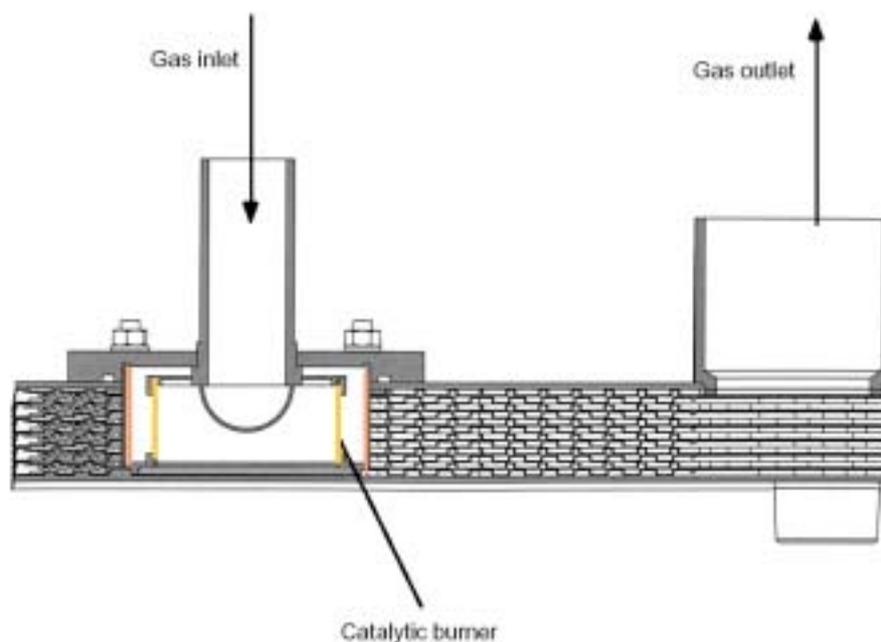


# Catalytic heat exchangers – a long-term evaluation

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Fredrik A. Silversand  
CATATOR AB

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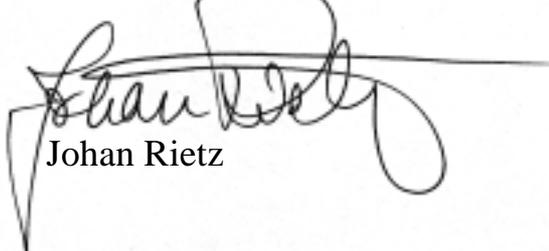
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SWEP International AB  
Sydkraft Gas AB  
Göteborg Energi AB  
Öresundskraft AB  
Lunds Energi AB  
AB Fortum Värme samägt med Stockholm stad  
Statens Energimyndighet

SVENSKT GASTEKNISKT CENTER AB



Johan Rietz

## Summary

A long-term evaluation concerning catalytic heat exchangers (CHEs) has been performed on the request of Swedish Gas Centre (SGC). The idea concerning CHEs was originally described in a number of reports issued by Catator almost a decade ago. The general idea with CHEs is to combust a fuel with a catalyst inside a heat exchanger to enable an effective heat transfer. The first design approaches demonstrated the function and the possibilities with CHEs but were defective concerning the heat exchanger design. Consequently, a heat exchanger company (SWEP International AB), which was specialised on brazed plate-type heat exchangers, joined the continued development project. Indeed, the new design approach containing Catator's wire-mesh catalysts and SWEP's plate-type heat exchangers enabled us to improve the concept considerably. The new design complied with a number of relevant technical demands, e.g.:

- Simplicity
- Compactness and integration (few parts)
- High thermal efficiency
- Low pressure drop
- Excellent emissions
- High turn-down ratio
- Reasonable production cost

Spurred by the enormous technical progresses, the importance of a long-term test under realistic conditions was clear. A long-term evaluation was initialised at Sydkraft Gas premises in Åstorp.

The CHE was installed on a specially designed rig to enable accelerated testing with respect to the number of transients. The rig was operated continuously for 5000 hours and emission mapping was carried out at certain time intervals. Following some problems during the initial phase of the long-term evaluation, which unfortunately also delayed the project, the results indicated very stable conditions of operation. The emissions have been rather constant during the course of the test and we cannot see any tendencies to decreased performances. Indeed, the test verifies the function, operability and reliability of the CHE-concept.

Apart from domestic boilers we foresee a number of interesting and relevant applications in heating and process technology. Since the Åstorp-CHE was installed, further improvements have been accomplished concerning emissions, operability and compactness. The CHE-concept has following a decade of development reached a milestone where a number of boiler manufacturers have shown their firm interest in the concept. Continued efforts concerning development, industrialisation and customisation are underway in order to put the CHE-concept on the market during the next few years.

## Sammanfattning

En långtidsutvärdering av katalytiska värmeväxlare har utförts på uppdrag av Svenskt Gastekniskt Center AB. Katalytiska värmeväxlare beskrevs ursprungligen i en serie rapporter från Catator för närmare ett decennium sedan. Katalytisk värmeväxling innebär att ett bränsle förbränns med en katalysator inne i en värmeväxlarestruktur. De första designförslagen påvisade funktion och tekniska möjligheter hos konceptet men också påtagliga brister avseende värmeväxlarnas konstruktion och funktion. Kontakt togs därför med ett värmeväxlareföretag som specialiserat sig på lödda plattvärmeväxlare (SWEP International AB). En ny design, som innefattade Catators katalytiska nät och SWEPs lödda plattvärmeväxlare, medgav signifikanta prestandaförbättringar. Den nya designen uppfyller sålunda en rad viktiga krav:

- Enkel konstruktion
- Hög termisk verkningsgrad
- Kompakt struktur med hög grad av komponentintegrering
- Lågt tryckfall
- Extremt låga emissioner
- Stort driftområde
- Rimlig produktionskostnad

I ljuset av de stora tekniska framstegen stod det klart att ett långtidstest behövde genomföras. Ett långtidsförsök startades därför i Sydkraft Gas lokaler i Åstorp. Den katalytiska värmeväxlaren installerades i en speciell rigg för att möjliggöra accelererade tester med hänsyn till antalet transienter. Försöket pågick kontinuerligt i 5000 timmar och emissionsmätningar genomfördes med jämna tidsmellanrum. Efter en del problem under den inledande fasen, som tyvärr också medförde projektförseningar, har försöket indikerat stabila driftförhållanden under hela perioden. Emissionsvärdena har varit stabila under utvärderingen och vi har inte kunna detektera några prestandaförsämringar. Långtidsförsöket verifierar således funktion, driftegenskaper och tillförlitlighet hos katalytiska värmeväxlare.

Förutom hushållsapplikationer förutser vi intressanta tillämpningsområden inom annan uppvärmning samt inom processindustrin. Ytterligare tekniska framsteg har gjorts i förhållande till den design som utvärderats i Åstorp med avseende på emissioner och effekttäthet. Efter nära ett decenniums arbete med katalytiska värmeväxlare har vi nu nått en milstolpe då vi lyckats attrahera åtskilliga pannstillverkare med den nya tekniken. Under den närmaste tiden kommer stora ansträngningar att ske avseende industrialisering och kundanpassningar i avsikt att nå marknaden inom några år.

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## 1. Introduction

A project concerning a long-time evaluation of catalytic heat exchangers (CHE) has been performed on the request of Swedish Gas Centre AB (SGC). The present CHE-design is a result of a co-operation between SWEP International AB and Catator AB, which was initiated during 1999. The principle of CHEs was originally treated in a number of reports issued by Catator during the period 1994 – 1997 [1-3]. These projects dealt with fundamental aspects and focused on system and catalyst development. A prototype unit was designed, constructed and evaluated.

The initial work clearly demonstrated the technical possibilities of the CHE-concept. The main problem was associated with the quality of the heat exchangers utilised at that time. Although the function of the CHE was satisfactory it was evident that a new type of heat exchanger needed to be developed in order to commercialise the product. The heat exchanger in the original design was a cross-flow heat exchanger, built for gaseous media at moderate operating temperatures. The catalyst consisted of plates/wire meshes, which were put into the channels of the heat exchanger.

Hence, a co-operative work was initiated with a heat-exchanger company (SWEP), which had specialised on brazed plate-type heat exchangers. Catator's wire-mesh catalysts (as cylinders) were successfully implemented into these heat exchangers and a simple and compact all-inclusive unit was developed.

There are really a number of advantages with catalytic heat exchangers:

- Simplicity and compactness
- System integration possible
- High thermal efficiency and quick thermal response
- Wide turn-down window
- Low emissions
- Fuel flexibility in the same design

The above statements are valid for the current design (SWEP-Catator) whereas the original design was more doubtful since the degree of integration was less. For instance, the original design needed a separate air-pre heater and a secondary combustion chamber. Also the emissions, although clearly acceptable at that time, were much higher in comparison to the present design. The original specification of demands stated that the emissions should be lower than the values listed below at any load of operation:

- Nitrogen oxides (NO<sub>x</sub>), < 10 ppm (v/v)
- Carbon monoxide (CO), < 50 ppm (v/v)
- Unburned hydrocarbons (UHC), < 50 ppm (v/v)

In order to derive one single expression for the emissions, we derived a concept, which we called the Emission Penalty Factor (EPF), with the following meaning:

$$EPF = 1/3[(NO_x)_m/10 + (CO)_m/50 + (UHC)_m/50] \text{ (m = measured value in ppm [v/v])}$$

The EPF-value should preferably be below 1.

Figure 1 below indicates the trends of development over the years. The EPF of the original CHE was rather high, mainly depending on CO- and UHC-emissions. The values of the EPF are presented versus the load density, which is the heat output divided by the geometric volume of the unit. Really, the original unit was inferior to the current design both concerning the emissions and the compactness. The original design also had a relatively narrow window of operation for acceptable CO/UHC-emissions.

Already the first generation of the new design (SWEP-Catator I, 1999) showed remarkable improvements in design, function and operability. The emissions were lower, the compactness and integration were higher and the window of operation was wider. Spurred by the enormous improvements, a second design was developed and evaluated (SWEP-Catator II, 2000). Indeed, the performance was improved further to enable operation at loads as high as 3 – 4 MW/m<sup>3</sup> with extremely low emissions and a high thermal efficiency. The long-term evaluation (the Åstorp-test) described in this report was performed with the second design of CHEs at loads varying from 0.6 to 3.5 MW/m<sup>3</sup>.

The development project continued in parallel with the Åstorp-test and further improvements were accomplished during 2001 (SWEP-Catator III). The usable load (loads with extremely low emissions) has been extended to values of about 6 MW/m<sup>3</sup>. Further development and improvements indicate that the convergence limit of the current CHE-concept will be about 10 MW/m<sup>3</sup> with extremely low emissions and a high thermal efficiency.

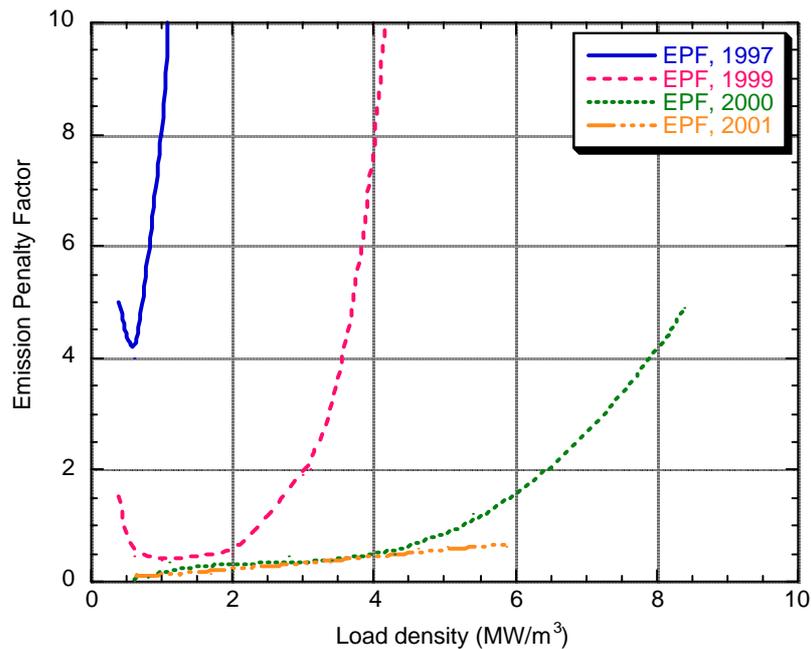


Figure 1 Trends of development  $EPF = 1/3[(NO_x)_m/10 + (CO)_m/50 + (UHC)_m/50]$  ( $m$  = measured value in ppm [v/v])

The third design complies with the most stringent emission standards existing at the moment (the Hannover-norm). According to this norm the NO<sub>x</sub>-and CO-emissions should be lower than 11 and 14 ppm (v/v) respectively when the measurements are performed according to a special norm (DIN 4702/8). The thermal efficiency is normally above 105%, when calculated on the lower heating value of natural gas. However, the thermal efficiency is depending on the inlet-water temperature to the CHE and can consequently vary.

The current CHE (40 plates) has a volume of about 3.4 litres and will enable operation at loads up to 23 kW. The CHE-design is an all-inclusive unit including all components for combustion and heat exchange. The idea is now to implement the CHE-design into condensing boilers and co-operation with a number of boiler manufacturers is underway.

The long-term evaluation (the Åstorp-test) was carried out to demonstrate the reliability of the concept and its components, i.e. the heat exchanger and the catalyst. It was decided to operate the CHE according to a compressed day-cycle to enable simulation of a large number of transients in a rather short time. The test was continuously run for 5000 h with emission mapping at a number of occasions. The project has been delayed depending on a freezing incident, which forced us to re-initialise the test.

This report covers the background of the project and describes the design and construction of the CHE and the test rig. The experimental data from the long-term evaluation are also presented and analysed.

## 2. Scope and objectives

The main objective of the project can be expressed as follows:

“To confirm and verify experimental and theoretical findings concerning thermal efficiency, emissions and reliability for catalytic heat exchangers under realistic conditions during long-term operation”.

The project covers a number of items according to:

- a) Dimensioning of a complete boiler rig
- b) Construction
- c) Commissioning
- d) Installation at Sydkraft Gas premises at Åstorp
- e) Emission mapping during the long-term test
- f) Evaluation & analysis
- e) Final report

The performance of the rig was evaluated according to a compressed day cycle, described later on, for about 5000 hours of continuous operation.

## 3. Background

The original ideas concerning catalytic heat exchangers were described in a number of reports issued during 1994 – 1997 [1 –3]. These projects resulted in a firm knowledge concerning different phenomena to take into consideration when designing CHEs for different applications. Since the heat exchanger part of the CHEs at that time was unsuitable for the application, the integration of the system was incomplete. Figure 2 relates a system layout and a section of a 50 kW-prototype. From the Figure it is obvious that components like start-burners, air pre-heaters and secondary burners were necessary to implement for proper operation. The complexity of the system made it difficult to arrive at the desired level of compactness. Also, the emissions of CO and UHC were rather high under certain modes of operation.

It was concluded that the design of the heat exchanger needed to be improved in order to comply with the demands concerning size, emissions and operability. Consequently, heat exchanger manufacturers were contacted and a co-operation with SWEP was initiated.

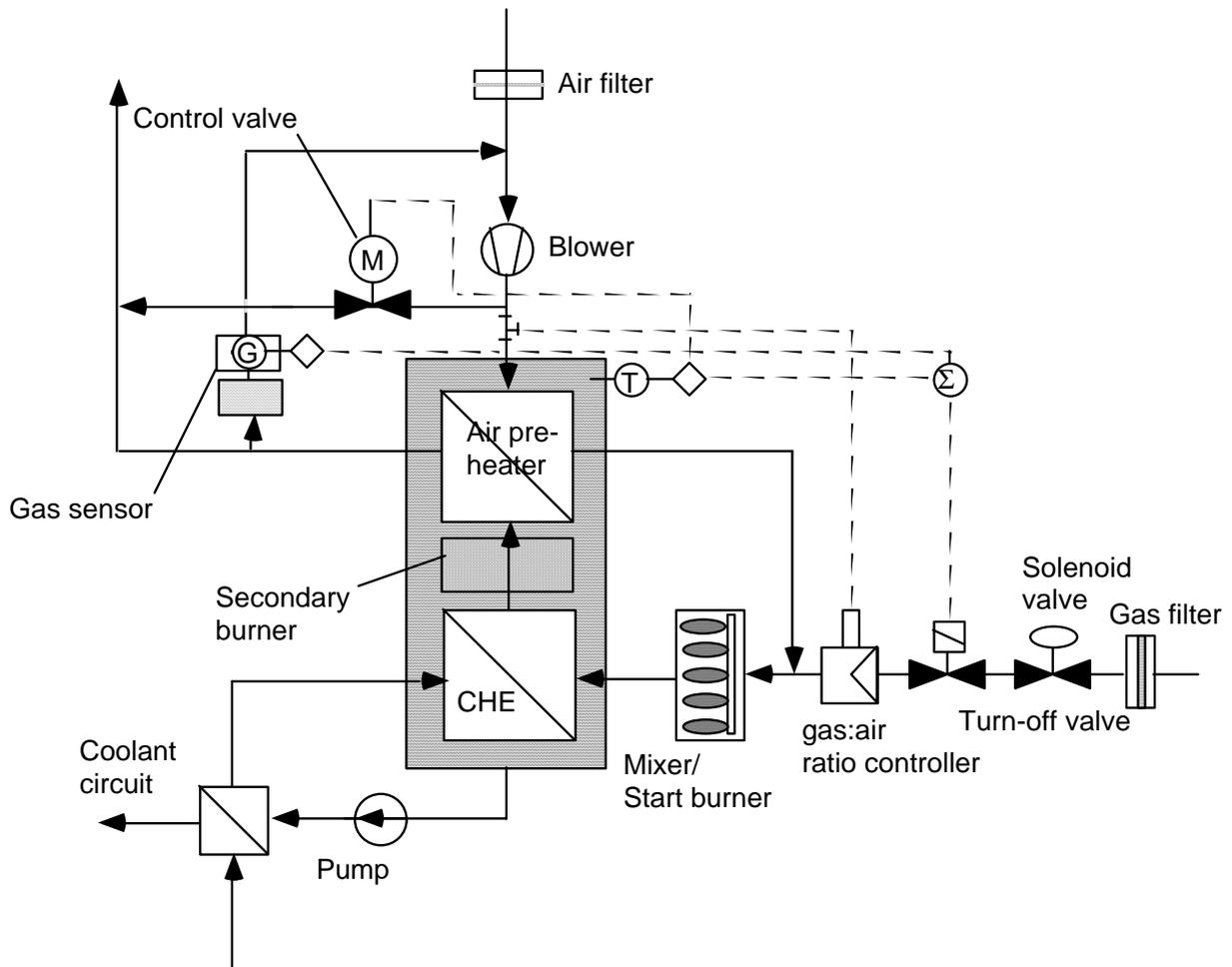


Figure 2a Previous design, lay-out.

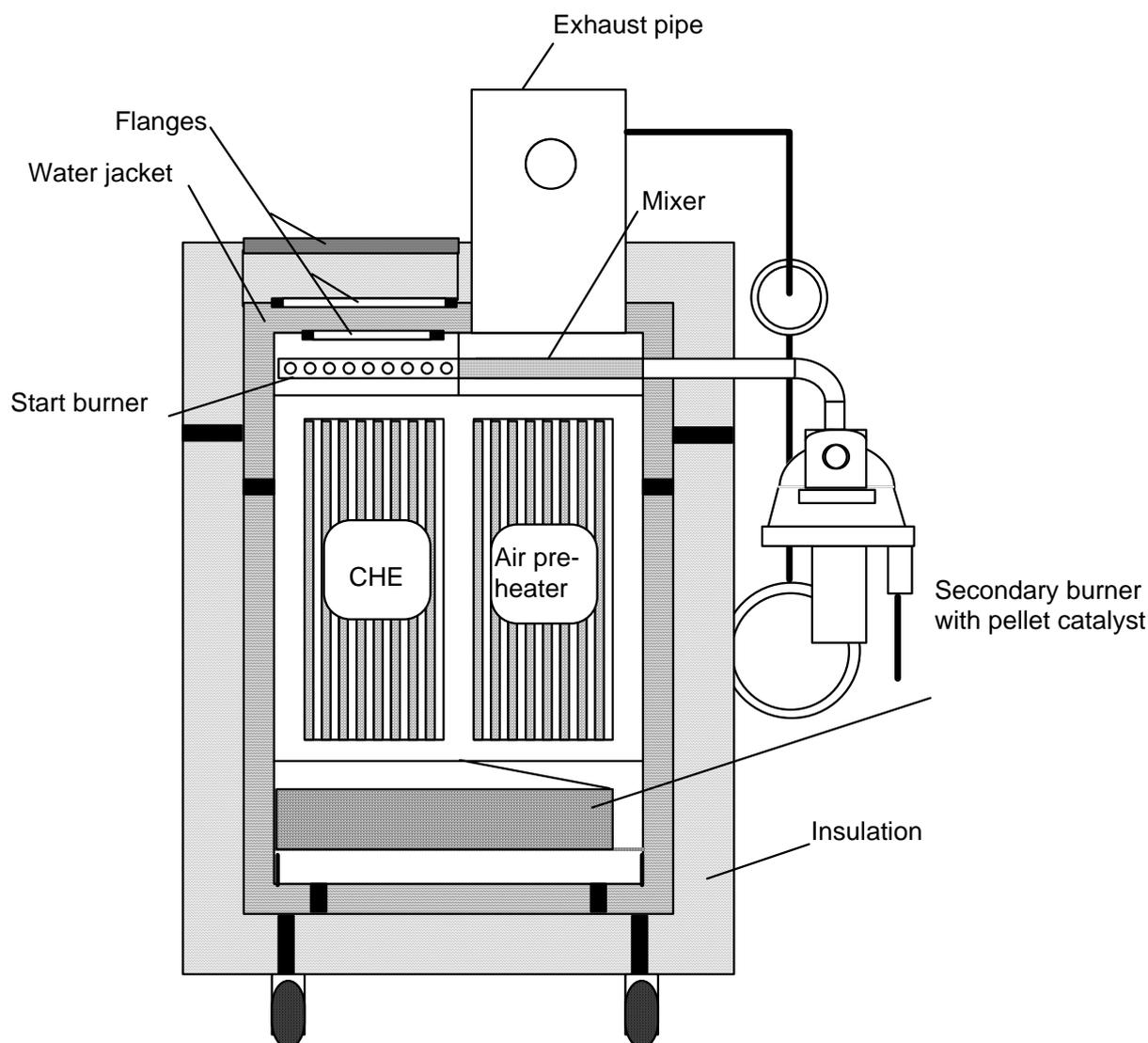


Figure 2b Previous design, section.  
 Dimensions:  $h \times b \times l = 675 \times 600 \times 600$ .  
 Approximately 50 kW of thermal effect.

A large number of combustion experiments had previously indicated a possibility to use wire-mesh cylinders as the combustion catalyst. Depending on the high thermal diffusivity in such structures, pre-heating was not necessary, i.e. the air-pre heater could be rationalised away. Furthermore by implementation of two wire-mesh cylinders in series it was possible to omit also the secondary burner. Start-up could be via flame combustion directly on the mesh surfaces, which enable us to remove also the start burner. The package of cylindrical wire meshes was then inserted into an inlet of a plate-type heat exchanger to enable effective cooling of the mesh catalyst and the hot flue gases, see Figure 3 below.

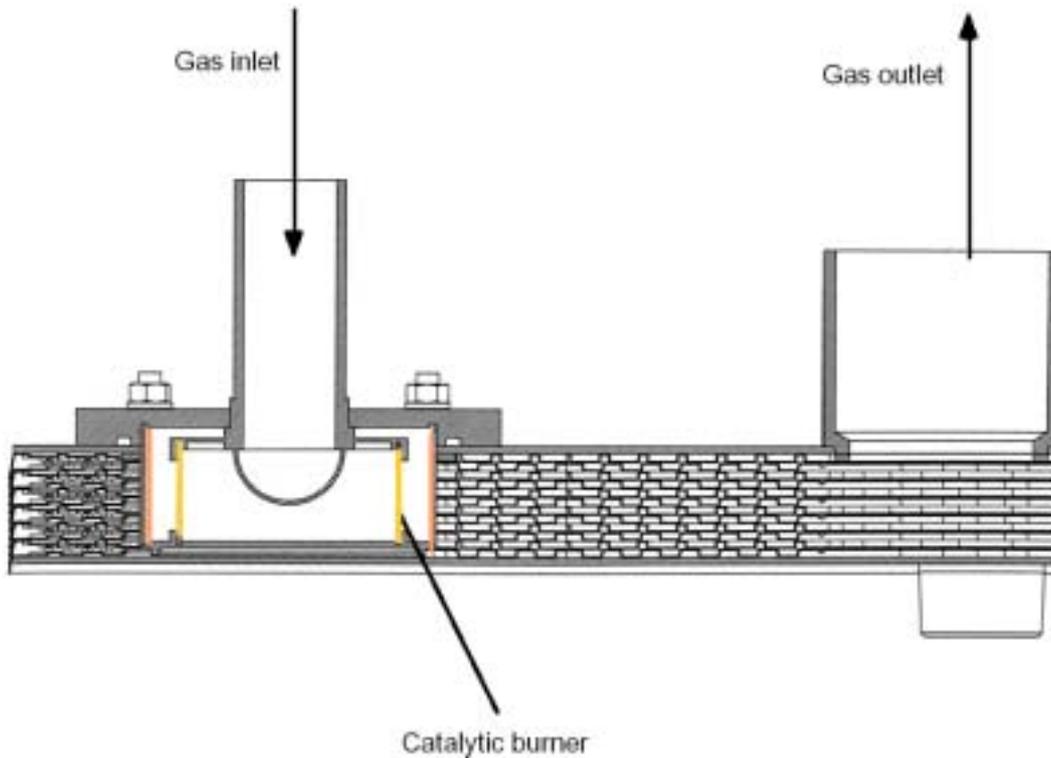


Figure 3 Current CHE-design

The exact design of the burner section has been changed a number of times and so have the composition and the structure of the catalytically active wire meshes. The design of the inlet section (i.e. the nozzle design) is another important area in order to arrive at even flow conditions all over the wire-mesh catalyst.

Consecutive design modifications have enabled us to improve the function and operability of the CHEs in steps. Thus, the best design alternative of today has undergone a number of modifications in comparison to the Åstorp-design, which is referred to below.

The Åstorp-CHE has a volume of 3.4 l and consists of 40 plates in parallel, which are brazed together to form a plate-heat exchanger. A catalytic burner comprising a primary and a secondary wire-mesh catalyst is placed in the inlet section on the gas side. Ignition is via flame combustion on the wire-mesh catalysts and the flame combustion mode is initiated by a glow plug.

Figure 4 is an emission mapping of the Åstorp-CHE versus the load. The  $\text{NO}_x$ -emissions typically increases from 1-2 ppm (v/v) at the lowest loads ( $<1 \text{ MW/m}^3$ ) to about 20 ppm (v/v) at the highest loads tested ( $8 \text{ MW/m}^3$ ). The CO-emissions increase in a similar way from levels below 10 ppm (v/v) to values above 500 ppm (v/v). The load-density of the Åstorp rig was restricted to values between 0.6 and  $3.5 \text{ MW/m}^3$  in order not to overload the catalyst/heat exchanger.

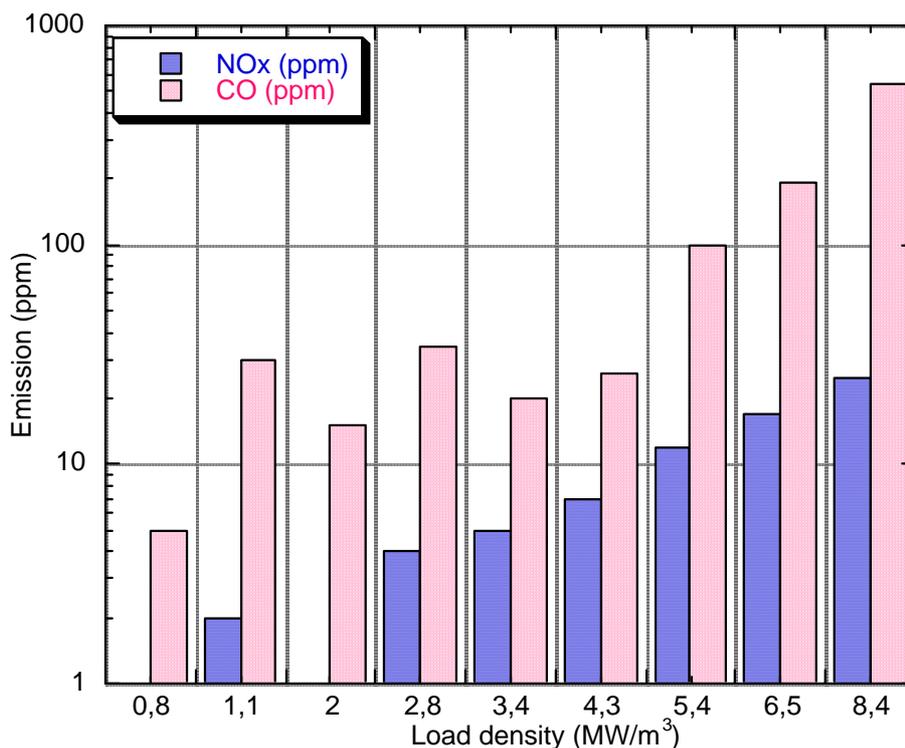


Figure 4 Emission status per 0010

Generally speaking, the thermal efficiency is a function of the flue-gas temperature and the excess-air ratio. Figure 5 relates the thermal efficiency to the flue-gas temperature and the excess-air ratio. To arrive at thermal efficiencies of 105% or above it is necessary to cool the flue gases to low temperatures ( $<40^{\circ}\text{C}$ ) to facilitate effective condensation. Hence, it is necessary to reduce the inlet-water temperature to values between  $30$  and  $40^{\circ}\text{C}$ .

The temperature difference between the cooling water and the flue gases in the CHE is normally restricted to a few degrees. Consequently, if the temperature of the inlet water is below  $40^{\circ}\text{C}$ , it is possible to arrive at thermal efficiencies as high as 105% all over the load interval. Figure 6 relates the thermal efficiency of the Åstorp-CHE to the load at an inlet water temperature of  $40^{\circ}\text{C}$ . By decreasing the water temperature further it is possible to increase the thermal efficiency somewhat.

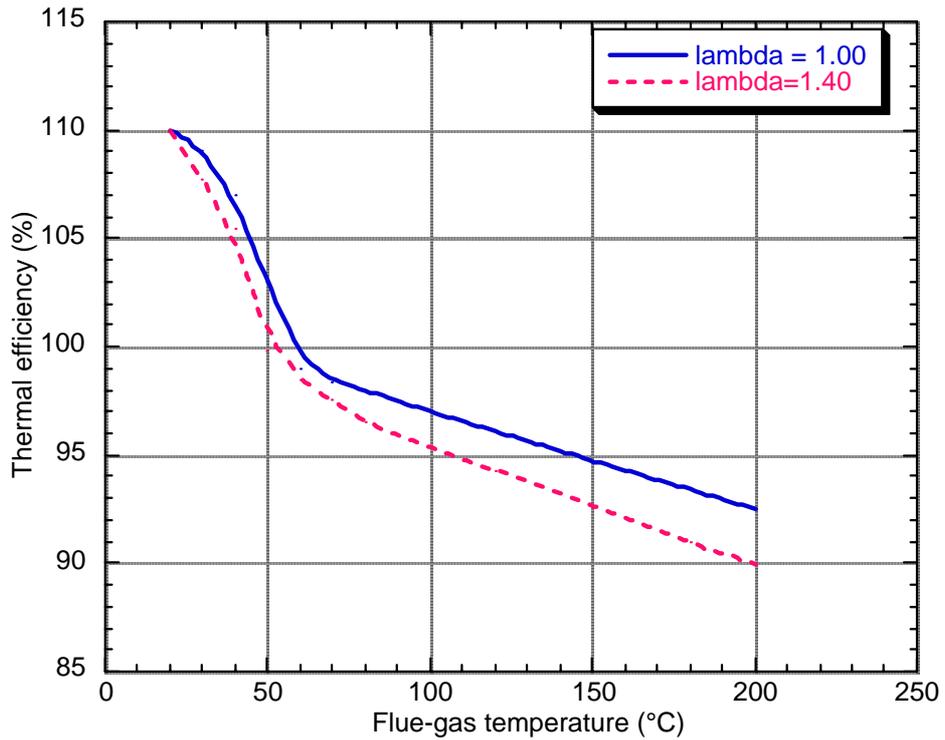


Figure 5 Thermal efficiency versus the flue-gas temperature at different lambda values.

The excess-air ratio of the CHE can be varied in a rather wide window. However, best performance with respect to the emissions is achieved at  $\lambda = 1.2 - 1.4$ . At lower lambda values, the emissions of nitrogen oxides will increase somewhat. At higher lambda values, the emissions of CO and UHC will increase.

Consequently, the Åstorp-CHE operates at lambda values between 1.2 and 1.4.

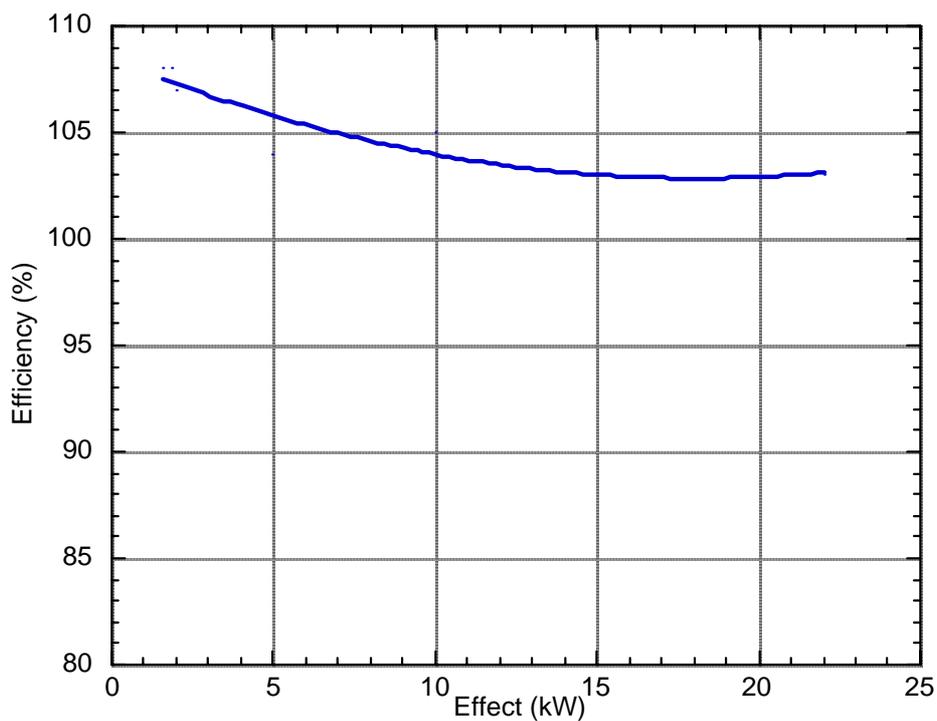


Figure 6 Measured thermal efficiency vs. load. Inlet water temperature to the CHE: 40°C.

The total pressure drop of the CHE is restricted to values below 7 mbar (see Figure 7 below), i.e. it is easy to find suitable fans and valves for the system under evaluation. The majority of the pressure drop is associated with inlet losses in the nozzle section. The pressure drop over the wire-mesh catalyst is in the region of 0.1 – 0.2 mbar.

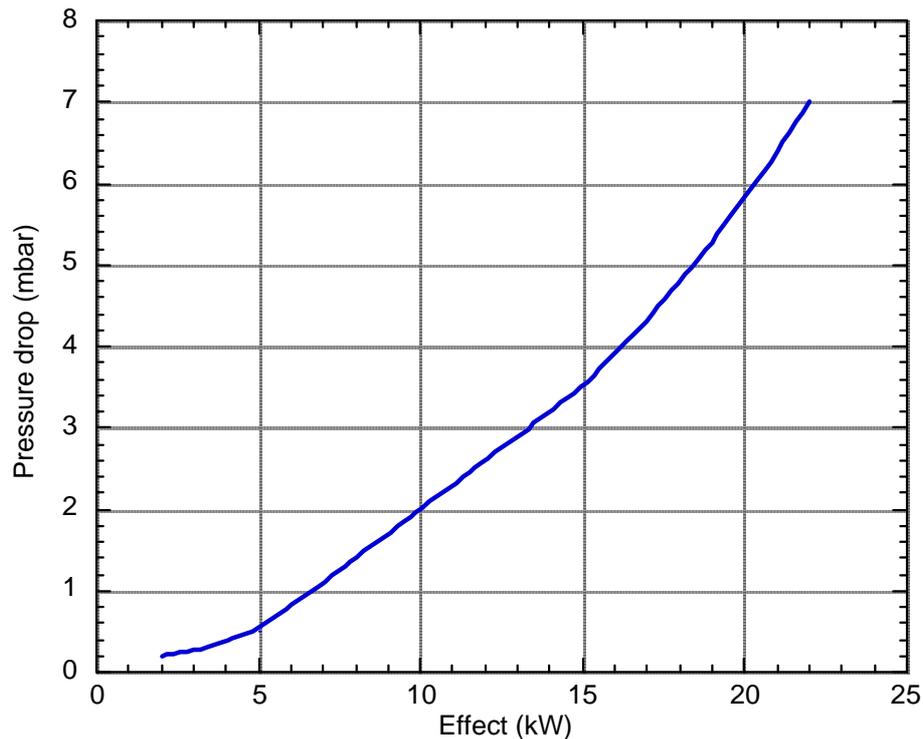


Figure 7 Pressure drop vs. load

The data described above relates to the Åstorp-CHE. Design improvements enable us to operate the latest designs at considerably higher load densities.

#### 4. Design principles and background of emissions

There are many possible design approaches concerning CHEs. The Åstorp-design and later derivatives were developed to comply with a number of demands:

- Simple and straightforward design
- Compactness and high degree of integration
- Few parts, i.e. easy to put together and to maintain
- Low production cost
- High thermal efficiency
- Low pressure drop
- Excellent emissions
- High turn-down ratio
- Multi-fuel possibilities

When all these factors were taken into consideration there were a number of relevant trade-offs to explore further. The emissions could, in principle converge to zero-levels if it was allowed to increase the amount of catalyst further (and the volume). However, the opinion here is clear: It is enough to comply with the most stringent regulations at the time and to focus more on factors like compactness, operability, durability and cost.

In order to reduce the emissions further it is essential to describe and to understand the processes behind nitrogen oxide formation and the emissions of CO/UHC in detail.

Nitrogen oxides ( $\text{NO}_x$ ) are primarily formed through three different reaction schemes: a) Thermal  $\text{NO}_x$ , b) Prompt  $\text{NO}_x$  and c) Fuel- $\text{NO}_x$ . Fuel- $\text{NO}_x$  is only formed when the fuel contains chemically bound nitrogen, e.g. when combusting bio-fuel or coal.

In Figure 8 the equilibrium content of NO in air is shown as a function of the temperature. The formation of NO is thermodynamically favoured only at high temperatures, as illustrated by the figure.

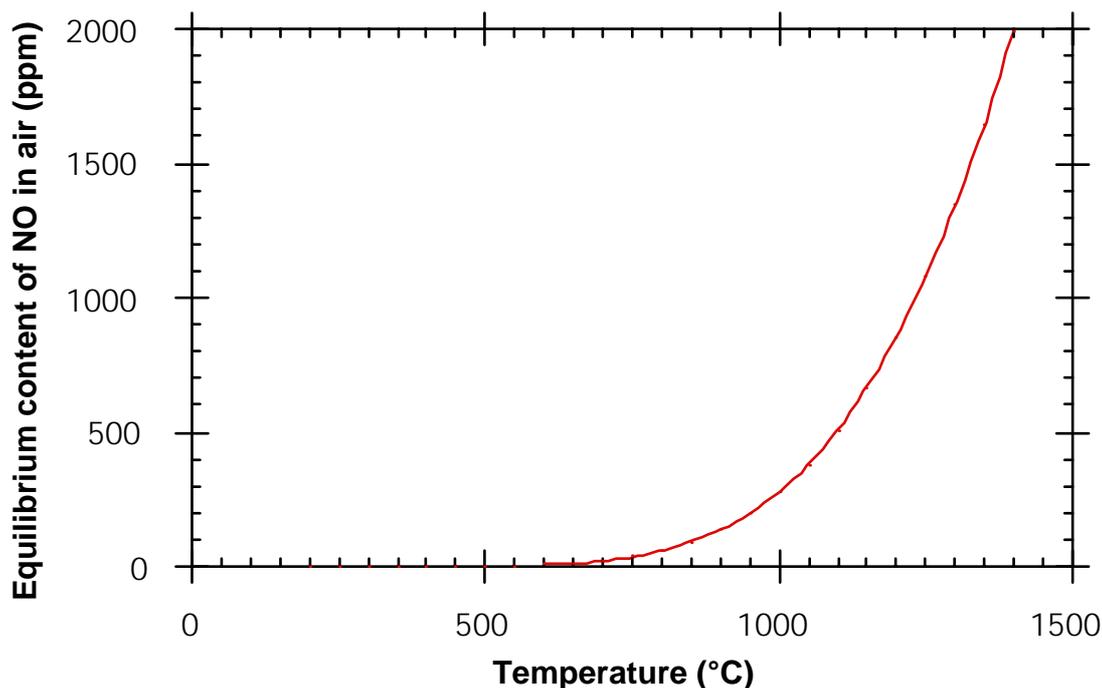
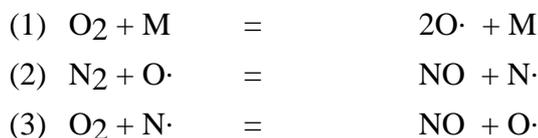


Figure 8 Equilibrium content of NO in air as a function of the temperature

Thermal  $\text{NO}_x$  is formed through radical reactions where oxygen and nitrogen radicals are important intermediates. The mechanism was proposed by Zeldovich in the 1940s and includes three elementary reactions:



M is an arbitrary molecule, which acts as a transmitter for thermal energy. Reaction (2) is assumed to be the rate-determining step, which leads to the following rate expression [4]:

$$\frac{dC_{\text{NO}}}{dt} = 2 k_2 C_{\text{O}} C_{\text{N}_2} \quad (\text{mol m}^{-3} \text{s}^{-1})$$

$$k_2 = 10^{7.8} \exp\left(\frac{-314000}{RT}\right) \quad (\text{m}^3 \text{mol}^{-1} \text{s}^{-1})$$

$$C_O = \sqrt{1.20 \cdot 10^3 T \exp\left(\frac{-54245}{T}\right) C_{O_2}} \quad (\text{mol/m}^3)$$

$C_{O_2}$  = Oxygen concentration (mol/m<sup>3</sup>)

$C_O$  = Equilibrium concentration of oxygen radicals (mol/m<sup>3</sup>)

The concentration of oxygen radicals may be higher than the equilibrium concentration. This phenomena, called radical overshooting, results in an increased rate of NO formation.

Prompt NO<sub>x</sub> is formed by fast radical reactions involving hydrocarbon radicals which attack molecular nitrogen to yield hydrogen cyanide and free nitrogen radicals. The nitrogen radicals then react with oxygen or oxygen-containing components to form NO. It is difficult to quantify the amounts of prompt NO<sub>x</sub> formed during combustion, although rate expressions have been proposed, e.g. [5]:

$$\frac{d X_{NO}}{dt} = 1.2 \cdot 10^7 X_{O_2}^b X_{N_2} X_{RH} \exp\left(\frac{-30240}{T}\right)$$

$X_i$  = Mole fraction of component i

b = Constant depending on the mole fraction of oxygen;  
b=0 if  $X_{O_2} > 0.02$

It is possible to get a rough estimation of the rate of NO formation by using the rate expressions presented above. Figure 9 shows the initial formation rate (ppm/s) of NO versus the temperature in a mixture containing 5 vol.% of methane in air. The formation rate will decline as the NO content approaches the equilibrium level. The figures in the diagram show the relative amount of thermal NO<sub>x</sub> at different temperatures. The formation rate of NO is strongly affected by the temperature, thus increasing from 20 ppm/s at 1000°C to 160 000 ppm/s at 1600°C. It is also evident that prompt NO<sub>x</sub> is the predominate source of NO<sub>x</sub> at temperatures below 1400°C.

In burner applications, the catalyst temperature will be around 1000°C. The residence time is normally in the region of 10-100 ms, thus indicating a NO<sub>x</sub>-content of 0.2-2 ppm at 1000°C.

It may be concluded that the formation of NO<sub>x</sub> can be decreased in the following ways:

- Combustion should be performed at temperatures below 1000-1200°C.
- The fuel content of the fuel/air-mixture should be decreased.
- The residence time should be as low as possible.
- The fuel should not contain chemically bound nitrogen.

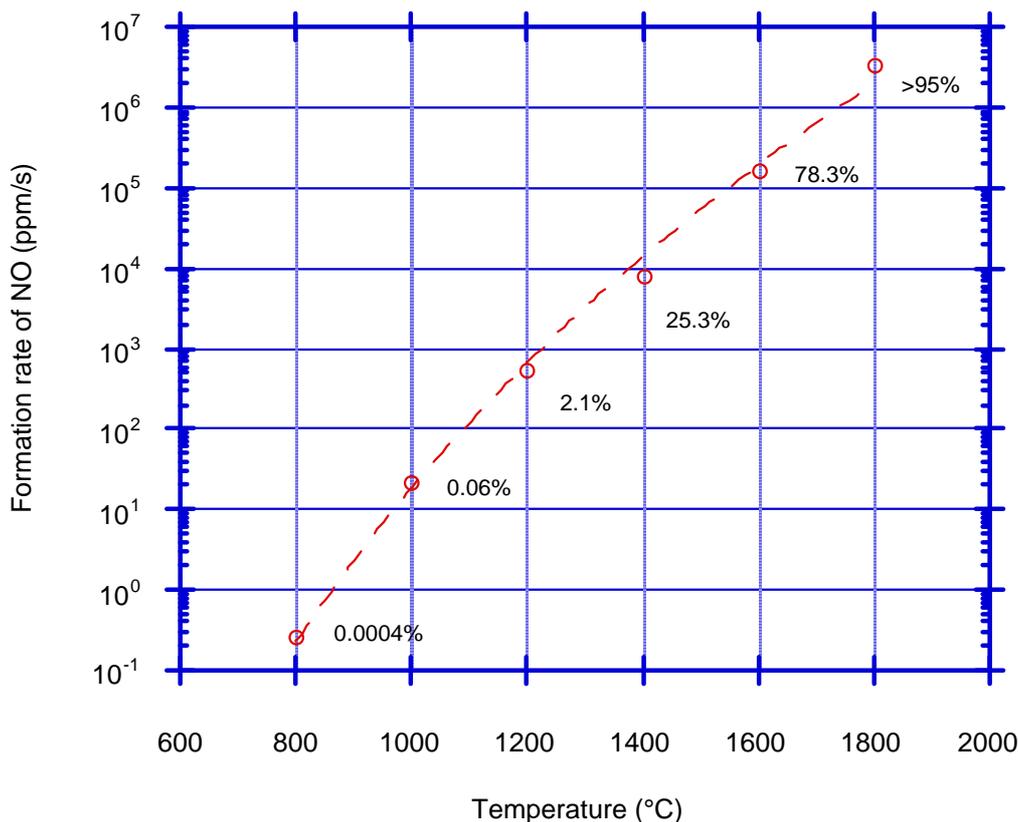


Figure 9 Initial formation rate of NO (ppm/s) as a function of the temperature in a mixture containing 5 vol.% methane in air; the figures in the diagram represent the fraction of thermally generated NO<sub>x</sub>.

The emission pattern concerning CO/UHC normally follows an opposite pattern, i.e. decreased emissions with increased temperatures and residence times. However, if the post combustion zone impinges on to cooled surfaces, the oxidation reactions will be “frozen” and the removal of combustible components will be impossible.

The emissions of CO/UHC increase dramatically at high loads due to poor gas-phase completion of the reactions. The gas-phase reactions are extremely temperature sensitive. Increasing the temperature of the flue gas from 700 to 900°C will reduce the residence time necessary for completion by a factor of 10. The residence time of the flue gases between the combustion catalyst (where the gas-phase completion occurs) is around 30 ms at full load in the CHE. By performing gas-phase radical calculations, it is possible to forecast the extent of gas-phase completion with respect to CO- and UHC-emissions. Figure 10 shows some results from the calculations. In this example the outlet concentrations (after the first catalyst layer) of CO and UHC are 1000 ppm respectively. As can be seen in the figure, UHC will react to produce CO, which in turn will be oxidised to CO<sub>2</sub>. Traces of UHC are combusted effectively at gas temperatures above 800°C whereas CO-combustion demands higher temperatures to be effective. At extreme temperatures, the equilibrium concentration of CO increases. In that situation it is not possible to reduce the CO-emissions.

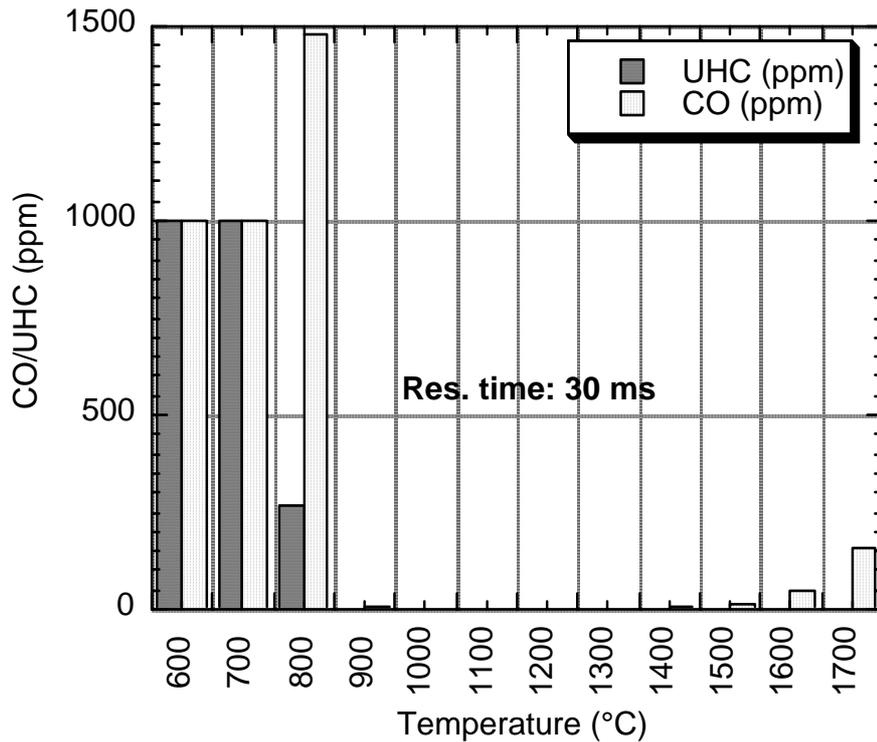


Figure 10 Radical initiated gas-phase combustion of CO (1000 ppm) and UHC (1000 ppm) at different temperatures and a residence time of 30 ms.

Hence, in order to achieve effective post-combustion, it is necessary to have enough residence time at a high enough temperature. Too effective cooling will effectively freeze the emissions of CO and UHC.

Apart from the design choices concerning the heat exchanger there is also a possibility to chose different catalysts, see Figure 11. The active material is usually dispersed on a carrier to increase the active area and the catalyst activity. The carrier is in turn applied on to a geometric substrate. The appearance of the geometric substrate may differ depending on the application. Important features are: contact area between the gas phase and the substrate, degree of turbulence caused by the substrate and the resulting pressure drop. Most catalysts can be produced in the form of *pellets* where the carrier itself constitutes the geometric substrate, see Figure 11. The form and dimensions of the pellets can, of course, be varied to a great extent, which simplifies the reactor dimensioning. The extremely high pressure drop in combination with poor catalyst utilisation due to pore diffusion limitations are serious drawbacks of this concept.

The catalyst may also have the form of a *fibrous material*. In these cases, thin threads of a ceramic material are woven together to form a pad with high porosity. The ceramic threads may be porous or non-porous. A ceramic pad prepared from porous threads may have a significant surface area which makes it suitable as a catalyst carrier. Indeed, such pads have been used to prepare diffusive catalytic burners for domestic applications and radiation heaters for industrial applications. The mass- and heat- transfer characteristics, as well as the catalyst utilisation, are excellent but the pressure drop and the poor mechanical strength are significant drawbacks.

The geometric substrate may also consist of a *foamed ceramic body* or a body of *sintered metal*. These substrate are highly porous and the internal surfaces are coated with a catalyst through a wash-coating procedure. The sintered metal concept is most interesting in energy production where thermal effect must be transferred from the catalyst body to the surroundings to avoid catalyst overheating. The poor conduction of ceramic bodies will lead to overheating and catalyst deactivation. Again, the high pressure drop is the major drawback of this concept.

In most industrial and automotive applications it is essential to achieve a high degree of conversion at a relatively low pressure drop. The *ceramic monolith* catalyst consists of an extruded ceramic body with parallel channels throughout the body. The dimensions and the geometry of these channels can be varied. The walls of the channels are normally coated with a catalytic layer through a conventional wash-coating impregnation procedure. In some cases the entire ceramic body is produced from a high-surface-area material which may be activated through an impregnation technique.

Ceramic monoliths are nowadays widely used in automotive applications, primarily due to the low pressure drop of the catalyst. The laminar flow conditions result in poor mass- and heat-transfer characteristics. This will in turn lead to larger reactor volumes and consequently to higher catalyst weights. The poor heat-transfer characteristics in combination with considerable thermal inertia also imply a poor thermal response during transient conditions with respect to the gas temperature. Ceramic monoliths are also susceptible to cracking due to thermal gradients within the body during rapid heating or cooling.

*Metal monoliths* can be produced by winding corrugated sheet metal. The geometry of the corrugation may be varied as well, as the thickness of the sheet metal. The metal support is coated with a catalytically active material through a wash-coating impregnation technique. Metal monoliths have a considerably higher thermal conductivity than ceramic monoliths and the thermal gradients are not expected to be especially severe. Metal monoliths are increasingly used in automotive applications where they are replacing ceramic monoliths.

*Wire meshes* or *wire gauzes* have also been used as geometric supports. The mesh or gauze is normally woven directly from an active metal, e.g. Pt/Rh (ammonia oxidation) or Ag (methanol oxidation). The surface area of such metal structures is low and they can only be used to catalyse extremely quick reactions. The activity can be enhanced if the wire mesh is coated with a porous ceramic layer through a wash-coating procedure. Thermal spraying is a suitable method for producing ceramic layers with superior adhesion to the metal substrate. It is also possible to produce rather thick ceramic layers with this technique. The surface area and the porosity of as-sprayed ceramic layers are low. To increase the porosity and the specific surface area, a modified spray technique has been developed by Catator. There are several advantages of catalytically active wire meshes. The mass- and heat-transfer characteristics are excellent, the pressure drop is low, the geometrical flexibility is high and the active material is effectively utilised. The major drawback is attributed to clogging effects at high dust concentrations, e.g. in solid fuel combustion.

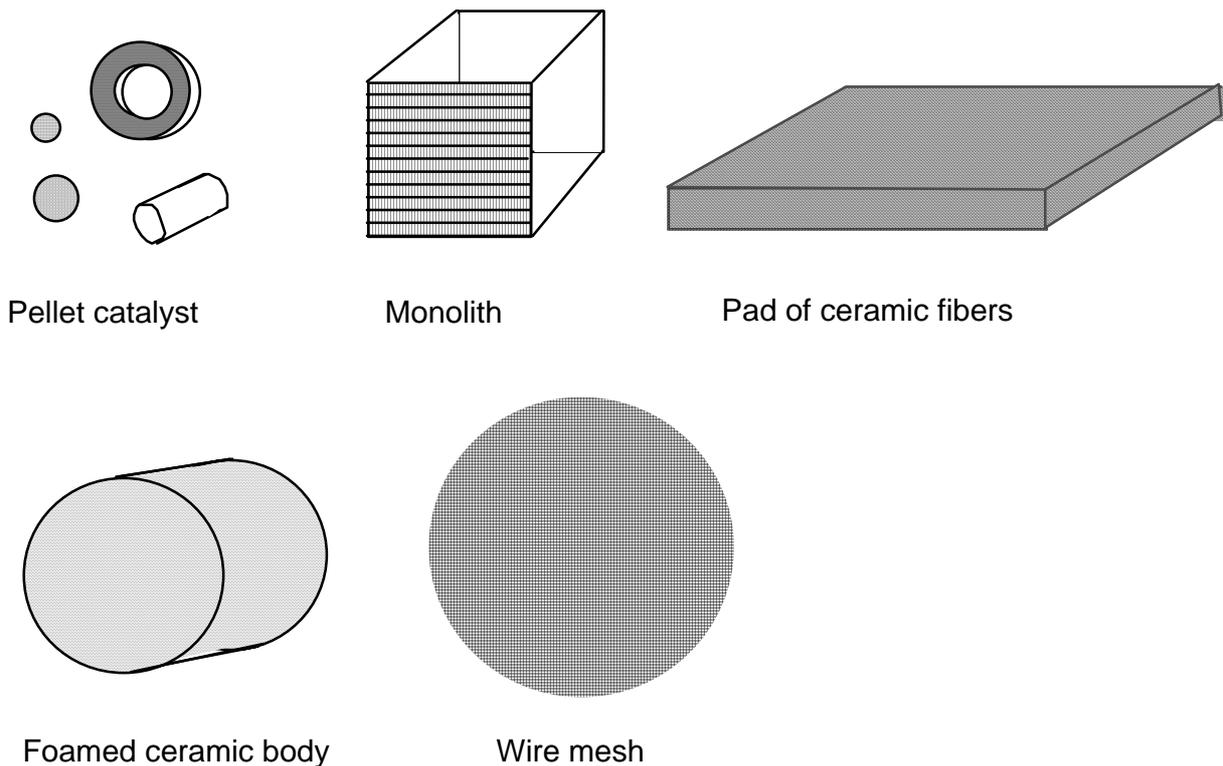


Figure 11 Different catalyst alternatives

In applications of energy production (i.e. catalytic combustion for energy production) it is possible to protect the catalyst from overheating by arranging the catalyst geometry to facilitate cooling through thermal radiation. The catalyst is cooled by thermal radiation to a cooling jacket surrounding the wire-mesh structure. The geometric flexibility offered by the wire-mesh approach makes it possible to construct catalytic burners working at a relatively low excess of air without over-heating the catalyst.

The geometric flexibility of wire-mesh catalysts is one of the most important features. It is possible to design a wire-mesh catalyst for almost any catalytic application and to fit it into almost any geometry. The preparation method for the catalyst will be similar in all cases.

In catalytic combustion, FeCrAlloy is used as the wire material. A porous layer of metal/metal oxides is supplied on to the wire mesh structure by means of thermal spraying. The porous layer is then treated chemically to increase the surface area of the catalyst and to render it catalytically active. In most cases (especially in methane combustion) palladium is used as an active phase. It is also possible to put cheaper transition metal exchanged barium hexaaluminate on to the wire meshes, although the light-up characteristics will be somewhat slower. However, there is a trade-off between performance and price/durability. The wire-mesh structure itself will tolerate operation at temperatures up to about 1000°C for very long times without oxidative ruptures. Figure 12 indicates the resistance to thermal degradation of a FeCrAlloy-wire ( $\phi$  0.4 mm) versus the temperature. From the Figure it is obvious that the wire will survive about 100 000 hrs at 900°C.

The most important deactivation phenomena to take into consideration are thermal sintering and evaporation of active phase. Thermal sintering is retarded by a number of stabilisation measures (trace element addition) during the catalyst formulation. The maximum possible temperature of the wire-mesh structure can be controlled via the mass-transfer characteristics of the catalyst (e.g. porosity, pore-size distribution, positioning of active phase etc). The goal with the ongoing catalyst development is to avoid extreme temperatures (i.e. runaway conditions) and to maximise the stability to thermal deactivation/evaporation at the operation temperature. This work includes geometrical aspects (mesh structure, wire diameter etc) as well as the morphological and chemical composition of the catalytic layer.

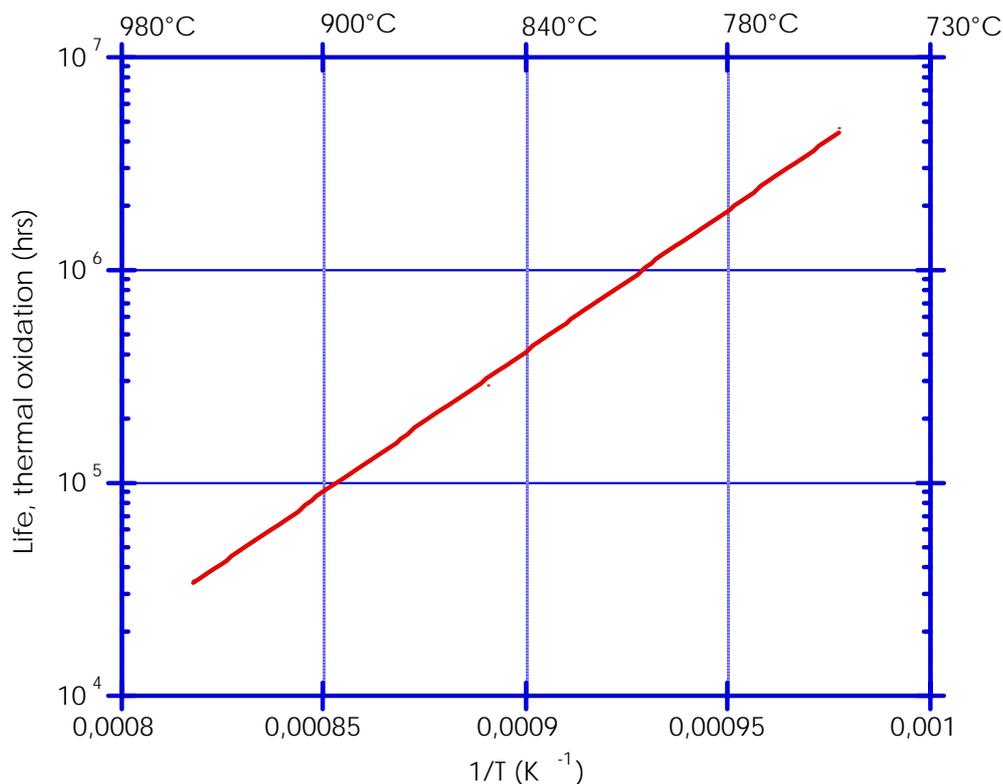


Figure 12. Estimated life time of wire-mesh structure (0.4 mm FeCrAlloy-wire).

## 5. Rig and methods of evaluation

The Åstorp-CHE was installed on a rig to enable long-term evaluation under transient operation conditions, see Figure 13. A secondary heat exchanger was installed to decrease possible problems with fouling inside the CHE due to formation of calcium carbonate. Also, this design enabled us to choose an appropriate inlet temperature of the water to the CHE, i.e. between 30 and 40°C. The load of the CHE was controlled in order to supply hot water with a constant temperature, normally between 60 and 70°C. A PLC-system was installed to vary the load situation by means of operating a battery of solenoid valves. By varying the number and types of solenoid valves which were open, the water flow in the secondary circuit and consequently the cooling capacity could be varied. The PLC-system was operated according to a compressed day cycle (CDC). The compressed day cycle enabled us to simulate one day of operation during one hour. The CDC-operation was repeated over and over again during the course of the long-term test (5000 hours). The CDC-data are given in Table 1.

Natural gas (type H, Danish gas quality) was supplied via a system of valves and the delivery pressure was 20 mbar(g). Air was supplied by means of a standard fan and the air:fuel-ratio was set by a valve, which was controlled by the pressure in the air line. The air-flow was controlled by the fan speed.

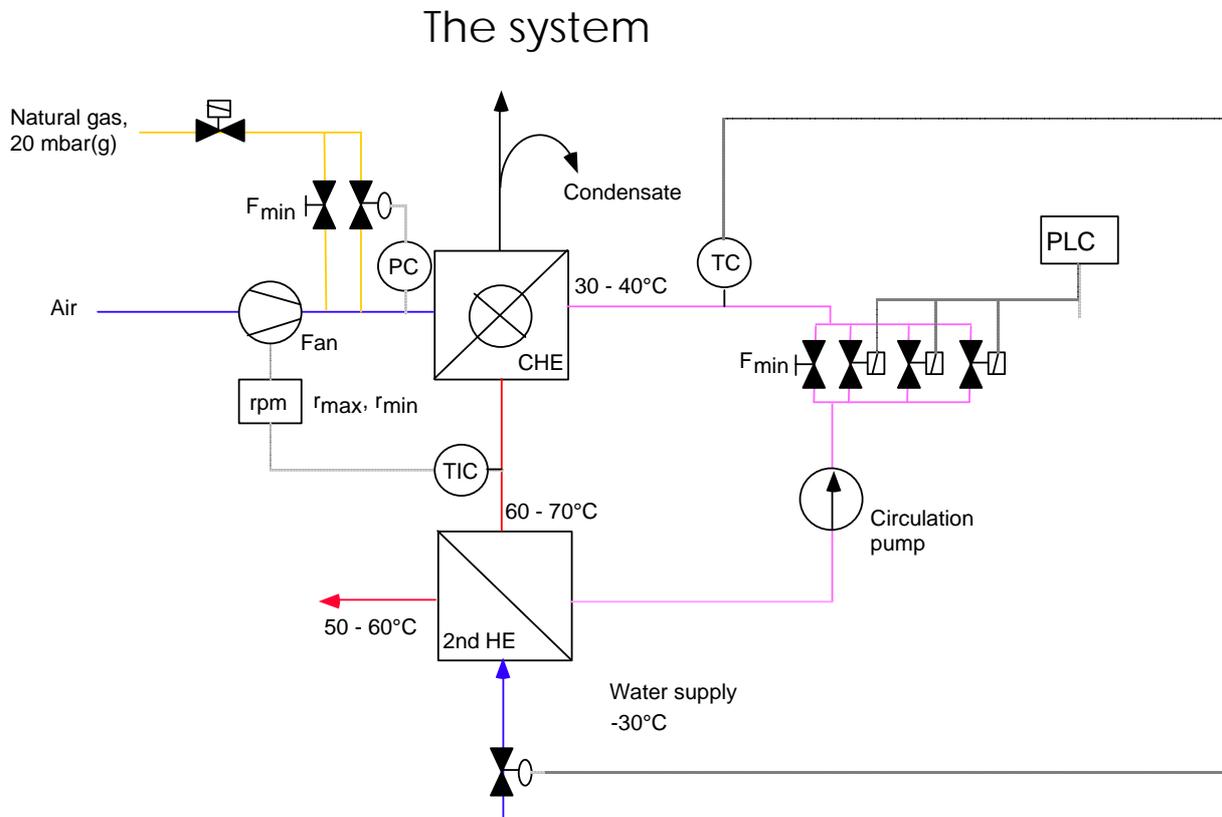


Fig 13 System lay-out

The rig was constructed and commissioned at Catators premises whereas the long-term evaluation was carried out at Sydkraft Gas premises in Åstorp. The effect density of the CHE was varied between 0.6 and 3.5 MW/m<sup>3</sup> during the test. However, since the Åstorp-CHE was installed, we have been successful in increasing the effect density to values of 6 MW/m<sup>3</sup> through different design modifications. A dynamic simulation program was developed to forecast the response of the rig system. This simulation tool enabled us to pre-study the effects of transient operation.

## 6. Commissioning

The rig was installed at Sydkraft Gas premises in Åstorp. Operation was according to a compressed day cycle where the load variations during one hour simulated the operation pattern during one normal day. Consequently, the rig has been operated for 5000 days (14 years) when we are talking about transients and mechanical fatigue but only 5000 hours when we are talking about thermal deactivation. Table 1 summarises the load variations and the duration of each load.

Table 1 Loads during the compressed day cycle

Step	Load (%)	Duration (min)
1	30	15
2	100	1
3	60	1
4	20	7
5	73	1
6	83	1
7	43	4
8	7	30

We encountered some problems during the commissioning of the rig at Sydkraft Gas premises. The temperature of the cooling water could reach higher temperatures than the expected values. Consequently we needed to install a water cooler upstream the CHE-rig to guarantee stable inlet conditions to the rig with respect to the coolant temperature. The limits in the safety system were set to close to the actual values in the delivery lines with respect to gas and air-pressures. Consequently we observed problems with unexpected shut-downs. Unfortunately one shut-down occurred at a moment with very cold weather conditions. This fact together with a simultaneous breakdown of the heating system at the location of the rig resulted in a severe freezing damage. The CHE and the secondary heat exchanger were damaged and so were components in the water supply system (pumps and valves). We also encountered problems with the electronics following flooding conditions at the location of the rig. Consequently it was necessary to replace a number of components in the rig to be able to continue the test. The test was re-initiated with the damage CHE since combustion tests let us believe that the CHE was intact enough for continued operation. However, the freezing damages had resulted in a lost tolerance within the CHE. This in turn resulted in increased emissions and accelerated problems with the tightening between the CHE and the mesh cylinders. After a few weeks operation it was decided to replace the CHE and to re-initiate the long-term evaluation from the beginning. The long-term test was re-initiated September 2001 and emission measurements have been performed at a number of occasions during the course of the test.

## 7. Long-term evaluation

As stated previously, emission mapping, was carried out at different times during the long-term evaluation. Emission measurements (at Åstorp) were by means of NDIR-technology (CO, CO<sub>2</sub> and UHC) whereas O<sub>2</sub> and NO/NO<sub>x</sub> were measured electrochemically. During the commissioning work complementary emission measurements were performed with FID (UHC) and chemiluminescence (NO/NO<sub>x</sub>). These instruments were however not possible to bring to Åstorp, but careful investigations show that there is a close correlation between the results of the different analysis methods.

Measurements were carried out every 500 hrs and the emission data were logged during one compressed day cycle. The lowest load corresponded to about 0.6 MW/m<sup>3</sup> whereas the highest load situation was 3.5 MW/m<sup>3</sup>. Highest emissions were, as expected, obtained at the highest load whereas the lowest load was associated with the lowest emissions. The emissions at all other loads were in between max and min.

Figure 14 relates the  $\text{NO}_x$ -emission as a function of the time on operation. There is a small scatter in the values but there is no evidence at all concerning increased emissions with time. The  $\text{NO}_x$ -emission (ppm) varies between 4 and 10 ppm, depending on the load situation.

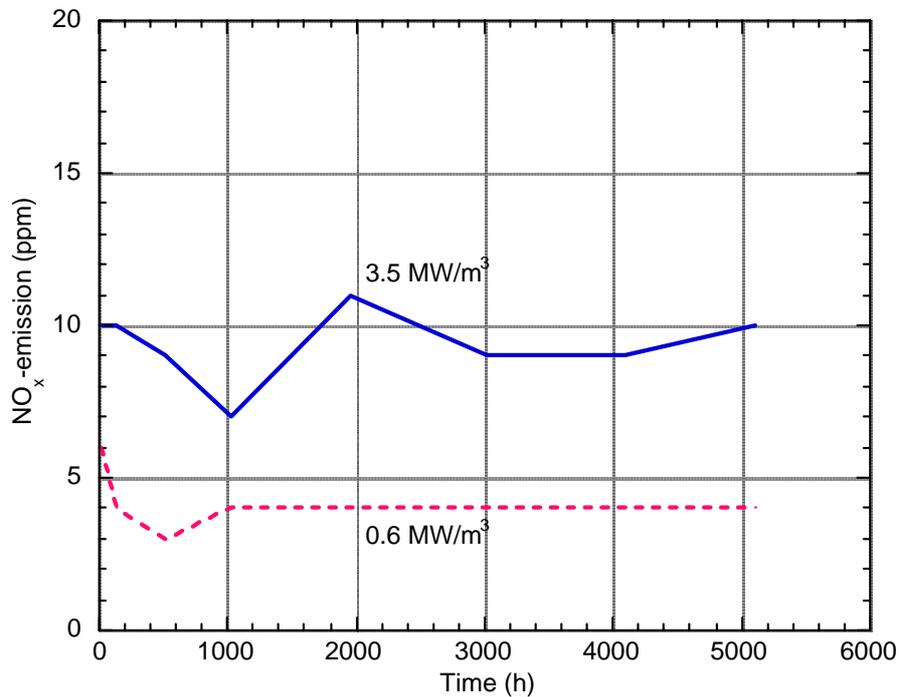


Figure 14  $\text{NO}_x$ -trend versus time on operation (ppm).

Similar results were obtained concerning the CO-emissions, see Figure 15. The CO-emissions varied between 20 and about 60 ppm (v/v) depending on the load situation. The measurements concerning UHC, indicated extremely low emissions all over the load interval. The UHC-emissions are mainly attributed to imperfect tightening between the heat exchanger and the catalyst. Such problems will be rationalised away following the industrialisation phase.

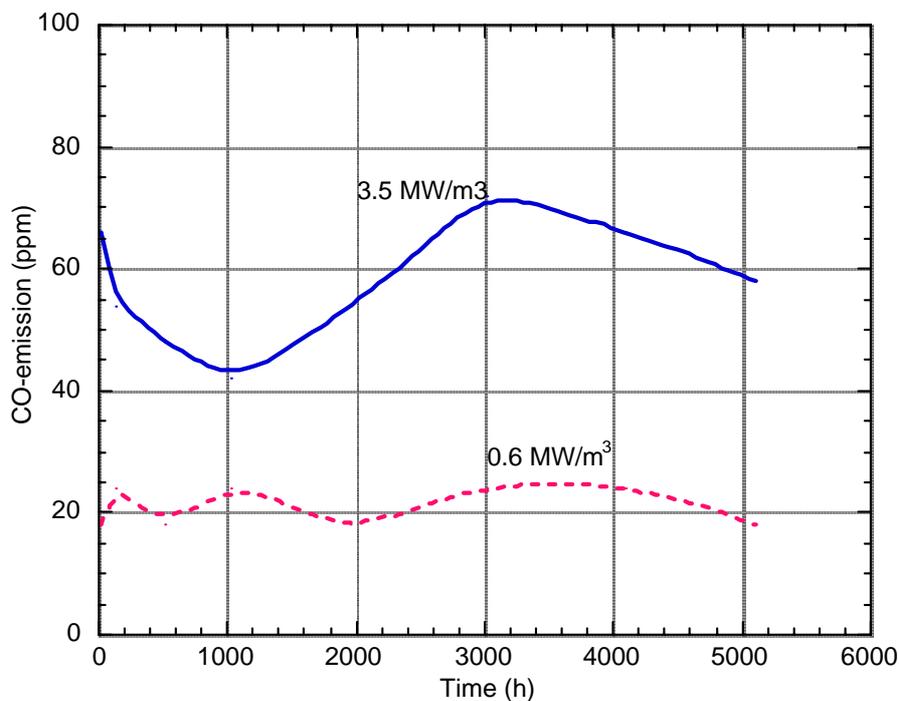


Figure 15 CO-trend versus the time on operation (ppm(v/v))

The CHE was removed from the rig after about 5000 hours of operation. The heat exchanger will be analysed for leakage and corrosion problems due to chemical impact of the condensing water. Possible problems with thermal fatigue will also be analysed with various methods. The catalyst has been subjected to activity testing in a micro reactor system to reveal possible catalyst deactivation.

Activity measurements were performed in a micro-reactor where a known mixture of carbon monoxide and air passed through a catalyst sample. The conversion was calculated and compared with theoretical values for a fresh catalyst. Since we only could use one single layer of catalytic wire mesh in the activity tests, we were obliged to analyse the results with a model for continuous stirred tank reactors (CSTR) due to the high axial dispersion.

The catalyst cylinders (primary and secondary) were cut into a number of samples associated with different load situations (uneven flow distribution along the circumference of the cylinders). The catalyst samples were rinsed from dust by means of a gentle washing with a weak acidic solution.

Figure 16 shows the results of the activity measurements for different samples (primary and secondary cylinders). The data are compared with theoretical estimations for a fresh catalyst according to a CSTR-model.

From the Figure it is obvious that there is a difference in thermal deactivation around the circumference, i.e. the largest impact of thermal deactivation is seen in the directions with the highest load. Also the secondary cylinder is more deactivated than the first cylinder, which might be explained by differences in the active phase. The second cylinder carries Pt as active phase and this component is susceptible to evaporation at extreme temperatures.

The conclusion is that we, as expected, have experienced some thermal deactivation. The observed deactivation has probably occurred during the initial phase of the test. The degree of deactivation can be reduced through a more uniform flow distribution. Improvements have also been performed concerning the active phases since the initiation of the Åstorp-test. In the development work concerning thermal stability of active phases, we use a specially designed rig for accelerated thermal deactivation.

However, the results from the Åstorp-test indicate that we are close to a suitable catalyst composition. The degree of deactivation is not serious in catalytic combustion since the main function of the catalyst is to generate free radicals for downstream gas phase reactions. Even if the activity of the catalyst is rather poor in activity tests, it will still generate these free radicals necessary for the combustion. The results from the emission mapping also indicate stable emission data during the entire test.

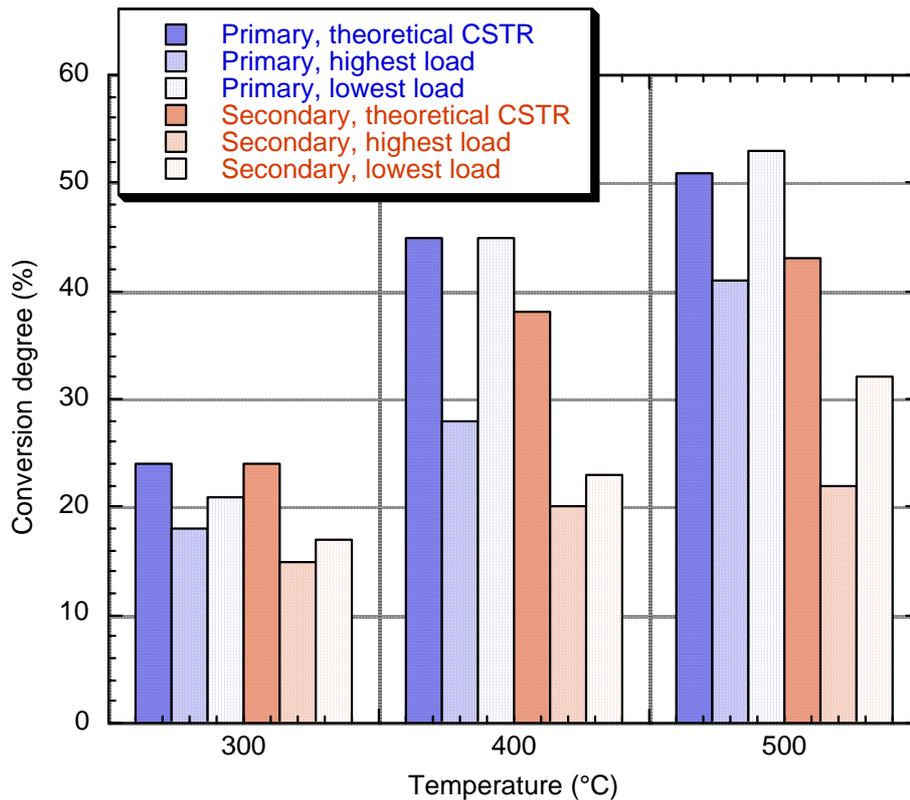


Figure 16 Results from activity measurements in a micro reactor. Combustion of CO in air.

## 8. Technical evaluation and analysis

There are really a number of aspects to take into consideration when analysing the data of the CHEs:

- Capacity versus size
- Emissions
- Excess-air ratio
- Turn-down ratio
- Thermal efficiency
- Fuel flexibility
- Durability
- Pressure drop

The current CHE is analysed according to these aspects below.

## **Capacity versus size**

The driving forces to increase the effect density are clear: compactness, decreased price and improved thermal response.

The effect density ( $\text{MW}/\text{m}^3$ ) has been increased from a value of  $3.5 \text{ MW}/\text{m}^3$  to a value close to  $7 \text{ MW}/\text{m}^3$  during the autumn of 2001. The CHE is an “all-inclusive” unit, which means that no secondary air/air-heat exchanger or condenser are necessary to implement.

We see no need in trying to improve the effect density further at this moment. In the long term, we forecast effect densities of about  $10 \text{ MW}/\text{m}^3$ . Still higher values will render us problems with decreased thermal efficiencies due to incomplete condensation.

For non-condensing types of CHE's, it is possible to increase the load further provided that measures are taken to improve the flow distribution, i.e. a symmetric flue-gas flow with multiple outlets. Effect densities in the region of  $20 \text{ MW}/\text{m}^3$  are expected

## **Emissions**

The emission status of the CHE is indeed an important area. The regulated emissions are CO and  $\text{NO}_x$ . The most stringent regulations at the moment are associated with the Hannover norm. The  $\text{NO}_x$ -emission should be below 11 ppm and the CO-emission below 14 ppm according to the Hannover norm (DIN 4702/8: measurements at 13%, 30%, 39%, 48% and 63% of full load).

The boiler manufacturers normally refer to DIN 4702/8 when comparing emissions. The CHE should preferably satisfy the Hannover-norm to be “the solution for the future”.

During the course of development, we have experienced problems to reach the emission goals, especially for CO at the highest loads. Extensive activities have been directed to emission control and we have converged towards the target values. Indeed, the development work performed during 2001 enable us to present the following values:

$\text{NO}_x$	5 ppm (DIN 4702/8), <10 ppm at maximum load
CO	15 ppm (DIN 4702/8), <60 ppm at maximum load

These values were obtained with a fresh catalyst. Deactivation might result in somewhat increased emissions.

The residual problems are still associated with CO-emissions. The CO-emissions arise from impingement of the combustion zone on to cooled surfaces, i.e. we “freeze” the reaction zone. The diameter of the gas inlet should be increased to enable gas-phase completion before impingement on to cold surfaces. Improvements can also be made through a better structure/coating on the secondary catalyst layer.

### ***Excess-air ratio***

No formal demands exist but increased excess-air ratios will decrease the thermal efficiency, especially at high flue-gas temperatures (incomplete condensation). The CHE can operate in a wide excess-air window: [1.05, 1.5]. The possible window of operation covers all demands forwarded by the boiler manufacturers.

### ***Turn-down ratio***

The CHE has an extreme turn-down ratio in comparison to conventional boiler-systems. Indeed, it is not the CHE itself which limits the turn-down ratio but components around the CHE, e.g. valves, fan, air/fuel-controller etc.

The current turn-down ratio of the system is 1:10. The CHE has a much higher turn-down ratio, possibly 1:25 or more. The boiler manufacturers are satisfied with the current status and request turn-down ratios in the region 1:6 – 1:10.

### ***Thermal efficiency***

The thermal efficiency is associated with the inlet-water temperature, the excess-air ratio and the efficiency of the heat-exchange process. The temperature difference between the inlet-water and the flue-gases is restricted to a few degrees. The excess-air ratio is in the desired region, i.e. 1.2 – 1.4. Consequently, the inlet-water temperature entirely governs the thermal efficiency of the unit.

General demands concerning the thermal efficiency are:	98 – 101% at 60/80°C
	105% at 30/40°C

These figures are reached with the current CHE-design.

### ***Fuel flexibility***

The fuel flexibility is an extremely important question and an advantage of the CHE-concept. There exist considerable problems with different gas qualities on the market and the boiler manufacturers need to produce a number of versions to comply with the different gas qualities.

The CHE is expected to tolerate different gas qualities without any problems. This is indeed a strong sales promoter of the CHE.

### ***Durability***

The durability is one of the most important questions for success. The complete system (CHE-system) should function properly for at least 10 years. It is allowed to replace the catalyst on maintenance, but the replacement interval must be at least 5 years.

The durability question splits into two relevant areas: mechanical stability and morphological stability. The mechanical stability is associated with the implementation of the catalyst into the heat exchanger and the methods used to produce mesh cylinders.

The morphological stability associate to the coating and the active phase of the catalyst and possible degradation through sintering and evaporation.

The Åstorp-test has demonstrated the durability of the catalyst and the heat exchanger during transient operation for 5000 hours. The results confirm the function, operability and reliability of the CHE-concept. However, the Åstorp-test must be followed by complementary confirmations concerning reliability, safety and durability. Such tests, which certainly are demanding, will be carried out as field tests in close collaboration with boiler manufacturers.

### ***Pressure drop***

The pressure drop is in control. The majority of the pressure drop on the gas side is associated with the nozzle. The boiler manufacturers have presented target values of 8 – 10 mbar. The present CHE shows a total pressure drop of 7 mbar at full load. Hence, the pressure drop is not a critical question.

## **9. Conclusions**

The state-of-the-art knowledge concerning the present CHE-design together with results obtained during the long-term evaluation confirms the assumptions concerning the advantages of the CHE-concept.

We are able to produce heat in an extremely compact device with excellent emission data and a high thermal efficiency. The present CHE-design complies with the most stringent emission standards at the moment (the Hannover-norm). The effect density is about 6 MW/m<sup>3</sup> in the current design, which presently can be considered as a unique value. The thermal efficiency is well above 105% if the cooling medium is cold enough (30 – 40°C).

The turn-down ratio of the CHE is at least 10:1, which is much higher than other solutions. Consequently, it is possible to reduce the number of starts/stops over a year to decrease the mechanical impact on the construction and the start/stop-emissions.

Since the pressure drop is low, it is possible to use standard components in the gas-and air supply systems. Suitable methods of initiating and controlling the combustion process, built on standard components, have been proposed. The cost of the CHEs is reasonable according to the price situation prevailing on the market.

The CHE is easy to scale according to specific needs with respect to the effect. Also, larger appliances can be built in modules, which comprises standard units. Another important feature of CHEs, is the possibility to combust also other fuels than natural gas in the same unit.

The long-term evaluation presented in this report confirms the function, operability and reliability of the CHE-concept. Indeed, the emissions were constant during the long-term test, thus indicating an inherent stability of the combustion catalyst and the catalyst structure.

The current design will now go through an industrialisation and a customisation phase in order to reach the market during the next few years.

## 10. Future perspective

The latest development together with the information obtained during the long-term evaluation confirms the potential of the CHE-concept. The first application will be CHEs for domestic applications (i.e. wall-hanged condensing boilers) in small appliances. Later on the goal will be to scale the CHE-concept also to other effect classes, e.g. small-scale water heating and large-scale appliances like district heating. There are also interesting fields of applications in the process industry. In some applications the coolant might be replaced with oils or other heating media. Also, small-scale steam generation is another interesting area of application.

The studies have so far been entirely focused on natural gas as the fuel. However, the CHE-concept opens a possibility to build heating units with the capacity to combust a variety of fuels in the same unit. Thus, fuel flexibility is indeed a very strong advantage of the CHE-technology.

There is still a potential to further improve the system with respect to emissions and operability. However, the present data are good enough to start a close dialogue with boiler manufacturers concerning customisation and commercialisation.

The exact design of the control system and the safety system are still open questions. In order to arrive at a suitable solution which take parameters like operability, maintainability and reliability into consideration, it is necessary to have detailed discussions with system manufacturers and authorities.

Really, the project which was initialised almost a decade ago has now finally reached a milestone; confirmation of the function, operability and reliability of catalytic heat exchangers in water heating.

Much of the efforts to put the CHE-concept on the market are now focused on industrialisation and customisation of the concept.

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**SE-205 09 MALMÖ • TEL 040-24 43 10 • FAX 040-24 43 14**  
**Hemsida [www.sgc.se](http://www.sgc.se) • epost [info@sgc.se](mailto:info@sgc.se)**

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