

EFFECTS OF SILICA DEPOSITION ON THE PERFORMANCE OF DOMESTIC EQUIPMENT IN THE NETHERLANDS

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Abstract

The effects of silica deposition on the performance of domestic appliances have been studied. Experiments on domestic boilers having different type of heat exchangers show that a large quantity of the silica particles formed in the flame deposit in the heat exchangers. The growth of the silica layer with time results in an increasing flow resistance over the heat exchangers and, as a consequence, a reduction of the boiler's thermal output. The degree of reduction in the thermal output strongly depends upon the configuration and material of the heat exchangers studied. Furthermore, the experiments reveal that the current measured in the ionization safety devices decreases in time due to silica deposition on the ionization probe, which ultimately results in boiler failure. Silica deposition in the studied hot water heater leads to an increased flow resistance across the heat exchanger. Consequently, the air intake from the surroundings reduces, and the CO emission increases over time. Analyses of the measurements show that the time to failure of the ionization device, the reduction in the thermal output of the boiler and the increased CO emissions of the hot water heater do not scale linearly with the concentration of siloxanes in the fuel. This effect is attributed to an increased density of the deposited silica at decreased siloxane concentrations.

Introduction

One of the renewable resources that can replace natural gas as fuel in combustion equipment is biogas. Biogases from fermentation (manure and/or biomass), landfill and waste contain mainly CO₂ and CH₄. However depending on the source, biogas contains varying quantities of contaminations such as halogenated compounds, sulfur compounds and volatile organic compounds, including organic silicon compounds [1-3]. These components, which are not found in traditional distributed natural gases, can have adverse effects on the integrity of the infrastructure, the safety and performance of end-use equipment. Therefore before injecting biogases into the natural gas grid biogases have to be upgraded by removing contaminants up to the level that should guarantee the safety and performance of end-use equipment.

Siloxanes, organic silicon compounds, and other silicon-containing compounds that are found in many types of biogas deserve special attention. Upon combustion, siloxanes are converted to silicon dioxide (silica, SiO₂) particles [4], which are known to deposit in gas turbines and engines [2, 5]. In gas appliances for heating and hot water preparation, silica particles may deposit on for example the heat exchanger and can cause deterioration in the performance [2, 6]. Gas appliances with narrow channels in the heat exchanger are expected to suffer adverse effects most quickly. 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 for example 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 (one of) the most sensitive applications to silica clogging caused by siloxanes. Moreover,

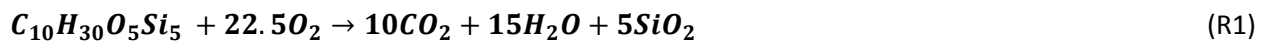
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any silica particles formed that are not deposited in combustion equipment are expelled into the air. Since combustion-generated silica particles smaller than 100 nm have been reported in the literature [e.g. 4, 7-11] the particles exhausted could contribute to the environmental burden of ultrafine particles.

In this study the deposition processes of silica in appliances and their consequences for appliance performance is examined in five domestic heating boilers having different configurations of the heat exchanger. Furthermore the effects of silica deposition in a flow-through water heater are studied. Given that silica is formed in the flame front [4], special attention is given to the effects of silica deposition on the performance of the ionization safety device. In addition, the effects of clogging of the heat exchanger on the efficiency, thermal output and on the CO emission have been studied. To test the concentration dependence the tests have been performed by using different fractions of siloxanes in the fuel.

Combustion of siloxanes in methane/air flames

Two types of siloxanes are used; L₂ (C₆H₁₈Si₂O) and D₅ (C₁₀H₃₀O₅Si₅) are used in this study. As an illustration the overall oxidation reaction of D₅ is shown below (R1).



It should be noted that reaction R1 is an overall representations of a chain of chemical processes [9, 14], similar to those in hydrocarbon oxidation. According to equilibrium calculations all silicon present in siloxanes should be converted to either SiO or SiO₂ upon combustion; after cooling all silicon should be present in the form of SiO₂(s). Silica yield experiments described in Ref. [19] show that the experimental yield of silica deposition was 89% for the conditions of the experiments. Given the experimental uncertainties, we assume that all silicon is converted to SiO₂(s).

Experimental

To study the deposition processes and their consequences for the performance of appliances, 5 modulating, condensing lean-premixed domestic boilers with a thermal load of about 20-25 kW, are used in this study. These types of boilers are commonplace in the Netherlands. Two of the domestic boilers selected have tubular stainless steel heat exchangers: one has rows of tubes and the other is a concentric cylindrical wound-tube heat exchanger. The three other boilers have aluminum heat exchangers: two have a lamella-type heat exchanger and the other has finned tubes, with fine channels. Table 1 shows an overview of the characteristics of the appliances studied in this work.

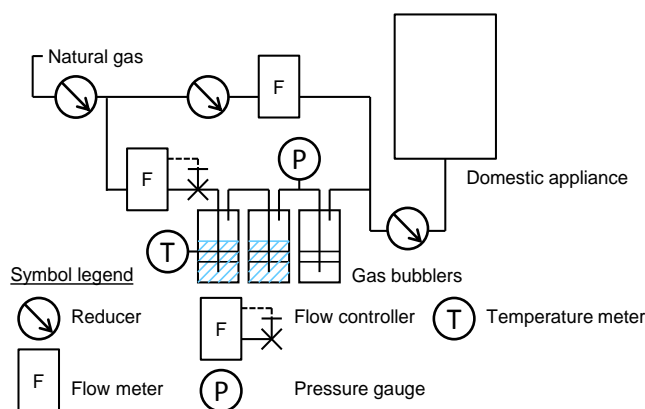
Table 1: Characteristics of the appliances used in this study

Appliance no.	Type	Max. Load, kW	Type heat exchanger	Material heat exchanger
1	Boiler	20	Lamella	Aluminum
2	Boiler	25	Tubes	Stainless steel
3	Boiler	25	Lamella	Aluminum
4	boiler	25	Concentric tube	Stainless steel
5	Boiler	25	Finned tubes	Aluminum
6	Hot-water-heater	28	Lamella	Stainless steel

The silica formed in the boiler can either be expelled via the air or the condensate. To collect the particles that have passed the heat exchanger before they are expelled into the air a High Efficiency Particulate Air (HEPA) filter is installed in the exhaust of one of the boilers that have a lamellar aluminum alloy heat exchanger. The filter is weighted before and after each experiment using a mass balance. Prior to weighing, the filters are dried in an autoclave at $\sim 50\text{ }^{\circ}\text{C}$ for about 48 hours. To complete the mass balance the condensed water that passes the siphon is collected, evaporated and the residue is weighted to determine the mass of silica that ends up in the condensate.

The sixth type of domestic appliance used in this study is a domestic 29 kW hot water heater. Before entering the burner the fuel in the hot water heater is partially premixed with air (the “primary” air). To complete the combustion a second flow of air (“secondary” air) enters the flame via diffusion during combustion. Given that clogging of the heat exchanger by silica may increase the flow resistance and reduce the flow of air to the appliance, we measured the oxygen and CO fraction in the flue gases of both the boilers and the hot water heater 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). The overall equivalence ratio is calculated based on the measured oxygen fraction in the flue gases.

Figure 1 shows the gas handling system used during the experiments to introduce siloxanes in natural gas. During the measurements the natural gas flows are measured using Bronkhorst EL-FLOW mass flow meters. Either L_2 or D_5 was added to the natural gas flow using gas bubblers. The temperature and pressure in the gas bubblers were measured during the experiment. The first two bubblers are filled with liquid L_2 or D_5 , while the last bubbler is kept empty to capture and prevent any liquid L_2/D_5 from entering the gas line to the domestic boiler. The L_2 or D_5 concentration in the fuel was varied by controlled mixing of the fuel leaving the bubblers with pure natural gas.

**Figure 1: Gas handling system to introduce siloxanes (L_2 or D_5) in natural gas**

Results and Discussion

Consequences silica deposition in domestic heating boiler 1

From the experiments performed in boiler 1 using different concentrations of siloxanes it follows that the yield of silica that "sticks" to the (lamellar) heat exchanger is about 94% and the other 6% was found in the HEPA filter installed on top of the chimney. Moreover, the experiments show that within the accuracy of the measurements the fraction of the silica that is deposited in the boiler is independent of the concentration of silica in the gas for the measured concentrations. In an independent study [16], the deposition process in the heat exchanger of the boiler has been modeled. The model predicts that more than 90% of the silica would deposit in the heat exchanger, consistent with our measurements. In agreement with literature [17] the model also identifies thermophoresis as the main deposition mechanism [16]. Since thermophoresis is independent of particle size for particles¹ <100 μm [18], the yield of deposition would remain constant, independent of the concentration, which is also in agreement with our (limited) experimental results.

To determine the impact of silica deposition on the performance (efficiency and load) of the domestic boiler having lamellar aluminum alloy heat exchanger, experiments were performed using different siloxane concentrations in natural gas, see also Table 2. Each experiment was continued until 50 grams of silica was produced (assuming 100% conversion of silicon to silica). During the start of each experiment the boiler was fixed at a thermal load of approximately 18 kW. During normal operation of the appliance, without siloxane admixture, the natural gas flow and thus the thermal load remains constant in time. However, as is illustrated in Figure 2 for experiment C (Table 2) a decrease in thermal output is observed when siloxanes are present in the fuel. This decrease in thermal output is caused by clogging of the heat exchanger resulting in an increased flow resistance, which (given the control system that varies the fuel input linearly with the air flow) will reduce the fuel flow and consequently the thermal output of the boiler in time.

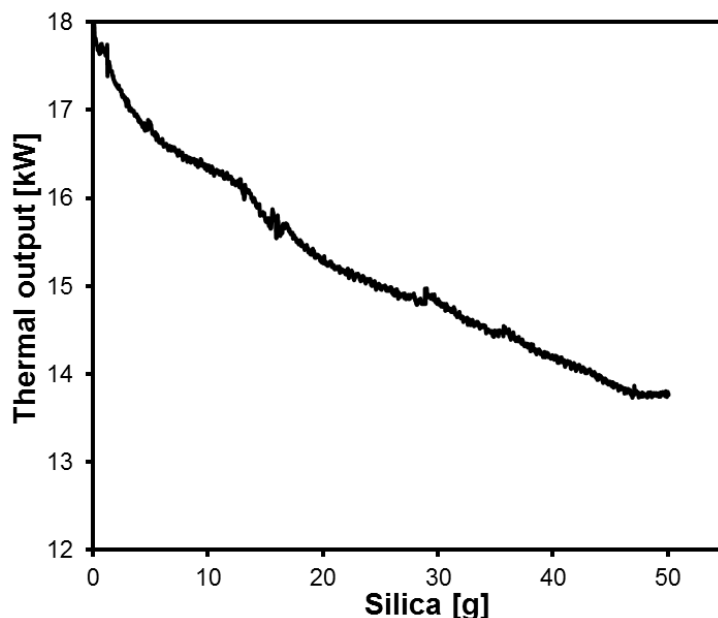


Figure 2: Thermal output as a function of the amount of silica produced for experiment C.

As can be seen from Table 2, lowering the siloxane fraction in the fuel results in a smaller reduction in the thermal output for the same amount of silica (50 g) produced. During the experiments no increase of CO emission was observed, which is expected since the fuel-to-air ratio is kept constant by the control

¹ In Refs [4, 16 and 4] it was shown that the silica particles and silica fractal-like aggregates formed in methane/air flames are smaller than 100 nm

system of the boiler. Here we remark that for boilers that do not have a control systems to keep the fuel-to-air ratio constant clogging of the heat exchanger can result in an increase in the CO-emission.

In Ref. [6] the dependence of the density of the silica layer formed in boiler 1 on the siloxane fractions in the fuel (table 2) is quantitatively studied by the analyses of SEM micrographs taken from samples of silica deposition layer cross-sections at different positions in the heat exchanger. The results show a reduction in the measured density of the silica layer with increasing siloxanes fraction in the fuel. As a result, if a fixed mass of silica deposits on an area in the heat exchanger the density will determine the silica layer thickness; a less dense and thicker layer increases the flow resistance more compared to a denser, thinner layer. From this observation we conclude that the non-linear behavior of the reduction in thermal output with siloxanes concentration (Table 2) in the fuel is attributed to changes in the density of the silica layer formed.

Table 2: Experimental results with different siloxane concentrations. Total amount of silica produced is 50g.

Exp.	Conc. [mg Si/m ³ _n] (siloxane type)	Time [h]	Thermal output reduction, [%]	Thermal reduction per gram of silica [%/g]
A	33.2 (D5)	440	20.6	0.41
B	56.3 (L2)	269	24.3	0.49
C	264.0 (L2)	58	26.6	0.53
D	1056.0 (L2)	14.5	33.3	0.67

The boilers studied have a combined ignition and ionization probe positioned close to the burner surface. This probe both ignites the premixed natural gas/air mixture during startup, and monitors the continual presence of the flame by measuring the ionization current through the flame. When the current has fallen below a limit value (e.g. 1 μ A in boiler 1) the boiler shuts itself off. To determine the impact of silica deposition on the ionization probe the current in the ionization safety and ignition device was measured in time during the experiments. Figure 3 shows the ionization current as a function of time for experiment D. At the high siloxane fractions of experiment D a boiler failure occurs after 1.2 operating hours because the ionization current has decreased to the point (1 μ A) at which the flame-detection safeguard is activated. After boiler failure had occurred the ionization probe was removed and replaced. After replacement with a new probe the measured currents were similar to the values before siloxanes were added. This shows that the silica layer on the ionization probe has an electrically insulating effect, which is responsible for the lowering of the ionization current.

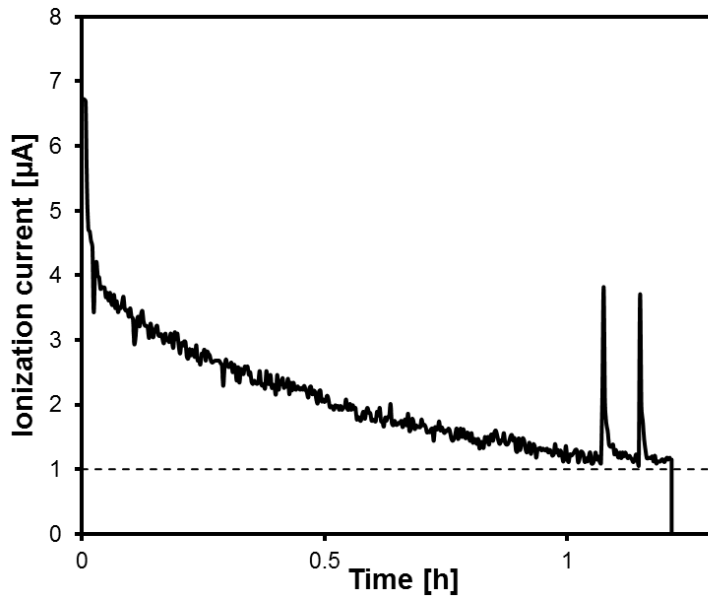


Figure 3: Ionization current as a function of time for experiment D. Dotted line shows the critical value at which the appliance fails.

The concentration dependence of the time to failure of the ionization probe experiments is studied by performing experiments with different siloxane concentrations in the fuel; 13.8 mg Si/m³_n, 56.3 mg Si/m³_n, 264 mg Si/m³_n and 1056 mg Si/m³_n. As expected, the results presented in Figure 4 show that the time to failure increases by lowering the siloxane concentration. However the concentration dependence is not linear; the time to failure increases (exponentially) for the same mass of silica produced.

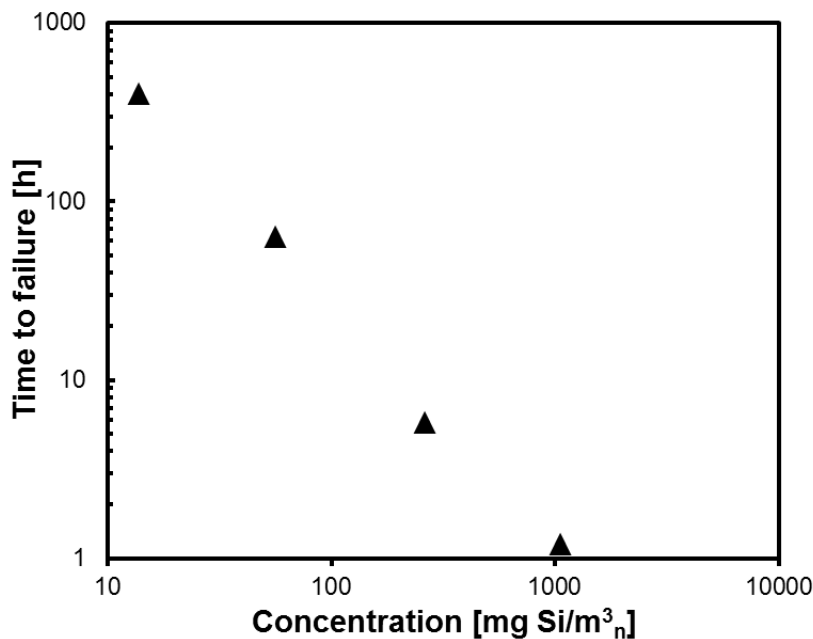
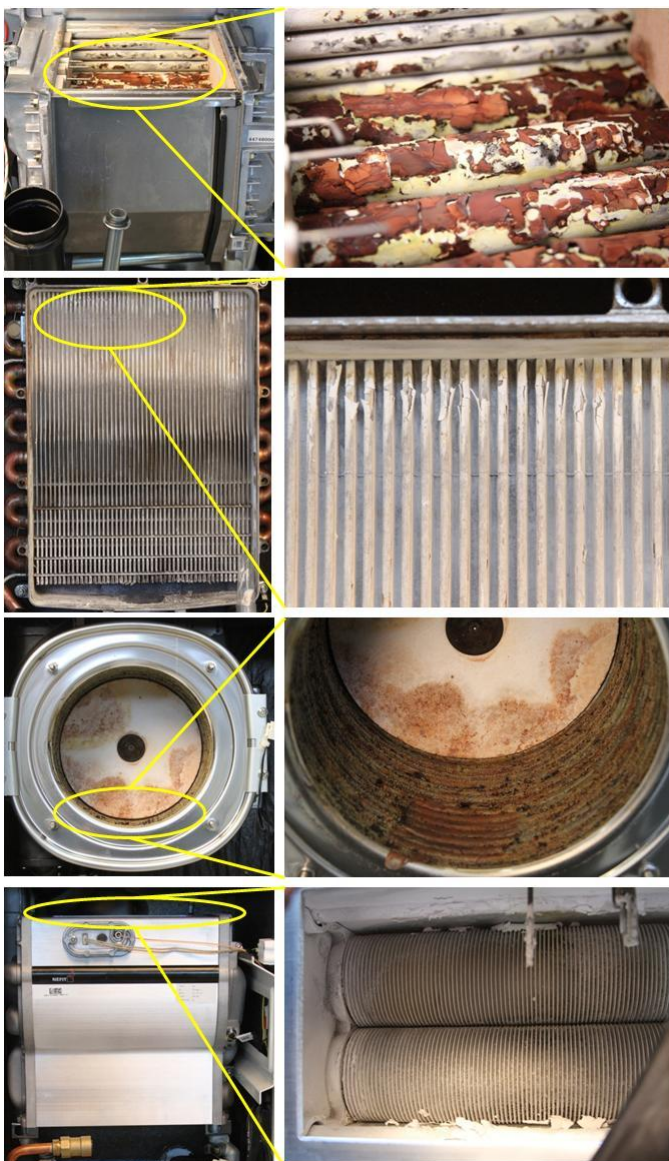


Figure 4: Time to failure of the ionization probe as a function of initial siloxane concentration in natural gas

Consequences silica deposition in domestic heating boilers 2-5

To study the effects of the clogging of heat exchangers by silica deposition, experiments in four domestic appliances with different configurations of the heat exchanger have been studied. Figure 5 shows the photographs taken after the experiments, described below, of the four selected heat exchangers. During the experiments, the boilers operated continuously for 850 hours on Dutch natural

gas at full load. Given that the average thermal load of the appliance is about 25 kW, 850 hours of continuously operation means a Dutch natural gas consumption of about 2360 m³ (equivalent to 1.6 year of annual use). A siloxane concentration of 7.5 mg Si/m³_n (corresponding to 1.2 ppm D5) is chosen for these experiments, which is expected to give a measurable degradation in the performance of the boiler within the duration of the experiment. Boiler failure occurs when the ionization current has decreased to the point at which the flame-detection safeguard is activated, as discussed above. After failure, the ionization probe was replaced. After 850 hours, the heat exchangers and ionization probes were examined; a layer of silica was observed on these parts in all 4 boilers. From Figure 5 it can be seen that in some cases a brown deposit had formed on the heat exchanger. It should be noted that the brown deposition seems more pronounced in the appliances with stainless steel heat exchangers. An EDS analysis taken from the stainless steel heat exchangers shows that the brown deposition consists primarily of silicon and oxygen atoms in the ratio 1:1. Also small fractions of iron and nickel are measured. The brown particles are also discussed [9] where it was assumed to be a mixture of Si, SiO and SiO₂.



Domestic boiler 2: Stainless steel tube heat exchanger

Domestic boiler 3: Aluminum lamella heat exchanger

Domestic boiler 4: Stainless steel concentric tube heat exchanger

Domestic boiler 5: Aluminum finned tubes heat exchanger

Figure 5: Photographs taken after the experiment with 7.5 mg Si/m³_n of the four selected heat exchangers Ref. [19]

Regardless of the appearance or composition of the deposit, the deposition in the heat exchangers led to an increased flow resistance in time, which in turn led to a decreased thermal output of the

appliances. In Table 3 the reduction in thermal output after 850 hours of operation of each of the appliances is presented. From Table 3 it can be seen that boiler 2 has the largest reduction, 63%, followed by boiler 4 (25.5%), boiler 3 (11.5%) and boiler 5 (2.5%). Given the large open spaces between the tubes in the heat exchanger of boiler 2, we had naively expected that this heat exchanger would be least susceptible to clogging, in contrast to the experimental results (Table 3). Examination of the heat exchanger shows that a thin layer of deposit is formed around the tubes. Eventually, the thin layer breaks off (resembling chipping paint) and large flakes are deposited on top of the next row (downstream) of tubes, effectively blocking the open spaces between the tubes. As a result, the flow resistance increases. Here we remark that this clogging mechanism is fundamentally different from the finned and lamellar heat exchangers. In light of both the apparent difference in structure of the deposited material, and the very strong effect on appliance performance at low siloxane concentrations, we recommend studying the depositions mechanism in appliances with stainless steel heat exchangers in more detail.

From Table 3 it can be seen that boiler 5 has the smallest reduction in thermal output. Inspection of the heat exchanger of boiler 5 showed substantial silica deposits on the cold sidewalls of the heat exchanger, which is attributed to circulation of combustion gases within the combustion chamber with thermophoretic transport to the walls [18]. From this observation we conclude that much of the silica is already removed before entering the (finned) heat exchanger, consistent with the only limited reduction in thermal output (Table 3).

Table 3: Results of experiments with concentration 7.5 mg Si/m^3_n in natural gas in boilers 2, 3, 4 and 5

Appliance	Concentration	Time	Thermal output reduction	Amount of silica formed in boiler	Thermal output reduction per gram of silica
[-]	[mg Si/m^3_n]	[h]	[%]	[g]	[%/g]
Boiler 2	7.5	850	63.0	23.5	2.68
Boiler 3	7.5	850	11.5	43.3	0.27
Boiler 4	7.5	850	25.5	35.5	0.72
Boiler 5	7.5	850	2.5	35.8	0.07

To determine the impact of silica deposition on the ionization probe, the time to failure of the ionization safety device was determined for each boiler (Table 4). From this table it can be seen that there is a direct relation with the initial current (at the start of the experiment) of the ionization safety device and the time to failure; boiler 3 has the smallest time to failure and has the smallest initial current ($7 \mu\text{A}$) while boiler 5 did not fail during the experiment (850 hours), and has the largest initial current ($30 \mu\text{A}$). Unfortunately, we were not able to measure the current of the ionization safety device of boiler 4.

Table 4: Results of the time to failure of the ionization probes in boilers 2, 3, 4 and 5

Appliance	Concentration	Initial current	Time to failure ionization probe	Yield of SiO_2 at time of failure
[-]	[mg Si/m^3_n]	[μA]	[h]	[g]
Boiler 2	7.5	16	395	13.8
Boiler 3	7.5	7	120	6.5
Boiler 4	7.5	unknown	697	28.8
Boiler 5	7.5	30	>850	>35.8

Domestic flow-through hot water heater

To determine the influence of clogging by silica particles on the CO emissions of a domestic hot water heater, experiments were performed with L₂ siloxane concentrations in natural gas as shown in Table 5.

Due to the clogging of the heat exchanger, the aeration of the hot water heater was reduced. The decrease in excess air factor increased the CO emissions from the appliance. The CO emission in the exhaust of the hot water heater is shown in Figure 7 as a function of the amount of silica produced during the experiments.

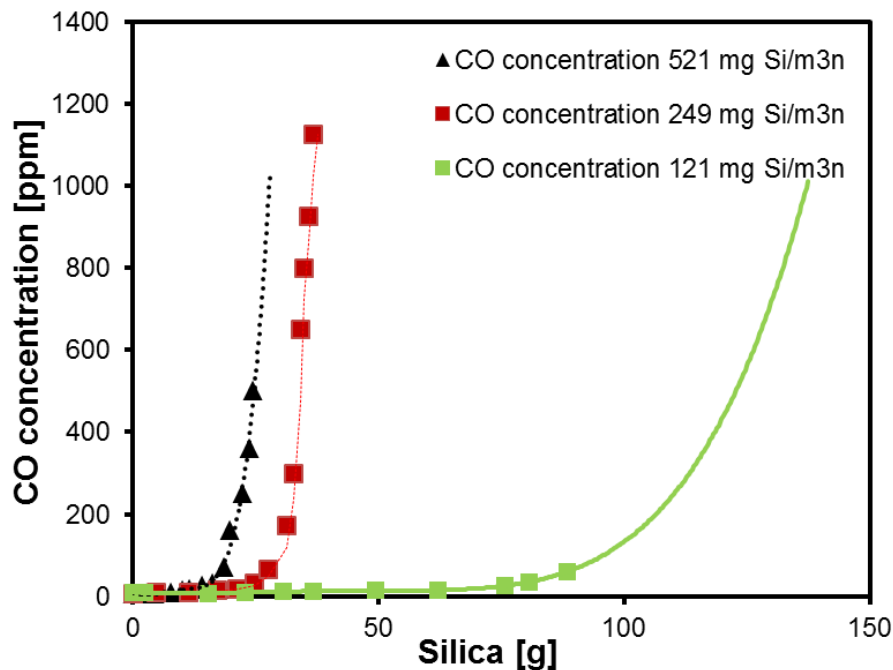


Figure 6: The CO emission for experiments E-G as function of the amount of silica produced

In Figure 6 it can be seen that the CO emission rises exponentially for each of the different concentrations. The maximum allowable CO concentration in the flue gases for domestic heating appliances is 1000 ppm (specified in the EU-approval standards for the individual appliances). Although 1000 ppm is allowed we note that this is substantially higher than the ~25 ppm that this appliance normally emits. This value (1000 ppm) was reached after 22.5 hours of operation and 36 g of silica produced for experiment F (Table 5). For experiment G the 1000 ppm CO limit could not be reached because the CO concentration in the surroundings had risen to 25 ppm (above the permissible exposure limit) and for safety reasons the experiment was aborted. Experiment E was also stopped before the 1000 ppm value could be reached due to time limitations. Therefore, CO emissions for the experiments E and G were extrapolated up to 1000 ppm CO as indicated in Figure 7. It should be noted that the excess air ratio decreased linearly during the experiment.

Table 5: Time and produced amount of silica at emissions of 1000 ppm CO

Exp.	L2 concentration [mg Si/m ³ _n]	Time to 1000 ppm CO [h]	Silica produced [g]
E	121	197.8	137.0
F	249	22.5	36.0
G	521	8.7	27.8

Table 5 shows the amount of silica produced when 1000 ppm CO is measured for the three siloxane concentrations. From Table 5 and Fig. 7 it is clearly seen that by lowering the siloxane concentration

substantially more silica must be produced to reach the 1000 ppm CO limit value. This nonlinear behavior, as also discussed for boiler 1, is assumed to be related to the density dependence of the silica layer in the heat exchanger with the concentration of silicon in the fuel.

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