.4 MJ/m^3 .

5. Results and discussion

5.1. Initial experiments on seven appliances

5.1.1. Effect silica deposition on the CO emissions

The experiments carried out in the instantaneous hot water heater with 11.2 mg Si/m^3 in the fuel showed a progressive increase in the CO emission with time, as shown in Fig. 3 (left). The increase in CO emission was caused by the increased flow resistance across the heat exchanger due to silica deposition (Fig. 3, right) reducing the flow of air that can be drawn in from the surroundings. Analyses of the white deposit on the heat exchanger (Fig. 3, right) by EDX shows that the white layer mainly

consists of silicon oxides. The reduced flow of air is clearly manifest in the steady reduction of the oxygen content of the flue gases seen in the figure. After $\sim 252 \text{ h}$ of operation (equivalent to $\sim 219 \text{ m}^3$ of gas consumption) the measured CO emission is above 2000 ppmv (dry, air free) and the measured CO/CO₂ level is higher than the “safety action level” of 0.02 used by service engineers as an indication that the safety performance of the appliance requires immediate remediation [29]. We also observe that during this period the oxygen content in the flue gases has decreased from $\sim 5\%$ under nominal operating conditions to $\sim 2\%$, the point at which the CO emissions increase sharply. From these observations, we conclude that the CO emission of the instantaneous hot water heater (appliance 1) is sensitive to silica clogging for the conditions studied. This appliance was therefore selected for further investigation.

In contrast, despite the visible deposition of in the heat exchangers of the partially premixed appliances 2 and 3 (shown in Fig. 4), no substantial changes in the CO emissions or oxygen concentration in the flue gas were observed, even after 1100 h of operation, as seen in Fig. 5. As such, these two appliances were not selected for further examination in the present study.

No significant increase in CO emission arising from silica deposition was observed for the four fully premixed domestic boilers (appliances 4–7 in Table 1). This is expected, since, as discussed above, the control system of these boilers is intended to

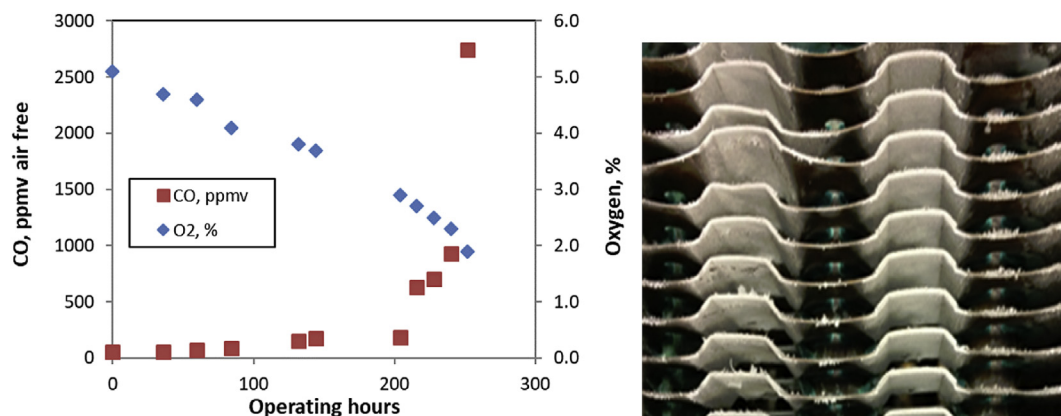


Fig. 3. Left: Measured CO emission and Oxygen content in the flue gases as a function of time for the experiment with 11.2 mg Si/m^3 in natural gas. The natural gas consumption is about $0.87 \text{ m}^3/\text{hr}$. Right: Top view of the heat exchanger, white layer on lamella is silica deposition.



Fig. 4. Left, heat exchanger appliance 2. Right, heat exchanger appliance 3.

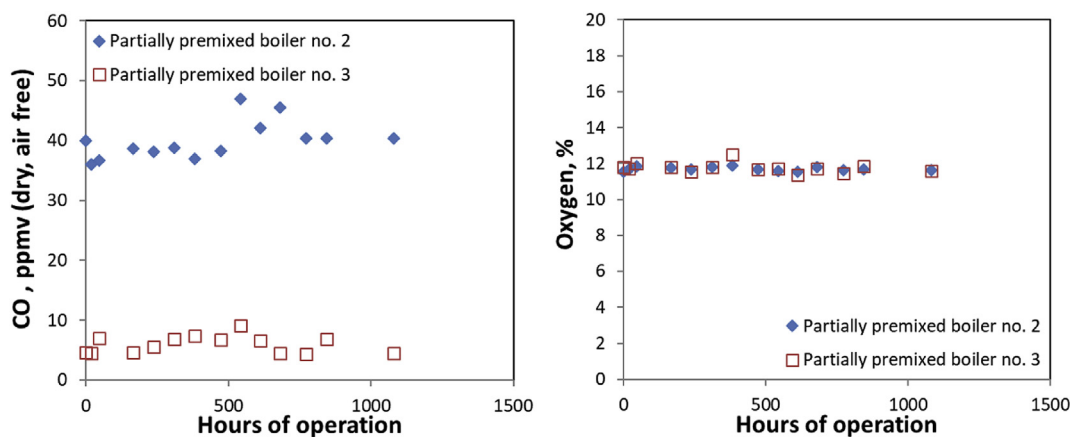


Fig. 5. Measured CO (left) and oxygen concentration (right) as a function of time for the partially premixed boilers (nos. 2 and 3), using 11.2 mg Si/m^3 in the fuel.

maintain a constant fuel/air ratio despite the decrease in air input to the appliance.

5.2. Effect silica deposition on the thermal input of the appliances

Since, in contrast to the fully premixed boilers, the partially premixed appliances have no coupling between any degree of clogging and the fuel input, no changes in thermal input was observed in these appliances during the course of the experiments, despite the substantial amount of silica deposited. Additionally, for the appliances (1–3) the temperature of the flue gases remained constant during the measurements, indicating that the efficiency was also not affected by the deposition of silica in the heat exchanger.

As discussed above, for the fully premixed boilers (appliances 4–7), the clogging of the heat exchanger by silica results in an increased flow resistance, causing a reduction in the air intake, whereupon the zero-pressure regulator automatically reduces the flow of fuel to maintain the fuel/air ratio at its nominal value. As an illustration, the reduction in thermal input with time, derived from the measured flow rate of the fuel to the appliance, caused by silica deposition in the heat exchanger is shown in Fig. 6 for appliance 7, and summarized for the fully premixed boilers in Table 2.

From Table 2 we see that the largest reduction in input is observed for appliance 7; 25% reduction in the thermal input after 1081 h of operation using 11.2 mg Si/m^3 in the fuel, which is

equivalent to 1719 m^3 natural gas consumption. This reduction is similar to that observed for an appliance with a similar heat exchanger studied previously [23]. Appliance 5 showed a reduction in thermal input of 17%, appliance 6 of 13% and appliance 4 of 9% after roughly 1000 h of operation. The measurements also showed that the efficiency of the appliances studied did not change significantly due to deposition of silica on the surface of the heat exchanger. Thus, the reduction in thermal input resulted directly in a reduction in thermal output of the appliance. The observed differences in the reduction in thermal input are directly related to the configuration and material of the heat exchanger.

As an illustration, the deposition in the heat exchangers of the two most sensitive appliances 7 (left) and 5 (right) after roughly 1050 h are shown in Fig. 7. The deposit in the stainless steel heat exchanger of appliance 7 consists of white and brown layers, and are generally present as a coating that partially blocks the heat exchanger. EDX analyses shown in Fig. 8 indicate that the brown deposit consists of the elements Fe, CR, O and Si. Based on the atomic fractions measured and given in Table 3, we assume that the brown particles primarily have stoichiometries that can be represented by a mixture of Fe_2O_3 , SiO and SiO_2 . Here we remark that at normal operation (without silicon present in the fuel) no substantial oxidation of stainless steel should occur, implying an interaction between silicon species and stainless steel. We further remark that in our previous study on Dutch domestic appliances, similar behavior was observed in the appliances having stainless

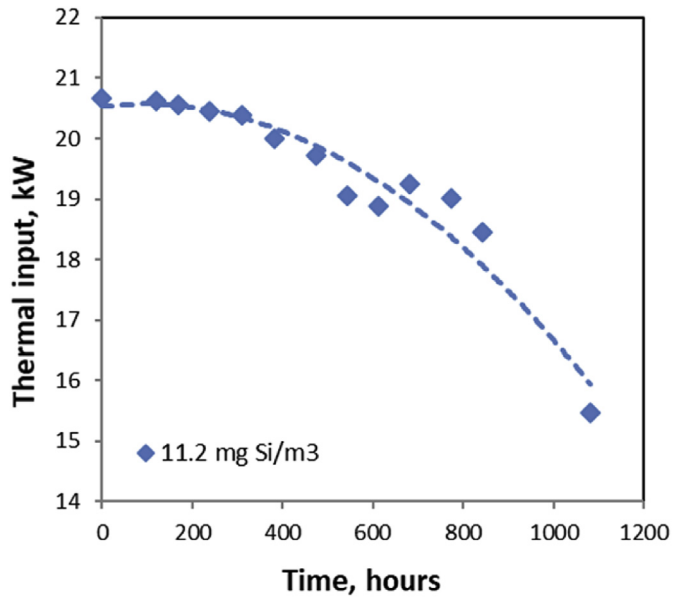


Fig. 6. Measured thermal input at full load of appliance 7, based on the natural gas flow into the appliance with a siloxane concentration in the fuel of 11.2 mg Si/m³.

Table 2
Effect silica deposition on reduction in thermal input with 11.2 mg Si/m³ in the fuel.

Appliance	Hours of operation	Gas consumption, m ³	thermal input reduction, %
4. Fully premixed boiler	953	1474	9
5. Fully premixed boiler	1030	2420	17
6. Fully premixed boiler	1058	2113	13
7. Fully premixed boiler	1081	1719	25

steel heat exchangers [23]. EDX analyses show that the white coating on the heat exchanger (Fig. 7, left and Fig. 14a, see below) consist of mainly Si and O atoms in the ratio 1:2, i.e., silica. The heat exchanger of appliance 5 (Fig. 7, Right) shows substantial amounts of silica deposition in the form of flakes on the walls of the heat exchanger, partially blocking the open spaces. EDX analyses of the deposits on the aluminum heat exchanger of appliance 5 indicate that the flakes consist of mainly silicon oxides and aluminum oxide.

Although the aluminum lamellar heat exchanger of appliance 4 is also covered with white layer (Fig. 9) that consists of mainly

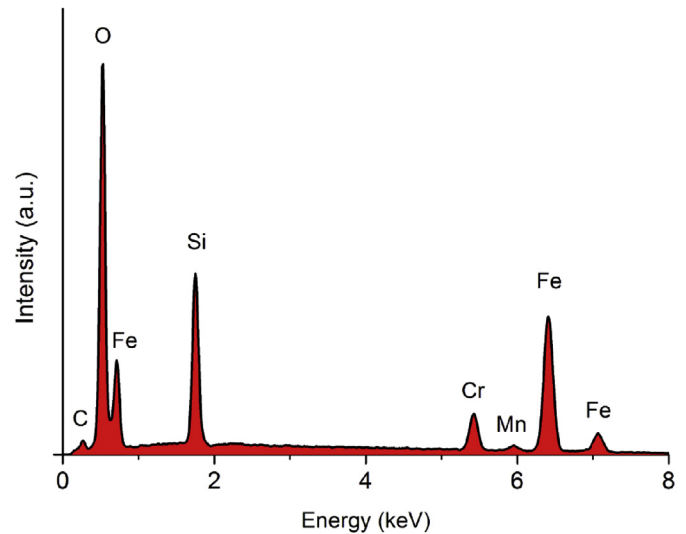


Fig. 8. SEM analyses of the brown deposit from the heat exchanger of appliance 7. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3
EDX analyses of the brown deposit in the heat exchanger of appliance 7.

Element	Wt, %	At, %
C	2.98	8.06
O	20.18	41.01
Si	10.13	11.73
Cr	8.33	5.21
Mn	0.28	0.16
Fe	58.10	33.82

silicon oxides (Fig. 10 and Table 4), only a small reduction of 9% in the thermal input reduction is measured. We attribute this to the large open spaces between the lamella and compactness of the deposited layer. As can be seen in Fig. 11, at the top and at the walls of the heat exchanger of appliance 6, large silica flakes are observed. Additionally, the lower baffle of the heat exchanger shows a fine layer of 'caked' silica due to condensation of water at this downstream part of the heat exchanger. Clogging of silica causes a reduction in thermal input of 13% after 1058 h of operation in this appliance.



Fig. 7. Silica deposition in the heat exchanger of the appliances 7 (left) and 5 (right) after roughly 1050 h of operation using 11.2 mg Si/m³ in the fuel.



Fig. 9. Silica deposition in the aluminium finned heat exchanger of appliance 4 roughly 950 h of operation using 11.2 mg Si/m^3 .

5.3. Effect silica deposition on the performance of the ionization safety device

The experimental results show that for all appliances having ionization safety devices the current measured by the device decreases with time due to progressive silica deposition on the ionization probe. Consequently, boiler failure occurred for three of the boilers studied because the ionization current had decreased to the point at which the flame-detection safeguard is activated. In the example presented in Fig. 12, boiler failure occurred after 430 h and a second, new, ionization safety device was installed. An interesting observation is that the installation of the second ionization probe resulted in an initial ionization current of $\sim 31 \mu\text{A}$ (compared to $38 \mu\text{A}$ for the original probe) and dropped down to $27 \mu\text{A}$ for the third probe, which is roughly $11 \mu\text{A}$ lower than the original ionization probe. The drop in the ionization current is most probably caused by the increased pressure drop over the burner because of silica deposition in the heat exchanger. This change in pressure drop causes a shift in the position of the flame front, affecting the transport of ions to the probe.

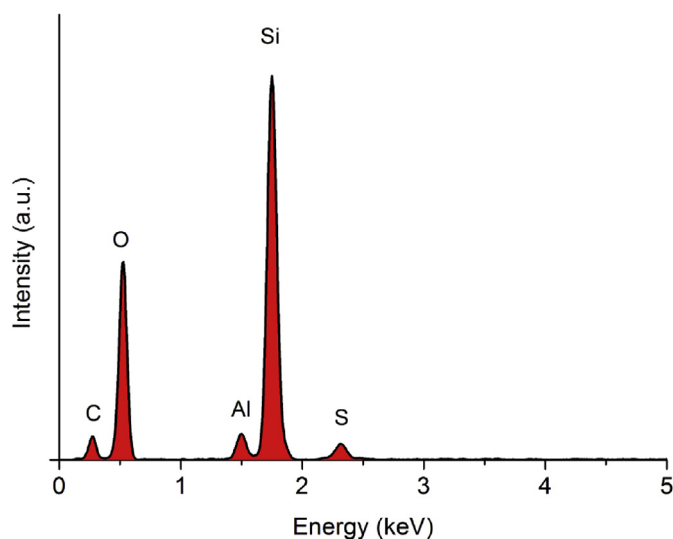


Fig. 10. SEM analyses of deposition samples taken from the heat exchanger of appliance 4.

Table 4
EDX analyses of the deposition in the heat exchanger of appliance 4.

Element	Wt, %	At, %
O	39.22	53.25
Al	3.24	2.61
Si	53.87	41.66
S	3.66	2.48



Fig. 11. Silica deposition in the aluminium heat exchanger of appliance 6 after roughly 1050 h of operation 11.2 mg Si/m^3 in the fuel. Left: top of the heat exchanger; right: bottom insert in condensing part of the heat exchanger.

5.4. Analysis of 'sensitive' appliances with varying siloxane concentrations

5.4.1. Appliance selection and assessment of impact during appliance lifetime

Based on the changes in CO emissions, thermal input and failure of the flame safety device, four appliances were chosen for further investigation using varying concentrations of siloxanes doped in natural gas, from 6.3 to 1.5 mg Si/m^3 . These were: three fully pre-mixed boilers, appliance 7 (largest reduction in thermal input), appliance 4 (most sensitive to failure of the flame safety device) and appliance 6 (large reduction in power and sensitive to failure of the safety device), and the hot water heater, appliance 1 (increased CO emissions).

We point out that the performance of the other appliances tested will continue to deteriorate with time, but more slowly than the appliances chosen. The differences observed between appliances are useful for illustrating the range of phenomena that can be observed in the field. However, when considering a maximum concentration of siloxanes in biomethane for a specific geographical area (such as for a given country or region within a country), then these differences and the degree to which they occur in the local population of appliances have a strong impact on the results. We shall return to this point below.

Varying the siloxane concentration down to 1.5 mg Si/m^3 in the fuel is intended to expose possible differences in behavior and to develop a transparent method of estimating the maximum concentration of silicon-containing species in biomethane that still results in appliance performance that is acceptable for the end user. The domestic equipment installed in practice is designed and approved to operate properly for the appliance lifetime (ordinarily 15–20 years) when fired with natural gas, which does not contain siloxane compounds. We must then make assumptions regarding the degree to which deterioration of performance would be tolerable for the end user.

The first assumption is that silica deposition may not cause more loss of performance than natural gas during the lifetime of the

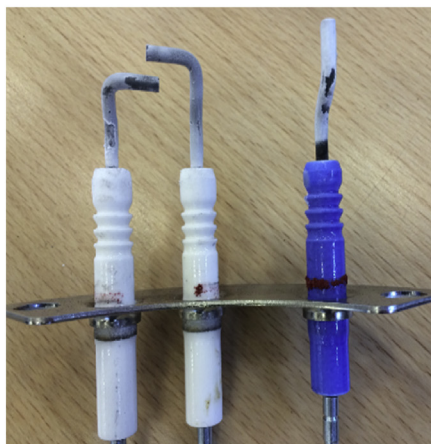
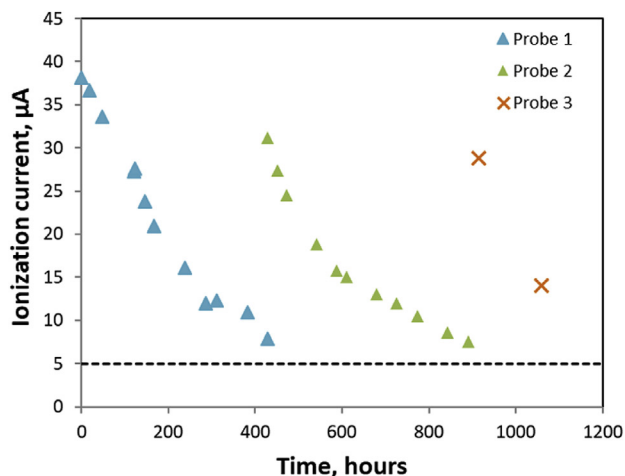


Fig. 12. Left, Ionization current measured as function of time for appliance 6. Right, silica deposition (white layer) on the ionization safety device of appliance 6.

appliance. Since it is not feasible to perform experiments for 15 years, we vary the siloxane concentration as given above to allow extrapolation based on the duration of the experiments performed. Further, for the purposes of the extrapolations made below, we assume that an appliance is fueled continually with biomethane with a fixed silicon concentration in the fuel. Additionally, we assume that there is no specific action for remediating the impact of silica deposition.⁴ These assumptions are considered a ‘worst-case’ condition for assessing siloxane impact on domestic appliances. Specific performance criteria for CO emissions, reduction of thermal input and failure of the flame safety device will be given below.

5.4.2. Effect of silica deposition on the CO emission of the selected appliances

As observed for the experiments at 11.2 mg Si/m^3 in the fuel, silica deposition does not result in a significant increase in the CO emissions for the selected fully premixed boilers (appliances 4, 6 and 7) when fueled with siloxane concentrations of 6.3 , 2.8 and 1.5 mg Si/m^3 . In contrast, the experiments carried out on the instantaneous hot water heater (appliance 1) show that clogging of the heat exchanger with silica resulted in a progressive increase in CO emissions with time, caused by the increased flow resistance across the heat exchanger and reduced air intake as discussed above, for the siloxane concentrations studied. Here we note that the strong effect of silica deposition at the lowest siloxane concentrations obviated the need for experiments at 6.3 mg Si/m^3 . As shown in Table 5, lowering the concentration from 11.2 to 2.8 mg Si/m^3 and subsequently to 1.5 Si/m^3 in the experiments increases the time to reach the safety action limit, essentially linearly. We remark that given the cumulative nature of silica deposition, it is convenient to express the effects in terms of mass of silica formed. For the experiments performed the CO/CO_2 safety action limit of 0.02 is exceeded when the same mass of silica has been produced (and deposited), $4.9 \pm 0.4 \text{ g}$. This observation implies that the effect of siloxanes in biomethane on this appliance can be extrapolated linearly from the measurements. It is important to note that from the point of consumer safety, the choice of limiting CO emission

(either expressed as actual emission or CO/CO_2 ratio) can be country and appliance dependent. In the UK this is $\text{CO}/\text{CO}_2 = 0.02$ for this appliance, but in other countries (such as the Netherlands) this can be 0.01 . Clearly, a lower limiting value is automatically translated into earlier ‘unacceptable’ performance and consequently a lower maximum concentration of siloxanes in the biomethane. Application of the data obtained here to other limiting performance criteria is straightforward.

Since different appliances are operated differently, and even different consumers can operate a given appliance differently, it is logical to consider the gas usage resulting in a mass of silica produced rather than the actual time of operation, also indicated in Table 6. The cumulative gas usage during the appliance lifetime (~ 15 – 20 years) for a hot water heater is much higher than studied here. To estimate the maximum silicon content in biomethane to prevent exceeding the safety action level within the lifetime of the hot water heater studied, the following relationship is derived from the results:

$$[\text{Si}]_{\text{CO}} = \frac{4.9 \cdot 1000}{V_{\text{gas, total}}} \frac{M(\text{Si})}{M(\text{SiO}_2)} \quad (1)$$

Where $[\text{Si}]$ is the allowed silicon concentration in biomethane expressed in mg Si/m^3 , $V_{\text{gas, total}}$ is the total gas usage in m^3 , $M(\text{Si})$ and $M(\text{SiO}_2)$ are the molar masses of silicon and silica, respectively. In many northern European countries such as the UK, the annual natural gas usage for water heating is $\sim 350 \text{ m}^3/\text{year}$. Thus, assuming the appliance is fueled with siloxane-containing biomethane for a lifetime of 15 years, the total gas used in the appliance is 5250 m^3 , and to accumulate the 4.9 g silica for this amount of gas used, the biomethane cannot contain more than 0.44 mg Si/m^3 .

5.5. Effect silica deposition on the thermal input of the fully premixed boilers

For the siloxane concentrations studied, progressive build-up of the silica layer in the heat exchangers is observed, leading to an increase in the flow resistance and causing a reduction in the thermal input for the fully premixed appliances (appliances 4, 6 and 7) investigated here. For all silicon concentrations used, the largest reduction in thermal input is observed for appliance 7, and we will discuss the results from this boiler here in more detail. Fig. 13 shows that the reduction of the thermal input with time becomes slower with decreasing silicon concentrations in the fuel.

⁴ Since silica deposition is cumulative, varying fractions in biomethane can be accounted for in the method described below. Furthermore, the absence of specific remedial action for silica deposition reflects the current practice. Parts sensitive to silica deposition, such as the ion probe, are ordinarily not replaced during the lifetime of the appliance. Specific aspects regarding remediation will be published separately.

Table 5

Amount of silica produced until the CO/CO₂ safety action level is reached for the hot water heater.

Concentration, mg Si/m ³	Duration, hours	Gas usage, m ³	Silica produced to reach safety action level, g
11.2	252	219	5.3
2.8	880	770	4.6
1.5	1825	1524	4.9

Table 6

Effects silica deposition on thermal input for appliance 7.

Concentration, mg Si/m ³	Time, hours	Gas usage, m ³	SiO ₂ produced, g	Thermal input reduction, %
11.2	1081	1719	41.2	25
6.3	1991	3096	41.8	26
2.8	2190	3523	21.1	32
1.5	4135	6517	20.9	28

When converting the data to the mass of silica produced, as shown in Table 6, we observe that at the two highest (11.2 and 6.3 mg Si/m³) and the two lowest (2.8 and 1.5 mg Si/m³) silicon concentrations the reduction in thermal input is similar at similar masses of silica produced. However, surprisingly, the impact of the two low fractions is about a factor of two higher than that at the higher silicon content: for example, at 11.2 mg Si/m³, the thermal input decreased by 25% after 41 g silica is produced, while at 1.5 mg Si/m³, the thermal input decreased by 32% after only 20 g silica is produced. Although not presented the results of appliance 6 show a linear reduction in thermal input with time for the four concentrations studied. Similar to appliance 7, the impact of the two low fractions for appliance 6 is about a factor of two higher than that at the higher silicon content. For example, at 11.2 mg Si/m³, the thermal input decreased by 13% after 51 g silica is produced while at 1.5 mg Si/m³, the thermal input decreased by 16% after 25 g silica is produced. Visual inspection of the heat exchangers of appliance 6 and 7 suggests a change in the deposition behavior in the heat exchangers and is discussed for appliance 7 in more detail below. Appliance 4 shows the lowest reduction in thermal input due to the large open space between the lamella (Fig. 9) of the heat exchanger. As a result, for the lowest concentrations studied

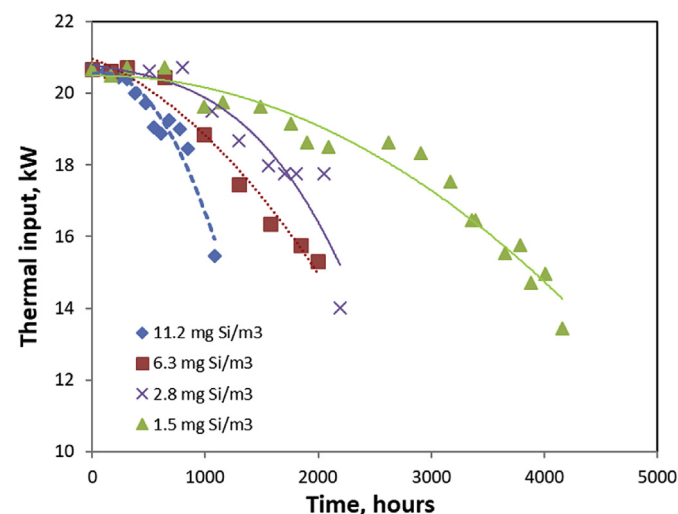


Fig. 13. Measured thermal input of appliance 7 for different silicon concentrations, calculated using the flow of natural gas into the appliance.

(2.8 and 1.5 mg Si/m³) only a minor reduction in the thermal input is observed with time for appliance 4.

The two photographs in Fig. 14a show the heat exchanger of appliance 7 after the experiments at 11.2 mg Si/m³ in the fuel. The figure shows yellow/white and brown deposits on the concentric tubes of the heat exchanger. The deposits form a solid coating on the surface of the tubes. As can be seen in Fig. 14b, at 1.5 mg Si/m³ in the fuel, the white/brown deposits are more in the form of a powder and macroscopic flakes that block the flue gas passage between the concentric tubes. This in turn magnifies the increase in flow resistance for the two lowest concentrations (2.8 and 1.5 mg Si/m³) relative to the higher concentrations (11.2 and 6.3 mg Si/m³). Furthermore, as discussed above, the fraction of metal oxides observed in the brown deposits increases when lowering the silicon content in the fuel. This suggests that the rapid silica deposition at high concentrations might act as a coating that prevents SiO₂/SiO₂-induced oxidation of stainless steel. As mentioned above, we note that in a previous study [23] using 7.5 mg Si/m³ in the fuel on an appliance with a stainless-steel heat exchanger with a different configuration of tubes than appliance 7 discussed here, large brownish flakes having predominantly Si and O in 1:1 proportion (with some minor metal components) also resulted in severe clogging of the heat exchanger. More research is needed to explain the origins of these phenomena.

To assess the impact of lower silicon concentrations in biomethane on the thermal input reduction during the appliance lifetime, we extrapolate the results obtained for the most sensitive appliance 7. Since within the uncertainty of the measurements the reduction in thermal input at 2.8 and 1.5 mg Si/m³ was the same at the same mass of silica formed, we extrapolate this data to lower concentrations linearly. Here we emphasize that the extrapolation presented below is limited to concentrations below 2.8 mg Si/m³. For a given degree of reduction (expressed in percent reduction) in thermal input deemed acceptable for the end user, we can obtain the corresponding mass of silica produced from the measurements from appliance 7 obtained at 1.5 mg Si/m³ in the fuel. These data are shown in Fig. 15, and a simple functional relation from Eq. (2) is derived:

$$y = -0.0138x^2 + 1.089x + 2.0731, \quad (2)$$

where x is the percentage thermal reduction and y is the mass of silica formed (g).

To develop limits for silicon levels in biomethane with rationale regarding the total gas usage and acceptable decrease in thermal reduction during in the lifetime of the appliance, Eq. (3) can be used:

$$[\text{Si}]_{\text{thermal input}} = \frac{y \cdot 1000}{V_{\text{gas, total}}} \frac{M(\text{Si})}{M(\text{SiO}_2)}, \quad (3)$$

where y is the amount of silica produced calculated via Eq. (2), V_{total} is the total gas usage during the lifetime of the appliance, and $M(\text{Si})$ and $M(\text{SiO}_2)$ are the molar masses of silicon and silica respectively and $[\text{Si}]_{\text{thermal input}}$ is the maximum silicon content in biomethane that maintains the thermal input of the appliance above the minimum value. For example, from Eq. (3) for a reduction in thermal input of 10%, the amount of silica formed is ~12 g. Assuming a yearly gas usage of 1600 m³, which is common for boilers in northern European countries such as the UK the total gas used for a lifetime of 15 years is 24000 m³. To accumulate the 12 g silica, the maximum mass that maintains the thermal input of this appliance above 90% of the maximum for this yearly gas use, the biomethane should not contain more than 0.23 mg Si/m³.

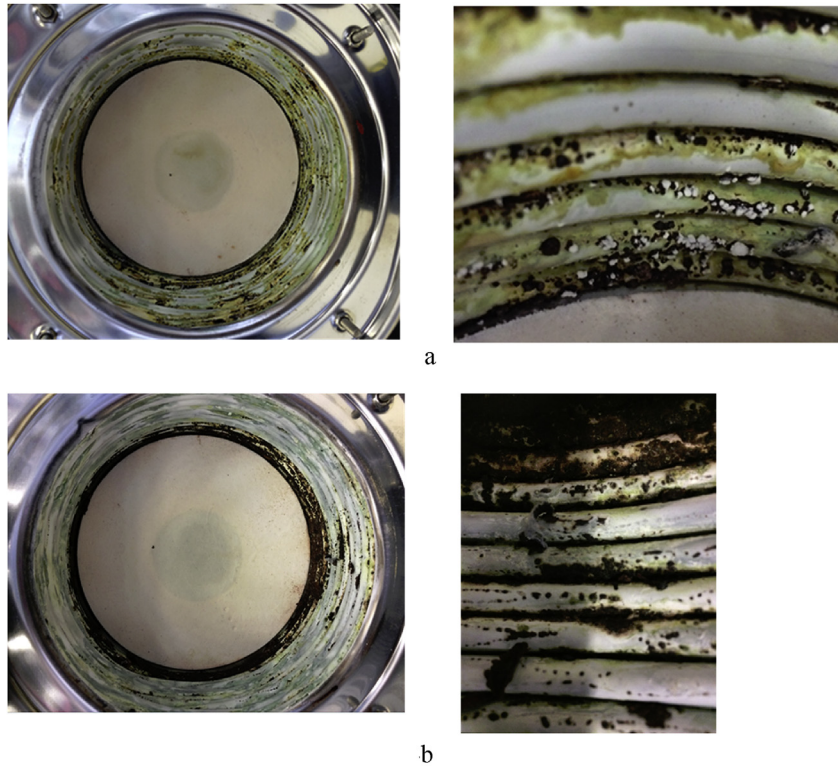


Fig. 14. a: Silica deposition on stainless steel concentric tube heat exchanger of appliance 7 at 11.2 mg Si/m³ in the fuel. b: Silica deposition on stainless steel concentric tube heat exchanger of appliance 7 at 1.5 mg Si/m³ in the fuel.

5.6. Effect of silica deposition on the performance of the flame safety device

Further experiments performed on appliances 4, 6 and 7 show that silica deposition on the ion probe of the flame safety device results in a reduction in the measured current with time for the concentrations studied. Consequently, as discussed above, at a given moment boiler failure occurs because the ionization current has decreased to the point at which the flame-detection safeguard

is activated. As an example, for appliance 6 the time to failure shown in Fig. 16 does not scale linearly with the concentration silicon in the fuel: at 11.2 mg Si/m³ failure was observed after about 430 h of operation and at 6.3 mg Si/m³ failure occurred after about 1500 h of operation, while no failure was observed for the experiments using 2.8 mg Si/m³ and 1.5 mg Si/m³ for the duration of the experiments. Similar results were observed for appliance 7 and for the most sensitive appliance 4, whose results are summarized in more detail in Table 7; Fig. 17 presents the time to failure vs. gas usage in a “log-log” plot. From this we conclude that the

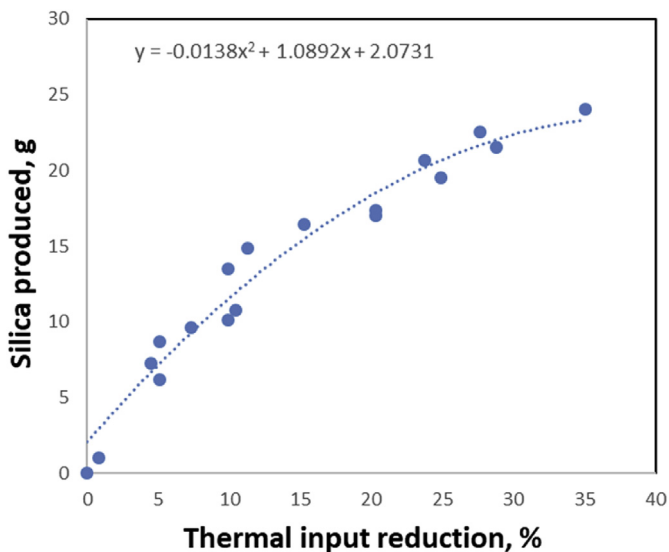


Fig. 15. Silica produced as function of the measured reduction in thermal input for appliance 7 when using 1.5 mg Si/m³ in the fuel.

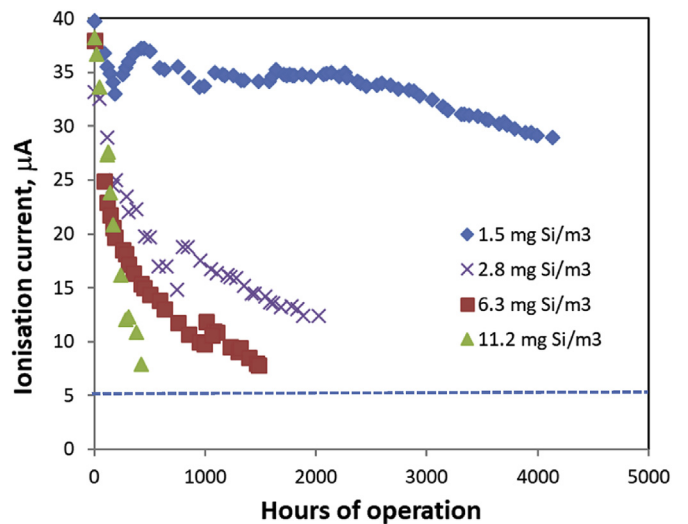


Fig. 16. Ionisation current measured at full load as function of time for appliance 6. The dotted line shows the critical value at which the appliance fails.

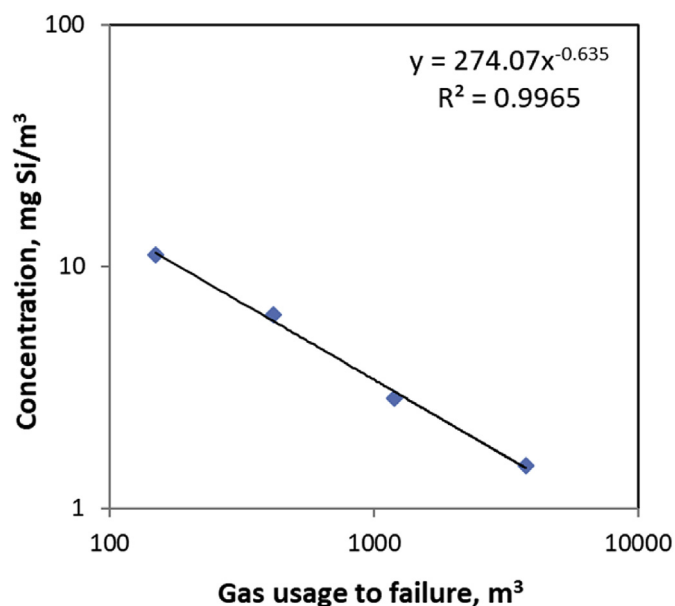


Fig. 17. Time to failure (Left) and gas usage to failure (right) of the ionization probe as a function of the silicon concentration (on log-log scale) for appliance 4.

Table 7

Time to failure, gas usage to failure and mass silica produced due to reduction of the measured current of the ionization probe for different silicon concentrations for appliance 4.

mg Si/m ³ n	Gas usage to failure, m ³ n	Time to failure, hours	Silica produced at time of failure, g
11.2	149	90	3.72
6.3	433	261	5.6
2.8	1208	728	7.2
1.5	4090	2464	12.1

measurements show that the time (and gas usage) to failure does not scale linearly with the silicon content in the fuel, but appeared to increase exponentially with decreasing silicon content. Our analysis of the relevant processes indicates that one of the contributing factors to the non-linear behavior observed is related to the fraction of silicon that is present in gas or condensed phases at the position where the ion probe is positioned. Appliances 4, 6 and 7 operate at an equivalence ratio of $\phi \sim 0.7$, and have an adiabatic flame temperature of $T_{ad} \sim 1850$ K. The thermodynamic calculations shown in Fig. 1 indicate that lowering the silicon concentration in natural gas from 11.2 to 1.5 mg Si/m³n results in a substantial reduction of the silica percentage present in solid phase from 70% to 10% at a temperature of 1850 K. A lower fraction of solid silica at lower concentrations means simply less solid available for deposition, giving a faster reduction in deposition with decreasing concentration than would be expected based solely on the total fraction of silicon in the fuel.

Based on the relation (4) derived from Fig. 17 we can estimate the maximum allowed silicon levels in biomethane to avoid failure of the ionization safety device for a given total gas usage;

$$[Si]_{ionization} = 274.1 V_{total, gas}^{-0.635} \quad (4)$$

As an example, for a lifetime of 15 years, the total gas used in the appliance is 24000 m³, and to prevent failure of the flame safety device for this amount of gas used, the biomethane should not contain more than 0.45 mg Si/m³.

6. Conclusion

The effects of silica deposition on the performance of seven different types of domestic appliances have been studied. The results show that silica deposition in the heat exchangers of these appliances increases the flow resistance across the heat exchangers, which consequently reduces the air intake from the surroundings. For the flow-through hot water heater, the reduction in air intake in the appliance results in a substantial increase in the CO emission with time, ultimately resulting in a safety risk for the end user. For this appliance, the time, and therefore gas usage, to reach the safety limit was dependent on the mass of silica formed from siloxanes and deposited in the appliance. This is a total silica mass loading effect and is independent of the concentration of siloxanes in the fuel. For the fully premixed boilers, the zero-pressure regulator limits the effect of the increased flow resistance to a reduction in thermal input, and thus in the thermal output, of the appliance. The extent of the reduction in thermal input is seen to depend strongly upon the configuration and the material of the heat exchanger. Furthermore, the rate at which the thermal input decreased depended on the siloxane concentration in the fuel, with the higher concentrations studied causing more rapid decrease than the lower concentrations. No significant reduction in the efficiency or changes in the CO emission were observed to arise from silica deposition in the fully premixed appliances. The experiments also showed that, for all boilers studied, the current measured in the flame safety devices decreases in time from silica deposition on the probe used to measure the ion current in the flame, which ultimately results in boiler failure. Here too, the results show that the time and gas usage to failure of the flame safety device does not scale linearly with the silicon content in the fuel, but appeared to increase exponentially with decreasing silicon content. Based on the results, together with assumptions regarding appliance lifetime, maintenance and gas usage, extrapolation methods have been proposed that can be used to assess the impact of low silicon concentrations in biomethane on appliance performance and safety with time. These methods can also be used to determine the maximum concentration of siloxanes in biomethane that preserves appliance performance during the appliance lifetime.

Acknowledgement

This research has been funded as part of the Network Innovation Allowance. We also gratefully acknowledge the (financial) support from the Cadent Gas, Scotland Gas Networks and Northern Gas Networks.

References

- [1] S.E. Rasi, Biogas Composition and Upgrading to Biomethane, PhD Thesis, University of Jyväskylä, 2009, <https://jyx.jyu.fi/dspace/handle/123456789/20353>.
- [2] R. Dewil, L. Appels, J. Baeyens, Energy use of biogas hampered by the presence of siloxanes, *Energy Convers. Manag.* 47 (2006) 1711–1722.
- [3] M. Schweigkofler, R. Niessner, Removal of siloxanes in biogases, *J. Hazard Mater.* B83 (2001) 183–196.
- [4] M. Ajhar, M. Travesset, M. Yüce, T. Melin, Siloxane removal from landfill and digester gas – a technology overview, *Bioresour. Technol.* 101 (2010) 2913–2923.
- [5] G. Soreanu, M. Béland, P. Falletta, K. Edmonson, L. Svoboda, M. Al-Jamal, et al., Approaches concerning siloxane removal from biogas – a review, *Can. Biosyst. Eng.* 53 (2011) 8.1–8.18.
- [6] A. Cabrera-Codony, E. Santos-Clotas, C.O. Ania, M.J. Martínez, Competitive siloxane adsorption in multicomponent gas streams for biogas upgrading, *Chem. Eng. J.* 344 (2018) 565–573.
- [7] B.M. Smirnov, M. Dutka, V.M. van Essen, S. Gersen, P. Visser, D. Vainchtein, et al., Growth of fractal structures in flames with silicon admixture, *Europhys. Lett.* 98 (2012) [66005 p1–6].
- [8] M.V. Dutka, A.A. Turkin, D.I. Vainchtein, S. Gersen, V.M. van Essen, P. Visser, A.V. Mokhov, H.B. Levinsky, J.Th.M. De Hosson, Size distribution of silica

- nanoparticles: its impact on green energy, *Funct. Nanostruct.* 1 (1) (2016) 1–12, <https://doi.org/10.24274/fn.2016.a1>.
- [9] S.E. Pratsinis, Flame aerosol synthesis of ceramic powders, *Prog. Energy Combust. Sci.* 24 (3) (1998) 197–219.
- [10] M.L. Eggersdorfer, D. Kadau, H. Herrmann, S.E. Pratsinis, Aggregate morphology evolution by sintering: number and diameter of primary particles, *J. Aerosol Sci.* 6 (2012) 7–12.
- [11] M.L. Eggersdorfer, D.K. Kadau, H.J. Herrmann, S.E. Pratsinis, Multiparticle sintering dynamics: from fractal-like aggregates to compact structures, *Langmuir* 27 (2011) 6358–6367.
- [12] M.S. Wooldridge, Gas-phase combustion synthesis of particles, *Prog. Energy Combust. Sci.* 24 (1998) 63–87.
- [13] L. Madler, H.K. Kammler, R. Mueller, S.E. Pratsinis, Controlled synthesis of nanostructured particles by flame spray pyrolysis, *J. Aerosol Sci.* 33 (2002) 369–389.
- [14] W.J. Stark, S.E. Pratsinis, Aerosol flame reactors for manufacture of nanoparticles, *Powder Technol.* 126 (2002) 103–108.
- [15] D.E. Rosner, Flame synthesis of valuable Nanoparticles: recent progress/current needs in areas of rate laws, population dynamics, and characterization, *Ind. Eng. Chem. Res.* 44 (2005) 6045–6055.
- [16] R. Strobel, S.E. Pratsinis, Flame aerosol synthesis of smart nanostructured materials, *J. Mater. Chem.* 17 (2007) 4743–4828.
- [17] S.L. Chung, M.S. Tsai, H.D. Lin, Formation of particles in a H₂/O₂ counterflow diffusion flame doped with SiH₄ or SiCl₄, *Combust. Flame* 85 (1991) 134–142.
- [18] H.K. Chagger, D. Hainsworth, P.M. Patterson, M. Pourkashanian, A. Williams, The formation of SiO₂ from hexamethyldisiloxane combustion in counterflow methane-air flames, *Proc. Combust. Inst.* 26 (1996) 1859–1865.
- [19] W.L. Flower, A.J. Hurd, In situ measurement of flame-formed silica particles using dynamic light scattering, *Appl. Optic.* 26 (11) (1987) 2239.
- [20] N. Nair, X. Zhang, J. Gutierrez, J. Chen, F. Egolfopoulos, T. Tsotsis, Impact of siloxane impurities on the performance of an engine operating on renewable natural gas, *Ind. Eng. Chem. Res.* 51 (2012) 15786–15795.
- [21] N. Nair, A. Vas, T. Zhu, W. Sun, J. Gutierrez, J. Chen, F. Egolfopoulos, T.T. Tsotsis, Effect of siloxanes contained in natural gas on the operation of a residential furnace, *Ind. Eng. Chem. Res.* 52 (2013) 6253–6261.
- [22] A.A. Turkin, M. Dutka, D. Vainchtein, S. Gersen, V.M. van Essen, P. Visser, A.V. Mokhov, H.B. Levinsky, J.Th.M. De Hosson, *Appl. Energy* 113 (2014) 141–1148.
- [23] S. Gersen, P. Visser, V.M. van Essen, M. Dutka, D. Vainchtein, J. Th. M. De Hosson, H.B. Levinsky, Effects of Silica Deposition on the Performance of Appliances in the Netherlands, IGRC, 2014.
- [24] S.C. Surita, B. Tansel, Preliminary investigation to characterize deposits forming during combustion of biogas from anaerobic digesters and landfills, *Renew. Energy* 80 (2015) 674–681.
- [25] B. Tansel, S.C. Surita, Oxidation of siloxanes during biogas combustion and nanotoxicity of Si-based particles released to the atmosphere, *Environ. Toxicol. Pharmacol.* 37 (2014) 166–173.
- [26] P.N. Langenkamp, A.V. Mokhov, H.B. Levinsky, Angle-dependent light scattering study of silica aggregate growth in 1-D methane/air flames with hexamethyldisiloxane admixture: effects of siloxane concentration, flame temperature, and equivalence ratio, *Combust. Sci. Technol.* 189 (1) (2017) 132–149.
- [27] EN ISO 6976, Natural Gas – Calculation of Calorific Values, Density, Relative Density and Wobbe Index from Composition, 2005.
- [28] EN 437, Test Gases, Test Procedures, Appliance Categories, 2009.
- [29] BS 7967, Guide for the Use of Electronic Portable Combustion Gas Analysers for the Measurement of Carbon Monoxide in Dwellings and the Combustion Performance of Domestic Gas-fired Appliances, 2015.