REDUCTION OF EMISSIONS FROM FERROALLOY FURNACES

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ABSTRACT

The Norwegian ferroalloy industry has high ambitions regarding environmental standards. Basic research work has been performed to improve the fundamental understanding of ferroalloy processes and the environmental aspects. This paper will present work dealing with the understanding of formation and control of NOx, PAH and dioxins. During this work various techniques and methods have been applied, such as comprehensive industrial measurements, laboratory experiments, model development and application of Computational Fluid Dynamics (CFD). The main goal has been to reduce the environmental impact of ferroalloy plants, by means of improving the combustion processes done by introducing new charging routines and optimized furnace operations, instead of installing expensive gas treatment systems.

The Norwegian obligations in accordance with the Gothenburg protocol are to reduce the NOx emissions by 30%, compared with the 1990 level within 2010. Measures developed in this work have resulted in 40-60% reduction in NOx emission, and major reductions in PAH and dioxins for ferrosilicon and silicon metal plants. This has been achieved by introducing semi continuous charging and improved furnace operations. Semi continuous charging and optimized furnace operations are shown to reduce the blowing activity (i.e. emission of large quantity of SiO over the charge by direct channelling from the crater zone). It also reduces variation in off-gas temperature and dust production.

To understand the processes and to achieve our results we have used online equipment, with fast sample rates and response times, to measure the off-gas compositions and temperatures. Most of the measuring techniques used are based upon optical principles making use of the absorption- and emission spectrum of the gases. In addition a new prototype instrument is developed for continuous measurement of off-gas characteristics, total dust amount and off-gas temperature.

The presented work is a result of a long term co-operation research and development teamwork, between the industry and the research community, and has improved both the process and reduced the emissions. The work has introduced new process design and operation standards, and has resulted in ferroalloy production with better environmental standards.

1. INTRODUCTION

It has been a part of a long-term strategy for ferroalloy industry to reduce the air pollution. The effluents from a modern ferroalloy plant will normally not cause environmental problems on its own. No environmental damages or health problems caused by the emissions discussed in this report have been observed in the vicinity of modern ferroalloy plants. But all emissions may have potential environmental effect as an additive effect with other sources. The results of this research and development teamwork have improved both the process as well as the environment. The work has introduced new process design and operation standards, and this will be continued when the different plants and furnaces are upgraded.

Previous research in this area has investigated the waste gas dynamics of ferrosilicon furnaces [1]. Large variations in waste gas composition as well as off-gas temperature during the normal furnace operations were found. These variations were among others induced by various operations such as stoking and charging. Since high temperature trigger clogging, it has been essential in a previous work to understand the clogging phenomena of the ferrosilicon furnace off-gas channels and to minimize temperature fluctuations [2]. The present work is a continuance of earlier work and includes both ferrosilicon and silicon metal plants.

The necessary reduction of the NO_x emissions cannot be achieved by the ferroalloy industry by itself. The total emission of NO_x from the Norwegian metal producing industry is only in the order of 3% of the total Norwegian emissions [3]. The main sources for the NOx-emissions in Norway are land and sea traffic as well as emissions from the oil industry. Measures developed in the project have, in addition to reduced NO_x emissions, resulted in major reductions in Polycyclic Aromatic Hydrocarbons (PAH) and dioxins emissions as well as process improvements.

The Norwegian Ferroalloy Producers Research Association (Norwegian Abbreviation FFF) is an association founded by the Norwegian ferroalloys industry to carry out joint research on ferroalloy processes and products. FFF and The Research Council of Norway have been promoting this research work in order to understand and to improve the environmental standards for the ferroalloy industry. Dimensions of the furnaces are large, there are a large number of parameters having an influence on each other, variations in time and space are important, and many complex phenomena are involved in the process. It is therefore very difficult to draw conclusions about how different parameters influence each other. The presented research work includes results from comprehensive measurements at industrial furnaces, as well as theoretical work, modelling and laboratory experiments.

2. PROBLEM DESCRIPTION

The main goal has been to reduce the environmental impact of ferroalloy plants, by means of improving the combustion processes by introducing new charging routines and optimized furnace operations instead of installing expensive gas treatment systems. It is essential to have theoretical expertise concerning the process- and the combustion related problems to achieve the goals. It is of equal importance to explore new and powerful measuring principles and their industrial implementations (equipment). A successful analysis of processes must in any case be based on a fundamental understanding in order to execute relevant measurements. In some cases, where we could not find appropriate commercial measuring equipment, we have developed new equipment.

To achieve a complete overview of all factors, exhaustive measuring campaigns on the different plants have been carried out. Measuring campaigns with many simultaneous measurements, with fast sample rates and response times of selected parameters, have resulted in:

- Increased understanding of the process.
- Identification of emission levels.
- Identification of measuring errors and inaccurate interpretations caused by slow instrument response.
- Experimental data that together with Computational Fluid Dynamics (CFD) modelling has given a more complete understanding of the process.

2.1. Expected Off-gas Constituents and Their Environmental Impact

This work has mainly concentrated on formation and control of the combustion controlled pollution elements NOx, PAH and dioxins.

NO_x (NO_1, NO_2) causes damage on vegetation and wildlife, and increases the risk of bronchiae suffering. The reason is that NO_x contributes to acid rain. NO_x forms in combustion processes by reaction between N_2 and O_2. There are four main NOx formation mechanisms: thermal NOx, fuel NO_x, prompt NO_x and nitrous oxide mechanism. The two first mentioned are the dominant mechanisms in electric arc furnaces producing ferro-silicon and silicon-metal.

Thermal NO_x is formed by direct oxidation of nitrogen (from the air) at high temperature. Figure 1 gives a rough idea how the different mechanisms are influenced by temperature. The formation of thermal NO_x is increased by increasing any of the following three variables: peak temperature, time at high temperature and oxygen content at high temperature.

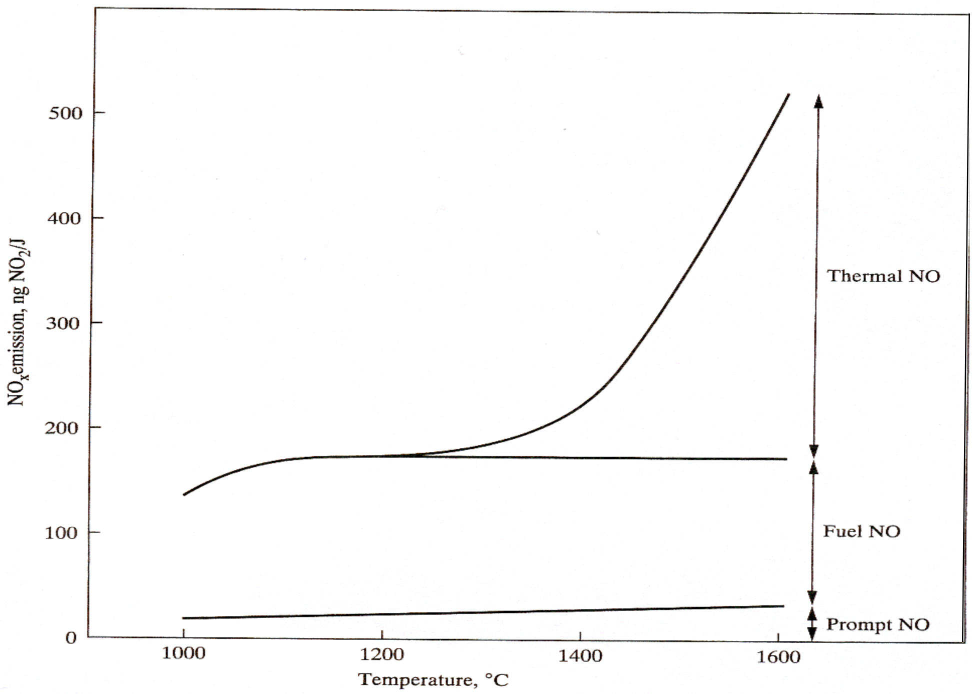

Figure 1: Approximate contributions from three NO_x mechanisms in coal combustion [4]

Fuel NO_x is formed by oxidation of the so-called fuel nitrogen, which means the nitrogen components present in the solid fuel. Formation of fuel NO_x is much more complex and less understood than thermal NO_x. Fuel rich conditions and interaction with specific intermediates whose presence is difficult to assess will reduce fuel NO_x. Fuel NO_x can also be important at much lower temperature than thermal NO_x.

PAHs (Polycyclic Aromatic Hydrocarbons) are a group of more than 100 different chemicals. Most PAHs in the environment are formed by incomplete burning of carbon-containing materials like oil, wood, garbage or coal. The PAH 16 EPA emission factors (recommended by U.S. Environment Protection Agency) are used to estimate national emissions of hazardous air pollutants, and has identified 16 priority PAHs, based on concerns that they do or might cause cancer in animals and humans. PAHs are destructed at temperatures above 800°C.

Dioxin is the name given to a class of super-toxic chemicals, the chlorinated dioxins and furans, mainly formed as a by-product of the burning of organic chemicals and plastics that contain chlorine. The dioxins forms between 250 and 450°C, and they are destructed at 800°C with a two second retention period or one second at 950°C.

3. FULL SCALE EXPERIMENTS

It has been performed measurements at different industrial FeSi/Si furnaces, all with feeding tubes through which the raw materials are fed. The off-gas composition- CO, CO_2, NO, NO_2, SO_2, O_2- and temperature have been measured at all campaigns every 5 seconds. In addition standard process data (like electric power, electrode position, electrode slipping, charging and stoking) have been logged. PAH and dioxins have been measured only in some campaigns, and we have also measured methane and nitrous oxide. The dynamic changes in the dust concentration have been monitored optically or with our self-developed thermophoretic sampler. The sampler collects dust in the off-gas channel within one minute, and afterwards the dust is removed and stored. A total sample rate of one sample per 4 minutes is possible. The samples are weighed and chemically analyzed later on. A prototype of an online optical instrument to measure simultaneously the total dust amount, chemical composition and off-gas temperature has also been developed to improve the dust measurements and process optimization.

3.1 Measuring Equipment

Accurate and continuous measuring methods are of vital importance to achieve increased process understanding, to control the process, to minimize emissions and to achieve better end-products. Measurements with fast response are important to understand processes with fast dynamics. This is of particular importance when we are dealing with control and strategies for minimizing emissions. The major instrumentation problems in the off-gas system of the ferroalloy industry are due to high temperatures, large amounts of dust and clogging and contamination of the measuring equipment.

Thermowells, used to protect temperature sensors, accumulate soot and silica particles, thereby insulating the thermowells. The result is much lower temperature peaks and very slow response. Optical measuring techniques have a great advantage because of fast response and little clogging and maintenance work. In this work we have gained experience with an online optical pyrometer that is measuring the temperature of the CO/CO_2 in the off-gas. The principle is to measure on a wave length where CO/CO_2 emits heat by radiation. This non-contact principle gives a true gas temperature, but the position of the measuring volume depends on the off-gas temperature and CO/CO_2 concentration.

We have used optical online instrumentation based on tuneable diode lasers (TDL) to measure gas components such as NO, H_2O, CO, CO_2 and CH_4. The laser beam is sent through a measurement volume from a transmitter (laser) to a receiver with a light sensitive detector. The instrument is protected from the process gas using windows that are kept clean by purging air.

To measure the dust we have used equipment based on transmission measurements across the off-gas channel. To measure the dust amount and composition we have developed a NDIR (non-dispersive infrared absorbance) sensor, where the amount of light absorbed is proportional to the concentration.

3.2 Experimental Results

Figure 2 shows typical measurements in off-gas temperature fluctuations at two different FeSi75-plants with different furnace operation, semi continuous charging at plant 1 and batchwise charging at plant 2. The temperature fluctuations at plant 1 are rather small and representative for semi continuous charging i.e. charging every minute. The high temperature bursts are triggered by avalanches (ref. paragraph 3.2.2) in the charge. The temperature peaks at plant 2 contributes to clogging in the off-gas channels and may enable NO_x formation inside the furnace, above the charge, where the temperatures are even higher.

Figure 3 shows correspondingly large fluctuations in the off-gas composition with batch charging. The charge avalanches causes outburst of large quantities of combustible gases, like CO, that rise from pockets of poorly carbonised charge materials.

Figure 4 shows how much smaller the fluctuations in off- gas composition can be with semi continuous charging and optimized furnace operations. Notice that the CO scale is just a tenth of the scale from the one in figure 3. The graphs in figures 3 and 4 both have a time span of one hour.

It was expected that there might be a good correlation between temperature and NO_x emissions. There is some correlation, but figure 5 shows a very clear correlation between dust concentration (mainly silica) and

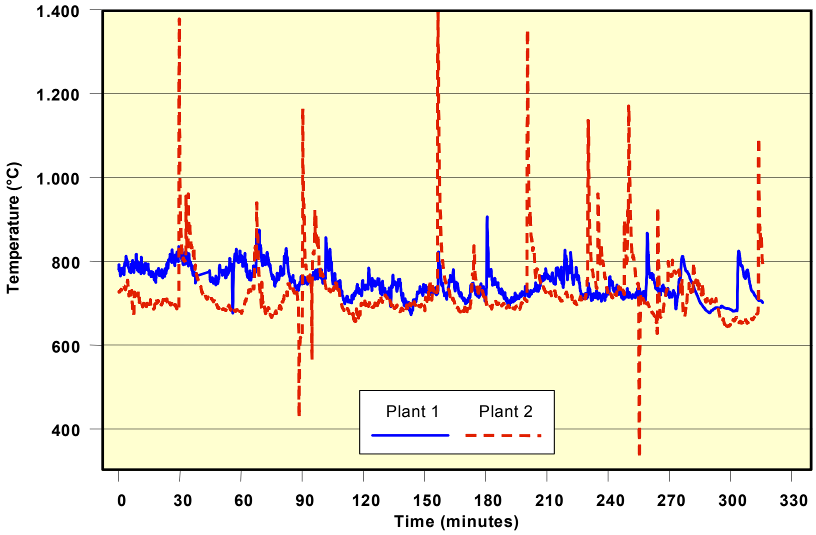

Figure 2: Different off-gas temperatures

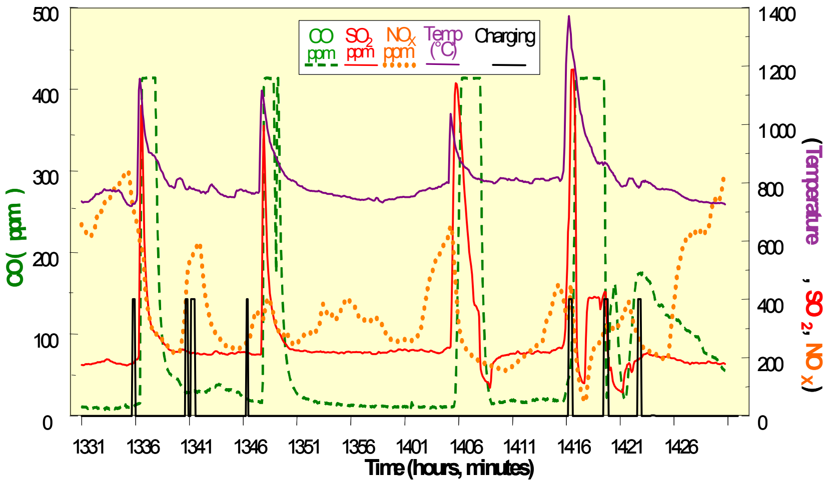

Figure 3: Off-gas composition and batch charging

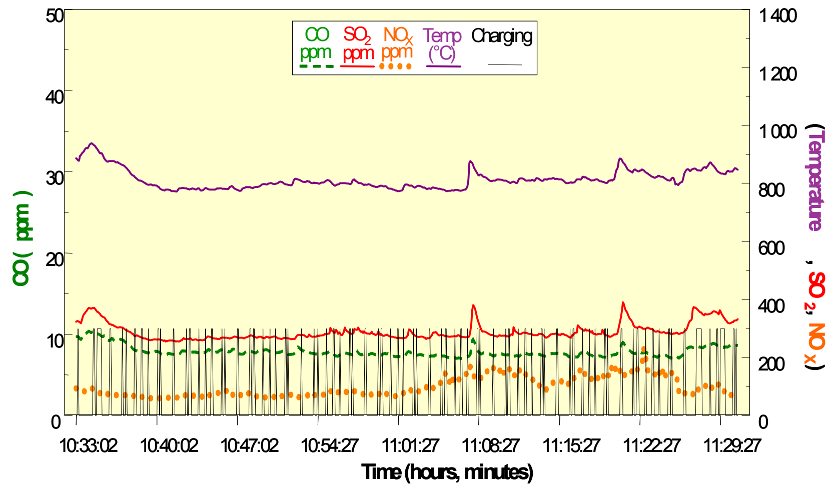

Figure 4: Off-gas composition and continuous charging

NO_x emissions measured at a FeSi75 plant. This correlation has been observed in all measuring campaigns. The experimental findings can be summarized as follows:

1. At low off-gas temperatures, NO_x concentration increases monotonously with dust concentration.
2. At low dust concentrations, NO_x concentration increases monotonously with the temperature.

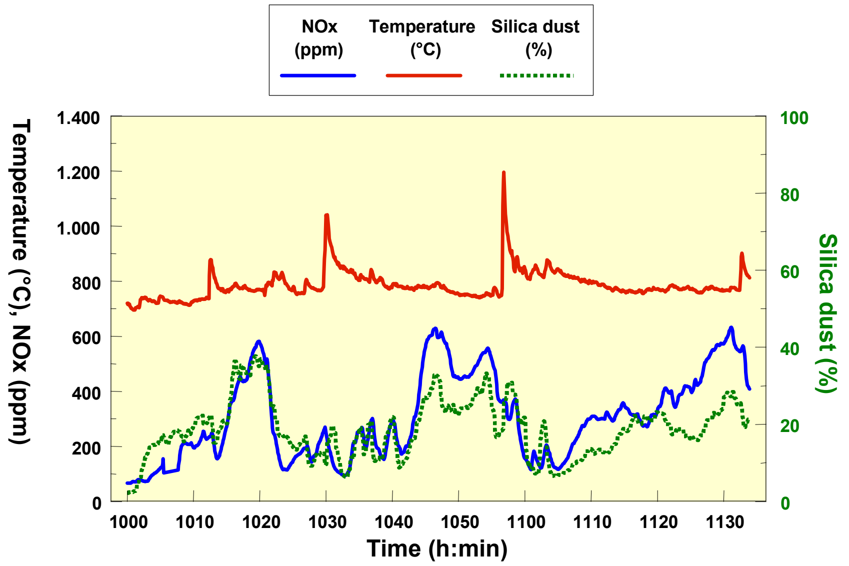

Figure 5: Comparison between temperature dust and NO_x

3. For the measurements taken during the measuring campaigns, the dust concentration has larger impact on NO_x concentration than the off-gas temperature.

Dust mostly comes from SiO combustion which produces high temperature zones locally. These locally high temperatures promote large production of thermal NO_x. The extra energy released by relatively small amounts of SiO may not be significant compared to the total enthalpy of the off-gases and consequently, changes in off-gas temperature may be small or even negligible.

3.2.1 Optimal Conditions

Only plants with semi continuous charging are considered for the so-called optimal conditions. At a Si- plant, during campaigns both in 2002 and 2003, a lowest level of approximately 50-70 ppmv@16%O_2 was measured, as seen in figure 6. In 2003, when the charging had been optimized, the periods with this lowest level were longer and more frequent and the low level was now even lower than before. In 2002, the NO_x level almost never moved below 70 ppmv@16%O_2, and the average NO_x level was more than twice as large. In another measuring campaign a furnace was stopped for about 15 minutes. It was then possible to observe the same lowest level of 50 to 80 ppmv@16%O_2. At another plant measurements were taken while the furnace was working with a power of approximately a third of normal, and the NO_x level was similar to the above-mentioned 50 to 80 ppmv@16%O_2.

Optimal conditions for minimum NO_x emission are a furnace with well distributed gas composition and where the temperatures are too low to produce thermal NO_x. Under these conditions only fuel NO_x will remain, having a value approximately independent of temperature (see Figure 1).

Spontaneous avalanches in the charge (i.e. collapse of large quantities of colder materials falling into the crater or other created cavities) occur from time to time as shown in Figure 7. Due to variable response time between instruments there can be a delay in some of the measured values. This avalanche is measured on a Si-furnace, while FeSi75-furnaces may have similar avalanches. The NO_x level was falling off right before the avalanche. As O_2 starts decreasing NO_x has a small peak going from 120 to 220 ppm and then flattens to a level lower than before the avalanche. N2O which was around zero goes to over 35 ppm under this avalanche. In addition a sharp peak in dust occurs as well as in temperature, SO_2, CO and CH_4. Dust must come from the sudden release (and combustion) of large amounts of SiO, while unburnt fine raw materials and soot are produced from heavy hydrocarbons released by pyrolysis of coal or coke. It is also worth noticing that the CO_2 concentration increases to 10%. Some typical features can be listed from the experimental observations of avalanches:

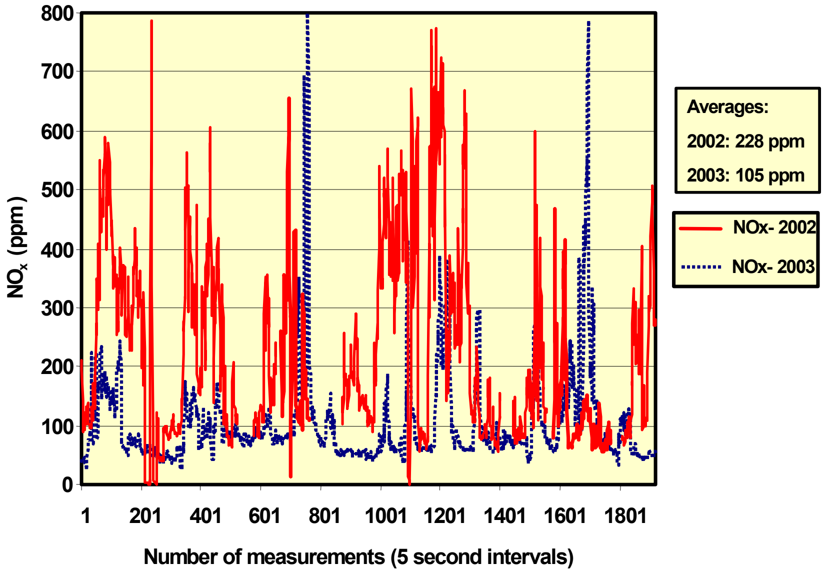

Figure 6: Optimizing of NO_x emissions

- Unreacted charge materials suddenly get in touch with hotter parts of the furnace resulting in high volatile release due to pyrolysis.
- The effect of an avalanche lasts approximately 1 minute. This is the time between the first change (going to a peak in some few seconds for most measurements) and the return to normal conditions (e.g. O_2 back to 16 vol. %).
- A distinct release of unburnt gases (CH_4, unburnt hydrocarbons and CO).
- Excess levels of combustion products: CO_2, SiO_2.
- Decrease in oxygen (from 16% to below 6% - can go as low as 0%).
- Relative changes vary from one avalanche to the other.
- NO_x seems to undergo a slight increase earlier than the other combustion products. A more intense avalanche does not necessarily mean higher NO_x. The average off-gas temperature exceeds 1400°C under an intense avalanche. This is above the temperature allowing thermal NO_x formation, implying that the low oxygen concentration then limits further NO_x formation.

3.2.3 Blowing

A clear correlation between high concentration of dust in the off-gas and high NO_x level has been established. Blowing is an extreme situation, where SiO rich gas from around the electrode tip is released through a gas channel in the charge. Then large quantities of SiO are burnt in air to silica dust. The observed correlation between NO_x and silica is also valid under blowing: blowing results in both high NO_x and silica.

As opposite to the avalanche phenomenon, which is always short in duration, the blowing phenomenon can last much longer. As long as channels are left open between the cavity below the electrodes (also called crater)

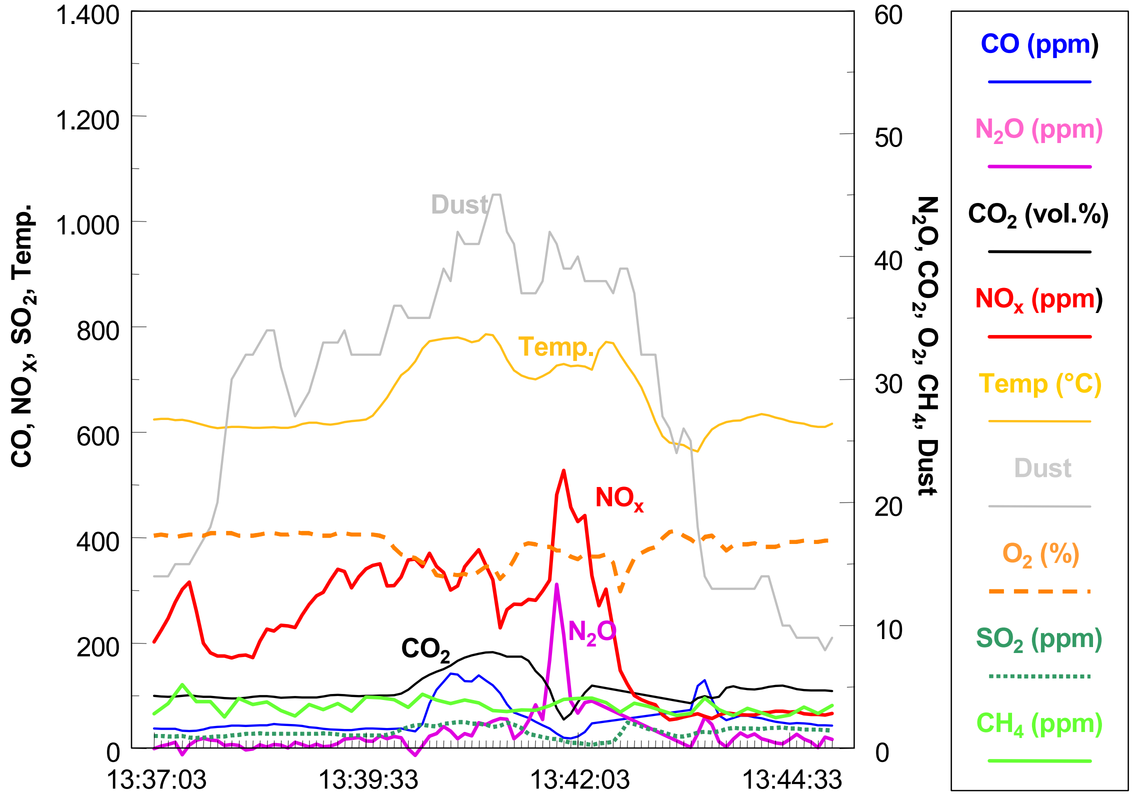

Figure 8: Off-gas measurements during blowing

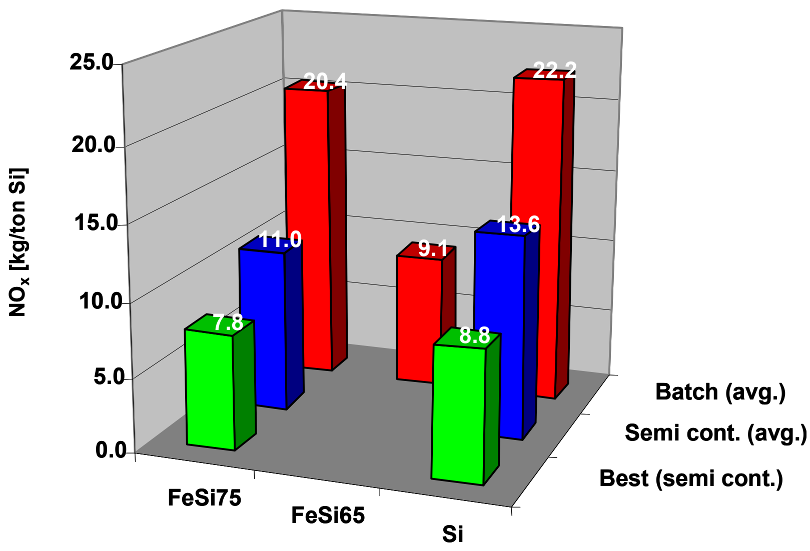

Figure 9: NOx emissions different charging routines and ferro-alloys

and the charge surface, the blowing phenomena takes place. Figure 8 shows a blowing phenomenon from a Si-furnace lasting for approximately 7 minutes. The increase in NO_x is more significant than for the avalanches. Now NO_x and N_2O formation takes place in local zones where SiO gas is released via channels through the charge surface. Here SiO gas burns with excessive local temperatures as long as oxygen is present.

4. ANALYSES AND CONCLUSIONS

The NO_x formation in ferrosilicon furnaces seems to be closely linked to the combustion of SiO and the fact that increased local temperatures connected to SiO combustion will promote NOx formation.

A possible explanation of the NO_x reduction with semi continuous charging is the reduction in heavy blowing activity. Measurements inside the furnace (with a more than 4 meter long water cooled probe [2]) have shown very low oxygen levels just above the charge. In oxygen poor zones, as we have measured right above the charge, small blowing and avalanche phenomena do not influence thermal NO_x formation significantly because of the lack of oxygen. NO_x only becomes significant when the flames burn in a zone where oxygen is available in sufficient quantities.

The thermal NOx mechanism seems to be the dominant mechanism in electric arc furnaces producing ferrosilicon and silicon-metal. The typical fuel NO_x level for a furnace is both estimated and measured to be in the range 50-100ppmv@16%O_2, with possible variations depending on furnace type and reduction material composition. Total NO_x levels less than 100 ppmv@16%O_2 have been measured for longer periods during some of our campaigns (see Figure 6).

Figure 9 shows a comparison of NO_x levels and charging methods from different ferroalloy plants with different charging routines, illustrating the potential with better charging routines. The figure shows the results of fifteen measuring campaigns carried out within a ten year period (1995-2005). Some of the improvements may be due to gradually better furnace operation, as the plants received information of the importance of improved charging routines.

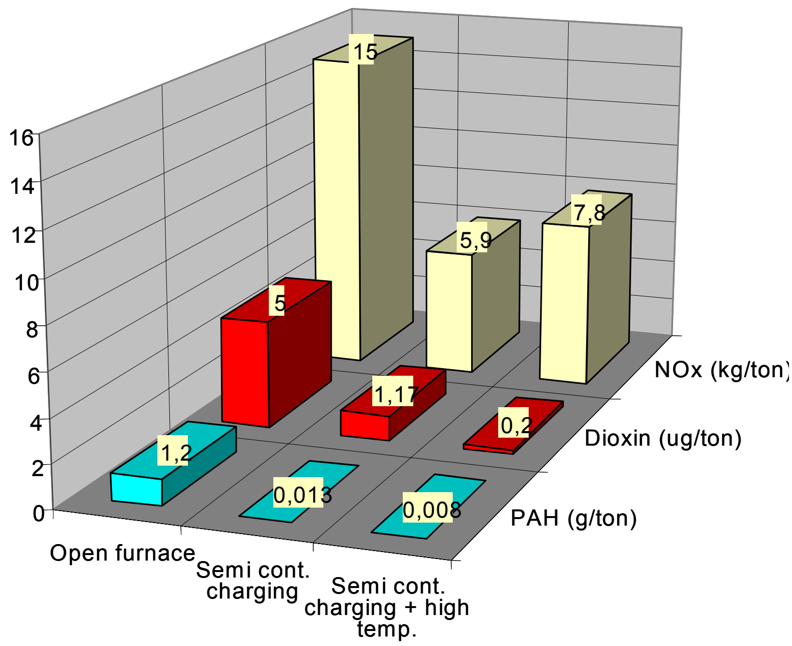

Figure 10: Possible improvements in PAH, dioxin and NO_x emissions

Figure 10 shows the reductions in PAH 16 EPA, dioxin and NO_x emission from two different FeSi75-furnaces. The open furnace is a traditional furnace with batch charging, and these are our reference measurements from 1995. The other one is a more enclosed furnace with feeding tubes through which the raw materials are fed semi continuous i.e. every minute. One full day was used measuring with semi continuous charging and standard off-gas temperature. The next day the off-gas temperature was increased from an average of 635°C to 812°C, by reducing the off-gas amount. This is within the temperature range where PAH and dioxin are destructed, and the temperatures inside the furnace are even higher. When the off gas temperature is increased the temperatures under the hood of the furnace can be in the range where thermal NO_x can be formed (Figure 1).

The average N_2O and CH_4 concentrations in the ferroalloy processes are typically a few ppm, except for some peaks as seen in figures 7 and 8. CH_4 was here measured at two Si-furnaces with an average of about 3 ppm, and N_2O are measured at one Si-furnace with an average of 0.3 ppm. These are very low values almost at the detection limit of the measuring instruments used. The oxygen content in the measured off-gas is about 14 -16%.

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