A STUDY OF CORROSION IN BALANCED FLUES DEPENDING ON OPERATION CONDITIONS

Bjarne Spiegelhauer, Danish Gas Technology Centre
Per Persson, Hovedstadsregionens Naturgas (Greater Copenhagen Natural Gas)
Marius Kildsig, Danish Gas Technology Centre

1. INTRODUCTION

The Danish natural gas companies have carried out a series of random sample inspections of flues on 500 domestic gas boilers to ascertain their condition regarding blockage and corrosion. The investigation showed that many flues were corroded and choked up in varying degrees. Subsequently, we have carried out a model calculation to establish whether operation conditions have an effect on the problem.

2. BACKGROUND

In the autumn 2000 the Danish natural gas companies initiated a project regarding corrosion and blockage of primarily aluminium flues from domestic boilers with closed combustion chamber. The purpose of the project was to investigate whether the sporadic reports about blockage in aluminium flues were isolated incidents or whether it was a general problem.

The proposal identified a number of interesting types of flue to investigate as well as a procedure for carrying out this investigation.

The results of the random sample inspection were closely followed by Danish Gas Technology Centre, the gas companies and the Danish gas authorities.

Figure 1: Example of corrosion in horizontal balanced flue

It turned out that approx. 11% of the flues showed serious signs of corrosion, and approx. 22% had begun to choke up. It was remarkable that systems with a horizontal balanced flue had problems more often than systems with a vertical balanced flue.

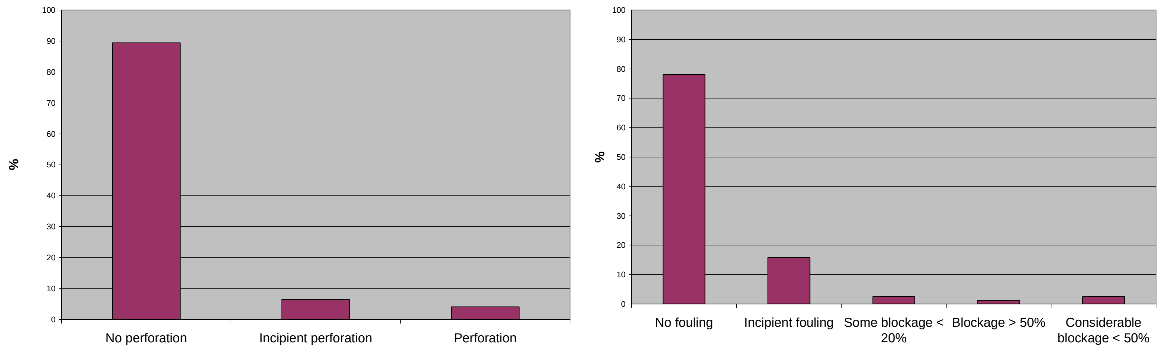

Figure 2: Corrosion and blockage

Another result of the investigation was that the gas consumption of the installation rather than the age of the installation would have an effect on corrosion. It was obvious that installations, where the exhaust air was led via an existing chimney, were more prone to corrosion problems.

Even though the main focus of the investigation was aluminium flues, it also covered stainless steel flues. As could be expected, stainless steel flues showed no signs of blockage, but - surprisingly - there were signs of corrosion.

When aluminium flues are corroding the aluminium oxide swells and causes fouling and blockage, whereas stainless steel flues are corroding by way of “pin holes” in the pipe rather than an even corrosion.

	Blockage	**Corrosion**
Flue material	Aluminium flues are much more choked up than stainless steel	Aluminium is slightly more inclined to corrode than stainless steel
Type of flue	Horizontal balanced flues are more likely to foul than vertical balanced flues	No noticeable influence
Gas consumption	Only slight influence	A growing influence
Year of installation	No influence	No influence
Number of bends	Some influence	No influence
Length of flue	A growing influence	A growing influence

Table 1: Various parameters’ influence on blockage and corrosion

3. ANALYSIS OF THE CORROSION PRODUCTS

Prior to this investigation corrosion problems were already known and several analyses of corrosion products had been made. Since these analyses showed different compositions of corrosion products, this time we chose to analyse the corrosion products from some of the flues inspected.

Six samples from three different installation configurations were selected for analysis. The samples were analysed by FORCE Institute using a procedure that is able to quantify the element boron (B) and heavier atoms.

These analyses showed that the corrosion products from aluminium flues contain nitrogen (N), oxygen (O), zinc (Zn), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P) and sulphur (S). In addition, one sample contained traces of chlorine (Cl).

The main elements of the analysed corrosion samples were oxygen, aluminium, sulphur and nitrogen. On average these elements made up approx. 99% of the samples on a mole basis and 98% on W/W basis. The average composition is shown in Table 2.

Element	W/W %
N	1.78
O	61.56
Zn	1.22
Mg	0.07
Al	26.22
Si	0.13
P	0.40
S	8.62

Table 2: Average of analysis results

Figure 3 shows the variation of the composition of main elements in the individual samples regarding aluminium, sulphur, oxygen and nitrogen. Figure 4 shows the corresponding variation regarding trace elements. The types are: Type 2: Takes air from chimney, Type 10: Horizontal balanced flue, Type 12: Vertical balanced flue.

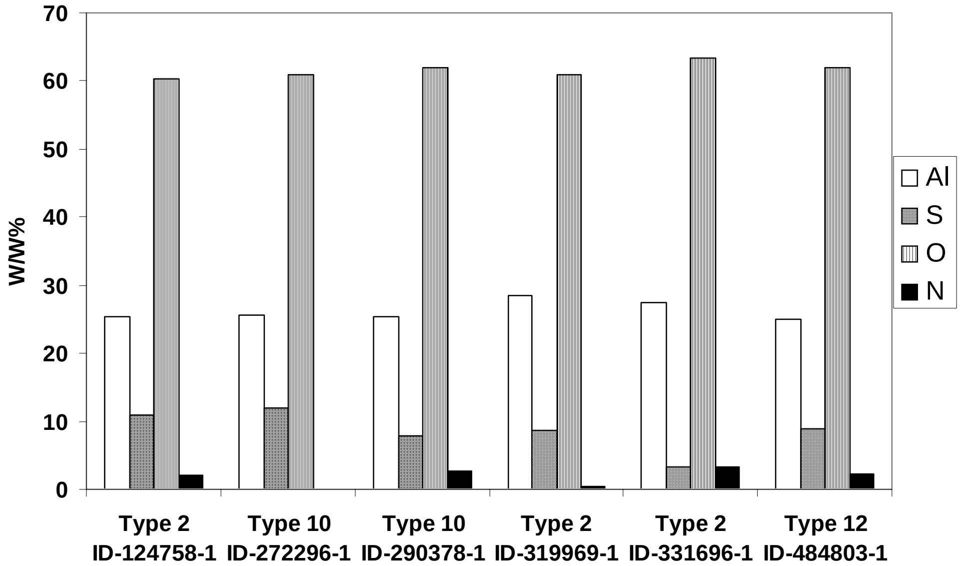

Figure 3: Analysis results for main elements. Type refers to the flue types defined.

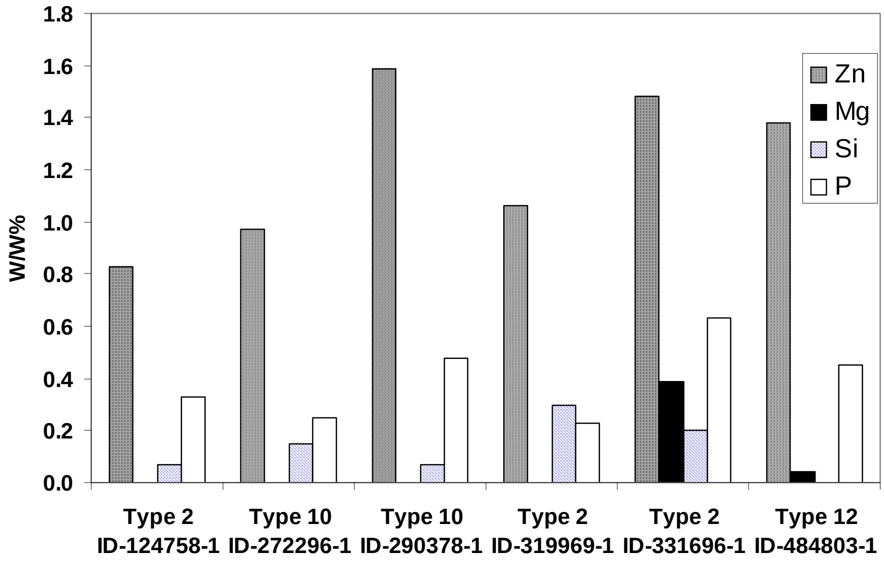

Figure 4: Analysis results for trace elements. Type refers to the flue types defined.

On the basis of the analysis results the chemical composition of the samples can be estimated. The samples primarily consist of aluminium salts ((Al_2O_3/$Al(OH)_3$, $Al_2(SO_4)_3$ og $Al(NO_3)_3$ and bound crystallization water. Crystallization water is water that is bound in its chemical structure and, therefore, will not evaporate during drying of samples. In addition, the samples contained small amounts of zinc, phosphorus, magnesium and silicon. All these elements are most likely to come from the original aluminium pipe.

Normally, aluminium is not considered a precious metal. Based on the general characteristics of the metal it would be expected to be water-soluble. However, aluminium reacts fast with the oxygen of the air, and the ensuing oxide film on the surface protects the subjacent metal. This phenomenon is called passivation of metal. In acidic and alkaline solutions the protective oxide film is dissolved and the metal is exposed to further corrosion caused by the oxygen or water from the flue gas. Due to its oxidising characteristics, pure nitric acid is not known to dissolve aluminium.

So, it is likely that the flue will corrode and choke up because of sulphuric acid and nitric acid condensation on the surface. These acids will dissolve the protective oxide film and make it possible for the oxygen of the flue gas to corrode the aluminium surface. The variations from installation to installation are probably caused by variations in each installation's tendency to condense acid on the flue. This was, at a first stage, attributed to differences in the boiler operation strategy (frequent start/stop, short operation periods vs. few long operation periods) and to differences in the cooling profiles of different flues.

4. CONCLUSION AND DISCUSSION OF THE RANDOM SAMPLE INSPECTION

The random sample inspections carried out showed that corrosion and fouling/blockage of aluminium flues is a general problem. Since the inspections also covered installations with stainless steel flues, this type was also included in the analysis.

It should be noted that the major part of the installations inspected had horizontal or vertical balanced flues, which are the type of flue that are most commonly used for gas installations. However, apart from those two types of flue, the inspection also covered a number of variations (18) of flues, including types where the exhaust air was led via an existing chimney.

Approx. 10% of the horizontal flues and approx. 12% of the vertical flues were corroded. In addition, it was registered that approx. 19% of the horizontal flues were beginning to get blocked, whereas only approx. 12% of the vertical flues showed signs of blockage.

Approx. 78% of the flues, where the exhaust air was led via an existing chimney, were blocked, and approx. 6% of those flues were corroded. In spite of the relatively small number of this type included in the investigation the tendency is fairly clear.

The investigation further showed that bends cause blockage of the flue, or perhaps rather that the fouling can choke up and not fall directly into the boiler. The results showed that 11% of the flues with two or more bends as opposed to 5% of the flues without bends showed signs of blockage.

It appears from the investigation that whereas the year of installation of the gas boiler does not have any significant influence on the blockage of the flues, there is a direct correlation between the gas consumption of the boiler and blockage.

From the start the flue systems, where the exhaust air was led via an existing chimney, were suspected to have sulphur deposits in these chimneys due to previous oil firing and these deposits were suspected to be carried along by the combustion air.

However, nothing supported this theory. The amount of sulphur oxide was not bigger in the corrosion products from those boilers. It is likely, then, that condensation of sulphuric acid and nitric acid on the surface will cause corrosion and blockage damages to the flue.

The results of this investigation indicated that flues from boilers with closed combustion chambers will have some corrosion irrespective of the material of the flue being stainless steel or aluminium. However, fouling and ensuing blockage was only found in aluminium flues.

5. SAFETY ISSUES

Fouling and blockage of the flue do not constitute any big safety hazard if it is a balanced flue in concentric pipes. If these types of flue get blocked the boiler's air-flow failure device will cut off the boiler. If the flue pipe gets perforated the flue gas will be recirculated to the combustion air; this will in the long term result in lift-off resulting in safety shut-off of the boiler.

In the case of flue systems, though, where exhaust gases and combustion air were led in separate pipes (split or balanced flue), perforation of the pipe caused by blockage might lead to flue gasses entering the dwelling, resulting in a CO poisoning risk. In general, we recommend to thoroughly inspect both the abovementioned types of flue system for corrosion and incipient blockage. It is most important, though, to have regular inspection of split flues.

For the time being there is no requirement for periodic inspection on boilers with closed combustion chamber. Therefore, it is very uncertain whether a defective flue will be detected in time. Furthermore, it may be difficult to find out whether a flue has begun to get blocked, as, in general, there are no cleaning and inspection possibilities on these flues, apart from disconnecting the pipes.

Several countries have requirements for cleaning and inspection possibilities on this type of gas boiler flues and the boiler suppliers already stock products that can be mounted on Danish boiler flues. In order to avoid any hazardous incidents relating to safety on domestic gas boilers with closed combustion chamber the authorities might consider introducing requirements for cleaning and inspection doors on all new installations and recommending the consumers to retrofit them on existing installations on one's own account. Furthermore, the authorities should consider introducing requirements for periodic inspection on all domestic gas boilers with closed combustion chamber and split flue with the flue gas pipe running in the dwelling - and not inside the combustion air pipe. Finally, in the case of new installations, they should consider to prohibit leading the exhaust air via an existing chimney

6. MODELLING OF SULPHURIC ACID CORROSION IN ALUMINIUM FLUES

The random sample inspection showed that aluminium as well as stainless steel flues from gas boilers can have problems with corrosion. The investigation clearly showed that aluminium flues had more problems than stainless steel flues: 35% of the inspected 352 aluminium flues had either blockage problems or corrosion problems, whereas only 6% of the 127 inspected steel flues had similar problems. The random inspection indicated that the corrosion was caused by the sulphur content of the natural gas. Following these findings the Danish gas companies initiated a further analysis of the causes of the corrosion of the aluminium flues.

The analysis showed that, as a first stage, sulphuric acid would condense in a normal standard flue and that, under the right conditions, this sulphuric acid would cause corrosion in aluminium flues. On this background, a mathematical model based on mass flow and energy balances was worked out. In addition, the model used a boundary layer theory that primarily is based on equilibrium curves between the acid/water film and the SO_3/water content of the air. This boundary layer theory was used to calculate the acid condensation.

We used a boiler with a closed combustion chamber as a standard case for the calculation. Table 3 shows the characteristics of this boiler.

Nominal effect	20 kW
Flue gas temperature from the boiler	200°C
Air excess	1.3
Start/stop frequency	2 min. (on) 8 min. (off)
Length of flue	5 m
Inner/outer diameter	0.06/0.1 m
Sulphur content of natural gas	10 mg/m^{3}n (4 mg S - H_2S, 6 mg S - THT Danish natural gas)

Table 3: Characteristics of the boiler for the standard case

Figure 5 and Figure 6 show the results of the calculations of the standard case. Figure 5 shows the total amount of acid (SO_3) condensing on the aluminium surface during a period of 1 hour 40 min. Figure 6 shows the variation of the strength of acid in the film through the same period 0.01 m from the flue gas inlet. From Figure 5 it appears that the amount of acid condensate increases every time the boiler starts and that there is hardly any evaporation when the boiler has stopped. From Figure 6 it appears that the strength of the sulphuric acid varies during the boiler start/stop cycle. This varying strength of acid is caused by a temperature controlled condensation and evaporation of water from the acid film, respectively. The film is thickest at the lowest strength of acid - which means that the acid is more mobile. Figure 6 shows that the strength of acid is 50% when the boiler starts. At 50% strength of acid the sulphuric acid is slightly corrosive. As the temperature rises, the water evaporates and the strength of acid increases at the same time as the acid mobility decreases. At 80% strength of acid the acid is expected to be considerably corrosive but only slightly mobile. When the boiler stops, the strength of acid will change almost instantly from 80% to 90% without a corresponding drop in temperature. At this change it is expected that the corrosiveness of the sulphuric acid will decrease. When the boiler stops, the flue temperature and thus the acid film temperature will fall. Because sulphuric acid is hygroscopic it will draw water from the atmosphere at falling temperatures. When the boiler stops the strength of acid will decrease, which is also shown in Figure 6.

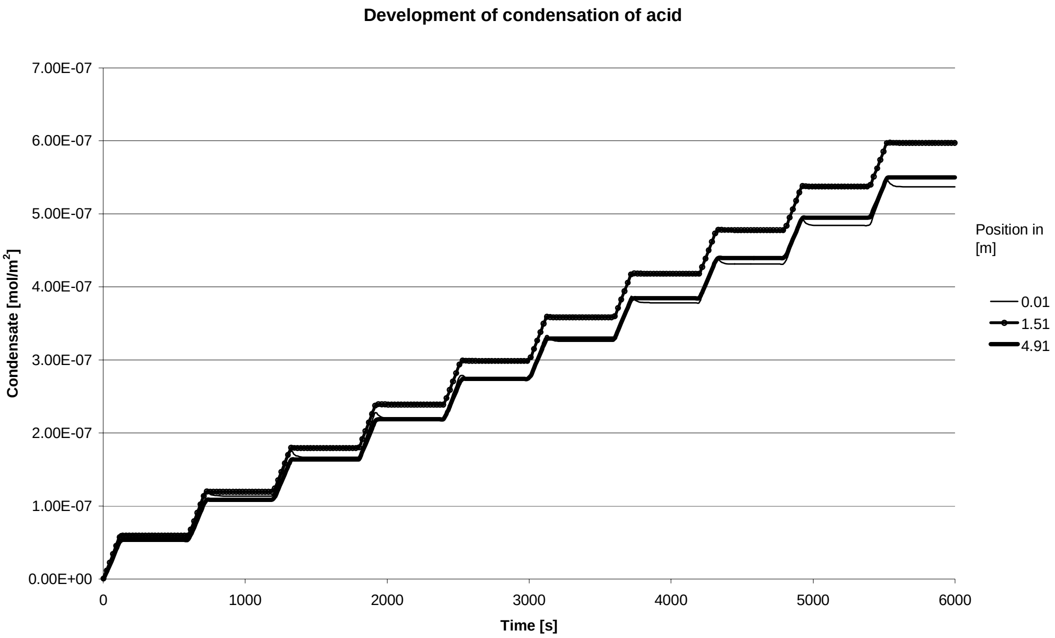

Figure 5: Total molar mass of SO_3 that has condensed on the aluminium surface of a standard flue during a period of 1 hour 40 min.

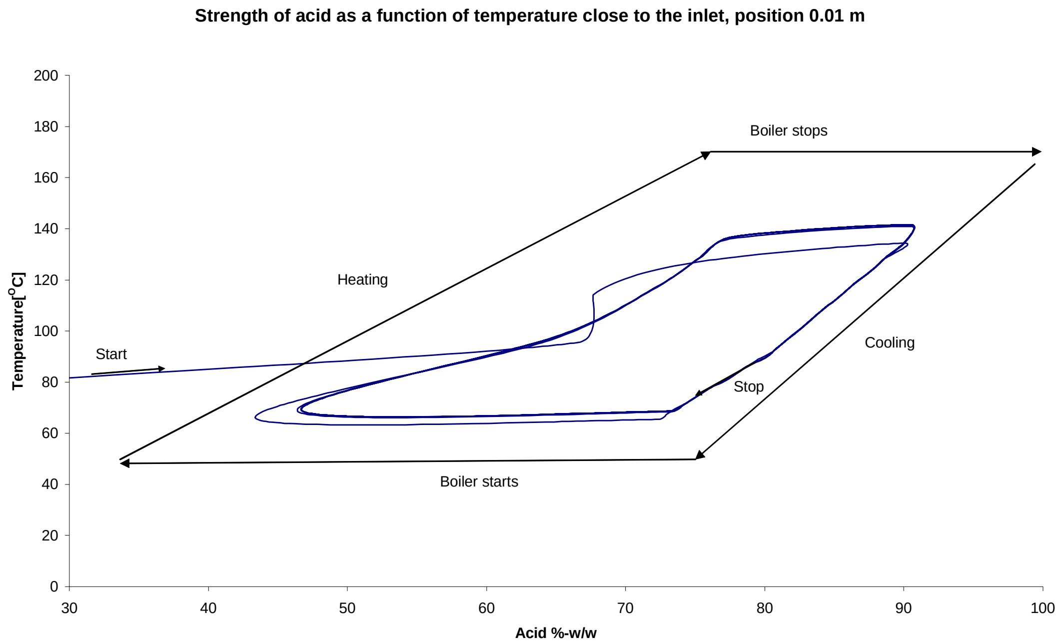

Figure 6: Mass ratio between water and acid in the acid film of a standard flue during a period of 1 hour 40 min.

A sensitivity analysis of the standard case showed that the condensed amount of sulphuric acid in the flue did not change significantly when parameters like air excess, λ, (1.6, 1.3), start/stop frequency, outdoor temperature (-10°C, 20°C), flue gas temperature (150°C, 200°C) and flue material (steel/aluminium) were changed. On the contrary, the analysis showed that the condensed amount of sulphuric acid increased when the sulphur content of the natural gas, the flue length and the gas consumption of the boiler increased. Based on the results of the sensitivity analysis we concluded that there is an approximately linear correlation between sulphur concentration in natural gas and the amount of condensed sulphuric acid.

In the standard case an acid film condenses evenly in the length of the flue, and the amount of acid increases gradually according to the operation time of the boiler, as shown in Figure 5. This means that the sulphuric acid has sufficient time to dissolve/corrode the aluminium flue. In practice, the amount of condensed sulphuric acid means that the film of sulphuric acid developed can only cause problems if either the acid or the corrosion products are accumulated in selected spots of the flue. The fact that the strength of acid varies with the start/stop cycle increases the risk that the acid accumulates in selected spots of the flue. Furthermore, the corrosion products are likely to accumulate in exposed spots of certain flues, since they tend to sift down and accumulate in the bends of the flue. It is estimated that both the effects mentioned above will influence the blockage/corrosion problems. The geometrical design of the flue, and other factors, will affect the velocity of a blockage/perforation process of the flue. In practice, the random inspection showed that blockage or perforation may occur after 3 to 10 years. Calculations showed that this will only occur if the acid/corrosion products do accumulate in selective spots of the flue.

7. CONCLUSIONS ON THE MODELLING STUDY

- Aluminium is a poor choice of flue material when acid condensation can occur.
- It is not possible to reduce the acid condensation by means of changing the way the boiler is operated
- The condensed amount of acid is approximately proportional to the gas consumption and the content of sulphur in the gas. One possibility of reducing the problem would be to reduce the content of sulphur in the natural gas. Danish natural gas contains approx. 4 mg S/m^3n and a further 6 mg S/m^3n is added for odorisation. Alternatively, corrosive-resistant materials could be used for flue material.

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