NO_X-EMISSIONS FROM THE SILICON PROCESS COMPARING WET AND DRY RAW MATERIALS PILOT SCALE EXPERIMENT

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ABSTRACT

SINTEF has carried out several pilot scale silicon process experiments in the past, but always with an open off gas system. In order to test the possibilities in running a semi closed furnace operation, a new off gas hood has been designed and tested. The off gas hood is designed to collect all off gases to gain insight into the phase compositions in the off gas and at the same time have the opportunity to monitor and maintain the charging/stoking of the furnace. The furnace hood has regulation and control of the air inlet into the combustion zone in two different heights. Both wet and dry raw materials are tested. The off gas temperature and composition was continuously monitored and analyzed during the experiment. In order to expand the knowledge on NO_X-formation in silicon metal production, such information is vital.

KEY WORDS: *Silicon process, pilot scale furnace, NO_X emissions.*

1. INTRODUCTION

Because of the negative environmental impact, the attention towards all kinds of NO_X emissions increases. The authorities' demand towards better surveillance and control of emissions increases as well.

Earlier and new industrial measurements towards FeSi- and Si-metal furnaces reveal quite high NO_X-emission. The measurements also show that the NO_X formation (mainly as thermal NO_X) is distinct connected to the formation of dust ($SiO \rightarrow SiO_2$) in the combustion chamber above the furnace surface, when the temperature is high and the access to N_2/O_2 is good. This means that stoking, charging and temperature straight above the furnace surface is important factors for the NO_X formation.

Silicon is produced in submerged arc furnaces, where quarts react via several sub reactions, with wood, charcoal, and coal. The required energy is supplied by carbon electrodes. The production route for ferrosilicon is similar, with addition of iron oxides. CO and SiO-gas escapes out on top of the furnace where it burn with air and form CO_2 and SiO_2.

Basically there are three main mechanisms producing NO_X; thermal NO_X, fuel NO_X and prompt NO_X. In ferroalloy industry, thermal NO_X is the most relevant, but fuel NO_X, from the oxidation of nitrogen components in the reduction material, can also be a significant source. Thermal NO_X is a result of direct oxidation of N_2 from the air at high temperature. NO_X-formation increases with combustion temperature, time spent at high temperature and the O_2 and N_2-contents present in the combustion chamber. The oxygen and nitrogen produce various oxides of nitrogen, mainly NO, but also a lesser degree of NO_2 and N_2O.

NO form nitric acid when dissolved in atmospheric moisture, result in a component of acid rain. In addition NO_X lead to formation of tropospheric ozone and thereby contribute to several forms of respiratory disorders. This is the main environmental impact of the NO_x emission.

In order to expand the knowledge on NO_X-formation in silicon metal production, a pilot scale experiment in a 160 kW silicon furnace has been carried out. A new off gas hood was designed with a view to be able to copy and manipulate the formation mechanisms for NO_X by controlling the flow of false air into the off-gas system.

The resulting NO_X-values corresponding to the different air inlet to the furnace top, showed significantly differences between the different air inlet geometries.

2. FURNACE

The experiment was carried out in a 160 kW single phase furnace with adjustable current and voltage supply. The furnace can be operated with both AC and DC. Maximum DC current is 8000 A and maximum voltage is 300 V. Maximum AC current is 5700 A and maximum voltage is 215 V. In this case AC was chosen. The furnace is connected to an off gas system, monitoring composition and temperature of the gas, and with filter collecting coarse and fine particles in the end.

Based on the observation from industrial measurements, the off gas hood was designed with the opportunity to control the false air inlet in to the combustion chamber, and at the same time be able to maintain the stoking and charging operations. A sketch and a picture of the furnace are shown in figure 1.

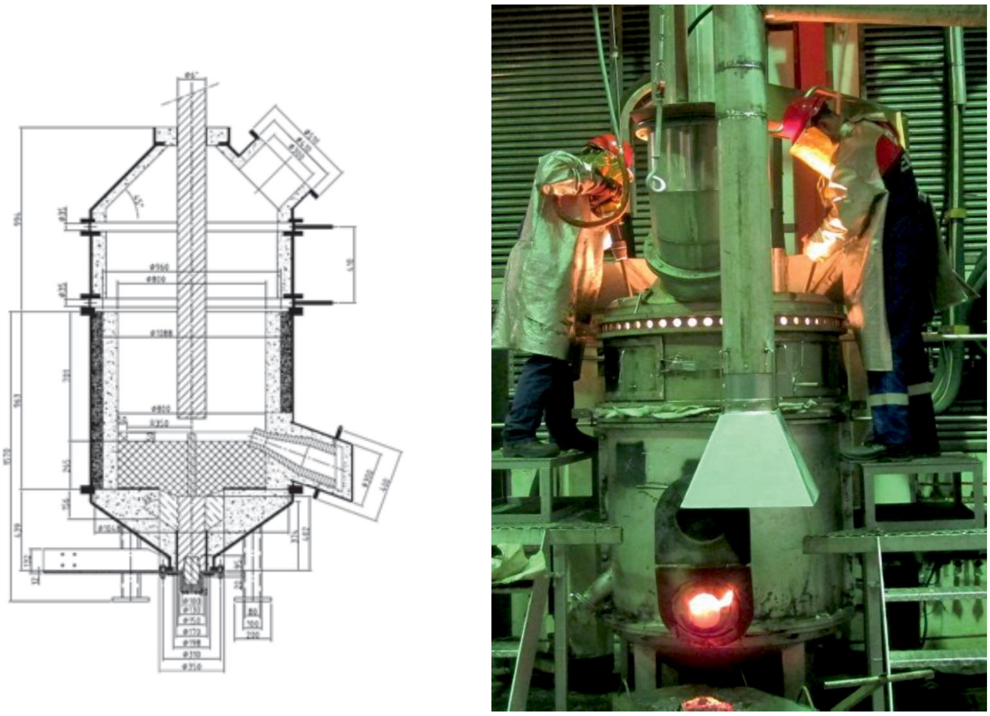

Figure 1: The figure shows a sketch of the furnace and a picture of the furnace in action

The furnace body is constructed with an outer steel mantle which is dividable horizontally just below the tap hole. The top is also dividable vertically in order to be able to apart the furnace pot into two halves. This particularly design reveal an option to fill the furnace with epoxy after ended experiment. The molded mass can then be removed in one piece. It is a very useful technic in post experimental studies, to cut the entire furnace in slices, and subsequently drill out samples from decided positions for analysis. Figure 2 shows a typical cross section of the furnace after ended experiment and a schematic overview of the different reaction zones.

The bottom lining was stamped with conductive SiC. In the bottom a graphite electrode was used with the power connected via copper tracks and a copper bolt below the furnace. In the side lining an Al_2O_3-based paste was used. The gap between the steel mantle and side-lining was filled with a 5 cm thick layer of silver sand (SiO_2).

Over the furnace hangs a 6 inches (15 cm) graphite electrode that can be adjusted up and down.

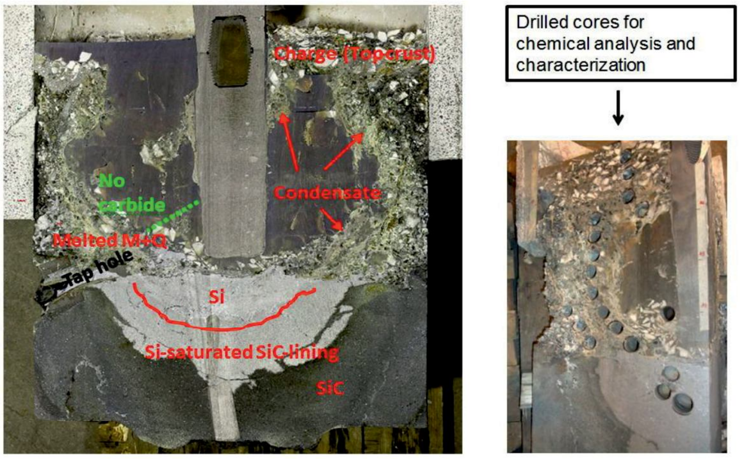

Figure 2: The figure shows a typical cross section of the furnace after ended experiment

2.1. Off Gas System

The hood was constructed with two sets of perforated rings. The holes perforating the ring had a diameter of 35 mm, giving a total opening area of each ring of 0,096 m^2. Each set of ring consist of one inner fixed ring one outer adjustable ring. The distance between the two set of rings were 500 mm.

The hood was also provided with two stoking gates and two gates for charging raw materials into the furnace.

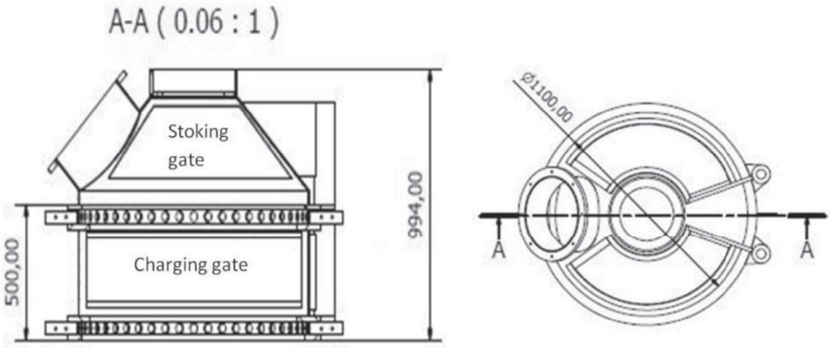

Figure 3: The figure shows a close up of the off gas hood

2.2. Furnace Operation

A critical factor to succeed the furnace operation in this scale, is a proper bottom lining. The conductive SiC lining was primary preheated for 500°C during 1 day and further baking with coke bed for 1 more day. The furnace is ready for raw material feeding after a total preheating equivalent to accumulated 1120 kWh. Raw material was charged into the furnace for 15 hours before the operation was stable and the furnace ready for the first tapping.

The furnace was run using AC power. The current was fixed at 4000 A, and the voltage fluctuate around 40 V. The resulting effect was stable around 180 kW. The furnace was tapped approximately every 250 kWh. During tapping the electrode was gradually adjusted down, to end up in the bottom when the furnace was "empty". After ended tapping the power supply was switched off in order to stoke down the furnace top with pneumatic tools. The electrode was then raised 5 cm and the furnace switched on. The furnace was then ready to rapidly be reloaded up to ¾ level, and then gradually refilled up to normal level (20 cm from pot edge).

Raw material used for this experiment was quarts (3-25 mm), coke (3-15 mm), coal (3-15 mm) and wooden chips (20-50 mm) in order to "ventilate" the charge. The raw material mix started with a carbon cover of 80 %, gradually increase up to 97 %.

The silicon pilot furnace was operating for 39 hours, producing with a silicon yield of 53 %. It was tapped 13 times, giving a total of 58,2 kg of silicon metal and 49,2 kg of fumed silica.

Through the experiment, after steady conditions was achieved, a series of trials where performed. In each trial a set of parameters were changed and corresponding off gas compositions measured. The parameters tested were:

- Position of false air inlet (open upper (U) or lower (L) perforated ring in the hood).
- Humidity/volatility of raw materials (wet (W) or dry (D)).

Wet raw material corresponds to coal (8,9 % humidity / 38,9 % volatiles) and wet wood chips (42,1 % humidity / 72,9 volatiles).

Dry raw material corresponds to coke (0,97 % humidity / 5,91 % volatiles) and dry wood chips (5,6 % humidity / 72,9 % volatiles).

Upper false air inlet is ~70 cm above charge level.

Lower false air inlet is ~20 cm above charge level.

Each run was finished with a tapping, followed by stoking and recharging of new raw materials for the next run.

The main purpose with the experiment was off gas analysis connected to NO_X-formation.

Data from power supply was continuous logged during the experiment. The effect/time-plot is showed in figure 4.

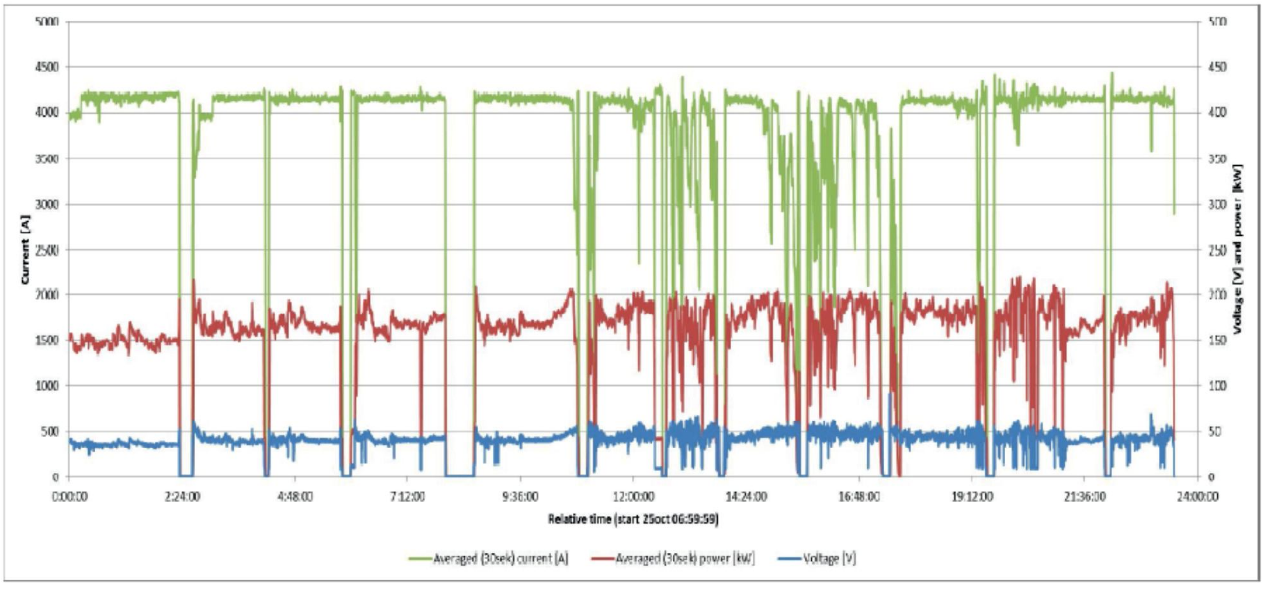

Figure 4: Current, voltage and effect output for the last 24 hours of the experiment

2.3. Measurements

Figure 5 shows a schematic overview of the furnace, off gas system and test points.

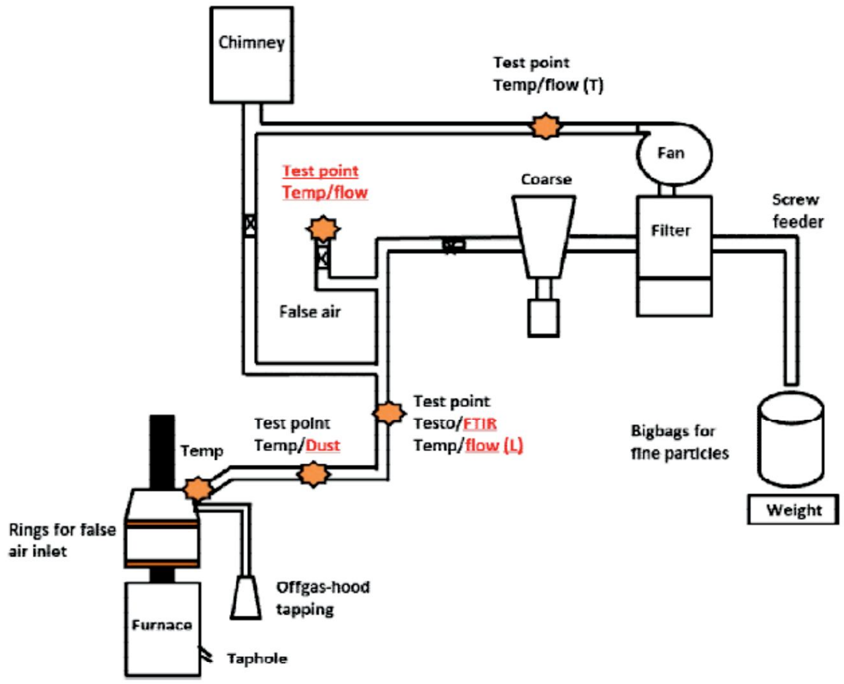

Figure 5: The figure shows a sketch of the furnace, off gas system and test points

3. RESULTS

Table 1 gives a summary of production and power consumption.

Table 1: The table gives a summary of metal produced, dust produced, and effect spent

Trial run nr	Time from start (hh:mm)	Time between tapping	Metal produced, kg	Silica produced kg	NOx, ppm	kWh pr production period	Furnace effect, kW	kWh/kg Si
1	0	0	0	4		1307	150	-
2	02:00	2	0	0,8	8	391	150	-
3	03:50	1,8	0	2	17	247	150	-
4	05:30	1,6	0	2,2	11	258	170	
5	07:10	1,6	0	2,7	26	242	170	-
6	10:15	3	5,8	4	47	-	175	
7	12:10	2	7,3	4,14	17	263	180	36
8	13:30	1,3	6,8	3,2	59	171	180	25
9	15:15	1,7	9,8	6,3	37	270	180	26
10	17:00	1,7	4,9	3,9	18	269	180	55
11	19:15	2,25	12,9	7,2	30	335	180	26
12	22:00	2,8	5,3	6	53	394	180	74
13	23:30	1,5	5,5	2,7	28	231	180	42

The temperature and off gas analysis was measured close to the furnace surface. To analyze the off gas a Testo 350XL [5] was used and the measurements where done continuously throughout the experiment. The measurements are done with a measuring cell with an accuracy of 2 ppm from zero to 40 ppm and 5% of measured value for measurements above 40 ppm. The Testo instrument measures CO, CO_2, O_2, NO, NO_2 and SO_2.

The purpose of the experiment was to study how the NOx emission was effected of:

- Position of false air inlet (open upper (U) or lower (L) perforated ring in the hood).
- Humidity/volatility of raw materials (wet (W) or dry (D)).

4 runs representing 4 different combinations of parameters, was selected to compare the average NOx emission within each run. The results are presented in the bar graph in figure 6. W= wet raw materials, D = dry raw materials, U = upper false air inlet, L= lower false air inlet.

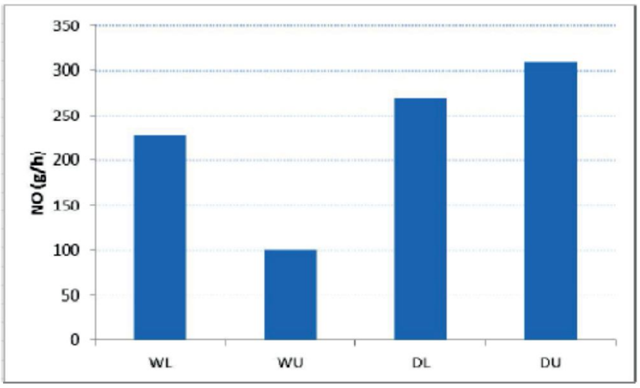

Figure 6: Average NOx emission within 4 different run, representing 4 different combinations of parameters

4. DISCUSSION

The resulting NO_X-values corresponding to the different air inlet to the furnace top, showed significantly differences between the different air inlet geometries. The experimental set up and the hood design was suitable in order to make a controlled off gas study within a fixed geometry. This specific geometry can also easily be transferred into mathematical modelling to verify modelling and simulation results.

Based on the data acquired from our experiment we can conclude the following for the pilot scale silicon furnace:

-Having the inlet of cold air close to the charge surface seems to produce more NO_x than moving it higher towards the off gas channel.

-Based on the NO_x results there is reason to believe that the velocity fields inside the hood influences the NO_x formation significantly.

Understanding the mechanisms in NO_x formation connected to the silicon process is of vital importance for working towards reduced emissions. A better understanding of the connection between the velocity fields above the furnace surface and the NO_x formation is needed.

The NOx emission seems to decrease significant by using wet raw materials (coal and wet wood chips), compared to using dry raw materials (coke and dry wood chips). This is probably due to addition of both water and hydrocarbons in the gas above the charge. Water evaporation contributes to decrease the gas temperature. The hydrocarbons will probably consume the oxygen for other competing reactions.

5. CONCLUSIONS

The NOx emission seems to decrease significant by using wet raw materials (coal and wet wood chips), compared to using dry raw materials (coke and dry wood chips).

The experimental set up and the hood design was suitable in order to make a controlled off gas study within a fixed geometry. This specific geometry can also easily be transferred into mathematical modelling to verify modelling and simulation results.

6. REFERENCES

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