Water Injection in the Fluewalls of an Anode Baking Furnace to Reduce Nitrogen Oxide Emissions

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Abstract

In the aluminium industry, the carbon anodes are baked in the anode baking furnace by means of the combustion of both the volatile matters emitted by the green anode and the extra fuel injected. The baking process generates pollutant emissions, most of them being treated by fume treatment centers. However, some of them persist, such as nitrogen oxide, one of the main sources of acid rain and acidification of fresh water.

Nitrogen oxide emissions are regulated in most countries and limits for this type of emissions tend to decrease. Therefore, it becomes challenging for some plants to operate their anode baking furnaces in compliance with new regulations. End of pipe solutions exist to treat nitrogen oxide emissions, but their implementations are often expensive. This makes source reduction of nitrogen oxide formation very interesting.

One method of source reduction is injecting water into the refractory fluewalls of anode baking furnaces, upstream from the combustion zone. In this article, the principle of operation as well as the implementation and effects of water injection on the anode baking process will be presented.

Keywords: Anode Baking Furnace, Nitrogen oxide, Water injection, Energy consumption, Anode cooling.

1. Introduction

The process of baking carbon anodes in an open-type anode baking furnace (ABF) produces fumes resulting from the combustion of gas or heavy fuel oil in the heating zone, and from volatile matters in the preheating zone. These combustion fumes containing several pollutants are collected via a ring main and sent to a fume treatment center to be treated, especially for soot and fluorinated gases. However, the most widespread treatment centers cannot remove all polluting emissions: nitrogen oxides (NO_X), for example, are not treated and typical concentrations of 20 to 150 mg/Nm^3 can be measured at the stack. Those gases contribute to the air pollution and the local regulations vary considerably from one plant to another. For instance, the local limit in Aluchemie is currently 150 mg/Nm^3 at the stack.

Due to growing environmental concerns, regulations relating to nitrogen oxide emissions are becoming more and more restrictive and some smelters must find urgent solutions to reduce NO_x emissions and maintain their authorization to operate. Smoke reprocessing solutions such as selective catalytic reduction exist; but, they are generally expensive and difficult to set up and maintain, which makes the reduction of NO_x generation at the source highly valuable.

The NO_x formed in the ABF are principally created during the combustion of natural gas and oil, their formation depends mainly on two parameters: the oxygen availability and the temperature of the combustion zone (Figure 1).

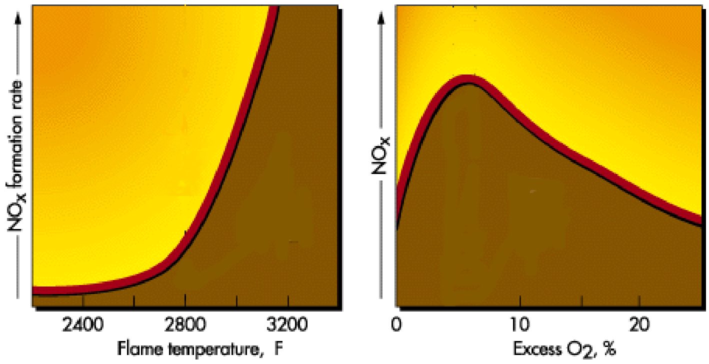


Figure 1. NO_x formation, from [1]

The measurements and modelling done in the past on ABFs have shown that the NO_x are mainly generated in the last heating section (HR3 or HR4), where the O_2 availability is higher (fresh air coming from the blowing area) as well as the temperature of the area.

Thus, to limit the formation of NO_x, the temperature along with the amount of oxygen of the fumes entering the 3rd heating section must be reduced. Experience shows that there is little lever to play with the burner design as the NO_x generation reduction is often coupled with a reduction of combustion efficiency and higher CO contents. The water injection in the fluewalls located in the blowing area of ABFs on the contrary has shown promising achievements together with other benefits.

Aluchemie is a carbon anode plant operating in Spijkenisse (The Netherlands) and producing 216 kt anodes of several formats each year. With the operation of 4 ABFs over the last years, the plant has seen an evolution of the local restrictions regarding the NO_x emissions and has tested several solutions. In this article, the operating principle of water injection will be described as well as the result of water injection tests carried out in Aluchemie.

2. Water Injection to Reduce NOx Generation

2.1 NO_x Generation in the Anode Baking Furnaces

NO_x is a generic term for the nitrogen oxides and refer mainly to nitric oxide (NO) and nitrogen dioxide (NO_2). These gases are atmospheric pollutants that are harmful for immune and respiratory function and are contributors to acid rain, smog, and ozone depletion.

The primary source of NO_x production in the industry is related to combustion processes. In the ABF process, where natural gas or heavy fuel oil is burnt, the thermal NO_x is the most relevant source.

There are three factors influencing NO_x formation: high temperature, high O_2 content, and high residency time at high temperature. Two ways to control NO_x formation in our standard industrial furnaces is to control excess oxygen or control flame temperature, as the residency time at high temperature is relatively short and difficult to control.

For the main part, the thermal NO_x are produced in the flame in the heating zone, and especially in the last heating ramp where the oxygen content and the temperature are high (up to 75% of the NO_x generation has been measured in HR3). The use of natural gas fuel produces usually more NO_x than heavy fuel oil.

2.2 Principle of Water Injection in the Anode Baking Furnace to Reduce NO_x Generation

The main objective of the water injection is to reduce the amount of NO_x formed during the natural gas combustion. Indeed, water injection in the blowing section fluewalls (in the section just upstream of the last burner ramp) will allow decreasing the temperature and diluting the oxygen in the combustion air and so, reducing the NO_x formation.

2.3 Other effects of water injection

The water injection may have other beneficial effects for the process:

- Acceleration of the anode cooling process: the injection of cold water in the hot blowing fumes vaporizes the droplets and so reduces the fumes temperature in the blowing zone which improves heat transfer between the cooling air and the refractories and helps to better cool the anodes.
- Reduction of gas consumption: the increase in steam content within the gas stream improves the heat transfer capability of the fumes and so lead to a decrease in gas consumption.
- Improvement of the baking homogeneity: due to the higher heat transfer coefficients, the steam content improves the heat transfer by radiation, thereby improving the heat distribution within a pit and reducing the presence of hot and cold spots.

However, some negative impacts of water injection are also expected, especially for the refractory condition: the injection of water into a hot furnace could have the potential of damaging refractory by creating thermal gradients and stresses in the refractory.

2.4 Previous Trials with Water Injection

The first water injection trials were carried out in 1980 [2] in Arvida. At that time, the objective of these tests was to improve the anode cooling efficiency, and the ramp was positioned on the third blowing section. The trials were promising; at the baked anodes unloading station, water had resulted in reducing the average surface temperature of the anodes by 140°C for an injection flow rate of 38 litre/hour/fluewall. Following these trials, a US patent related to the introduction of water in the cooling air was issued [3].

Some other trials were carried out in 2012 in Aluchemie with an injection into peephole 3/blowing zone 2, but the trial was stopped due to recurrent issues with blockages in the nozzles. The ramp and the nozzles were modified in 2019 to allow reliable use of the ramp and a new trial was carried out.

3. Modeling Results

The effect of the injection of water droplets in the blowing zone has been studied with several models.

3.1 Effect of Water Injection on NO_x Generation

A. Principles of the NO_x Model

The effect of water injection on the NO_x generation has been modelled with an evolution of RTAP pulse model [4] which focused on the behavior of the flames during the gas injection. Both thermal NO_x (Zeldovitch model) and prompt NO_x have been taken into account in the simulations, even if the prompt NO_x has a small contribution in this case.

The transient approach for pulsed combustion had to be adapted for NO_x prediction because the fluewall temperature was considered as constant for all configurations in the initial pulse model. With this constant temperature, the heat transfer from gas to walls was not properly described and thus the outlet temperature of the gas was not correct (on the furnace, the gas outlet temperature is controlled and kept constant at ~1200 °C). A steady-state approach has thus been defined and validated to investigate NO_x emission: a wall heat flux on the fluewall is then prescribed to get the correct outlet gas temperature. This steady-state approach cannot be used for predicting accurately the wall heat transfer but should only be used for NO_x prediction.

With this approach, the average gas velocity and temperature are properly calculated and thus the NO_x production rate is more accurate. The geometry used in the model consisted of the three heating sections of Aluchemie's furnace. The mass flow rate of gas injected is based on the results of the pulse model. The air flow rate entering the heating zone was adjusted to reflect the real gas flow/air flow ratio.

B. Results of the NO_x Model

In the model, water is injected as droplets of prescribed diameter in peephole 1 of the last blowing section with a 1 L/min flow rate (droplet diameter = 250 µm) and evaporates as shown in Figure 2. The impact of this water injection is given in Table 1. The water injection affects both the fumes temperature which is reduced by 250 °C and the oxygen content which is reduced by 6.8 %. According to the model predictions, water injection at a flow rate of 1 L/min in the first blowing section reduces the NO_x emission by 43 % (Figure 3).

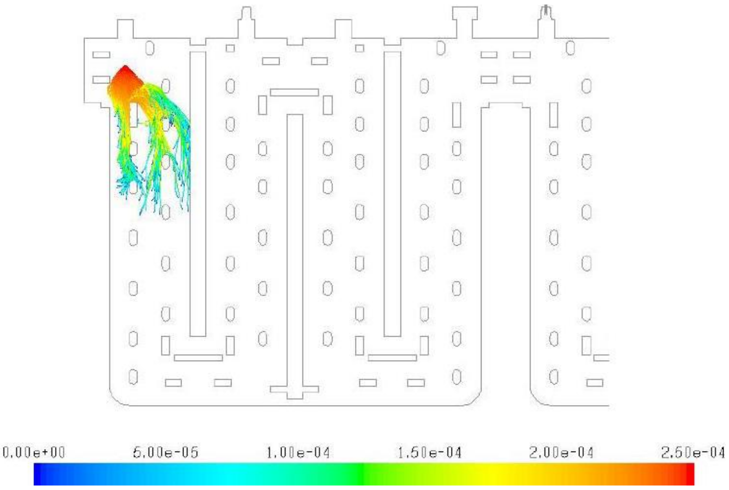


Figure 2. Droplet diameter (m), injection of water in the first blowing zone, peephole 1.

Table 1. Impact of water injection on air flow temperature and composition at the outlet of the first blowing zone

	Reference				**Water Injection**			
	BL1	**HR3**	**HR2**	**HR1**	**BL1**	**HR3**	**HR2**	**HR1**
O_2 (kg/kg) outlet	0.233	0.106	0.051	0.069	0.217	0.099	0.05	0.067
Outlet Temperature (°C)	1054	1231	1226	1167	807	1223	1218	1169

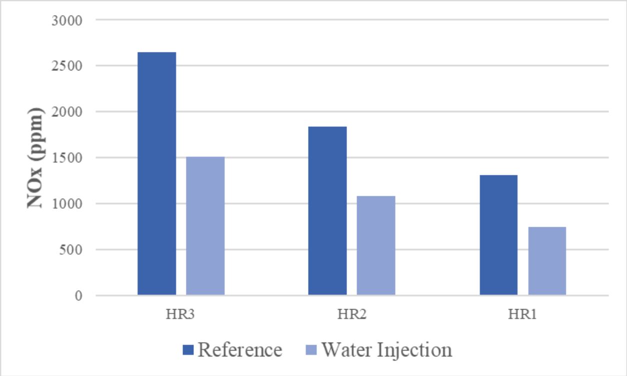


Figure 3. Evolution of NO_x concentration at the outlet of each heating section for the reference and the water injection with 1L/min flow rate

3.2 Effect of Water Injection on Anode Cooling

A study of the effect of water injection on anode cooling was carried out with a 3D transient model [5]. This model calculates the temperature evolution in all materials (fluewalls, packing coke, anodes) during blowing and cooling. It has shown that the water injection at 1 L/min in the blowing ramp could decrease the anode temperature at unloading by 60 °C in average.

4. Trial Results

4.1 Objective of the Trial

The objective of the trial was to identify the effects of water injection at various flow rates on different parameters: NO_x generation, anode temperature, fumes temperature, and gas consumption. The reliability of the ramp over the trial period as well as the effect on refractory temperature have been also measured. Some additional trials have been done to check the impact of water ramp position and nozzle type.

4.2 Technical and Functional Properties of the Water Injection System

The function of the water injection ramp (Figure 4 (a)) is to inject water continuously during a baking cycle in each fluewall line, at a constant flow rate between 0 and 2 L/min and in the form of a spray. The ramp has been designed to enable easy maintenance and easy and safe moving by cranes. The ramp is equipped with one fluid spray lance per fluewall, enabling to inject water inside the peepholes from 0 to 100 mm deep. Lances nozzles were defined and validated following pre-tests on site. Nozzles spray (Figure 4(b)) can inject water at an angle between 0° and 45°. Each lance has a simple isolation valve for water, and water is injected continuously during the baking cycle. The ramp water circuit is designed to have a constant water pressure between 1 and 3 bars along the ramp during the operation.

Figure 4. (a) General view of the water injection ramp in Aluchemie; (b) View of one nozzle spray injecting water in peephole 1 in Aluchemie

4.3 Trial set-up

A series of trials was carried out in Aluchemie on Baking Furnace 2, in a straight line. Water was injected in blowing zone 1 (Figure 5) at different flow rates, ranging from 0.5 to 1.2 L/min and at a depth of 0 mm. Each trial lasted for 6 hours with a water injection in fluewalls 1 to 4. Fluewalls 5 to 7 were used as the reference.

A gas analyser (TESTO) was used with a fume extraction in preheating zone 3 (PH3) at 1-meter depth in order to analyse the effect of water injection on NO, NO_2, O_2, CO and CO_2. The NO_x levels were determined at the starting of the water injection ramp, after 3 h of injection, and at the stopping of the water injection; and each measurement lasted for 10 minutes.

Additional fumes thermocouples were placed in the blowing zone, in peephole 3 of the first blowing zone (BL1), to evaluate the impact of water injection on the temperature of the fumes entering in the heating zone. A thermal camera was used to take pictures in the area where the water was injected to evaluate the impact on thermal gradients in the refractory.

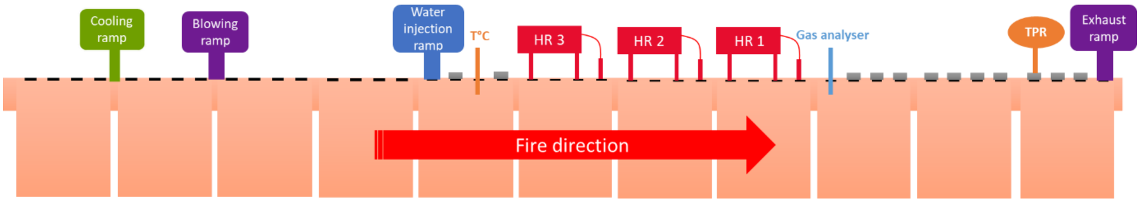


Figure 5. Schematic representation of the trial set-up

Most of the trials were done with the first nozzle design (Figure 6) and some additional trials were done with the second design that allows to get smaller droplets. The second type of nozzle however allows a flow rate of maximum 0.5 L/min due to the higher pressure drop.

Figure 6. Pictures of the two types of nozzles used in the study

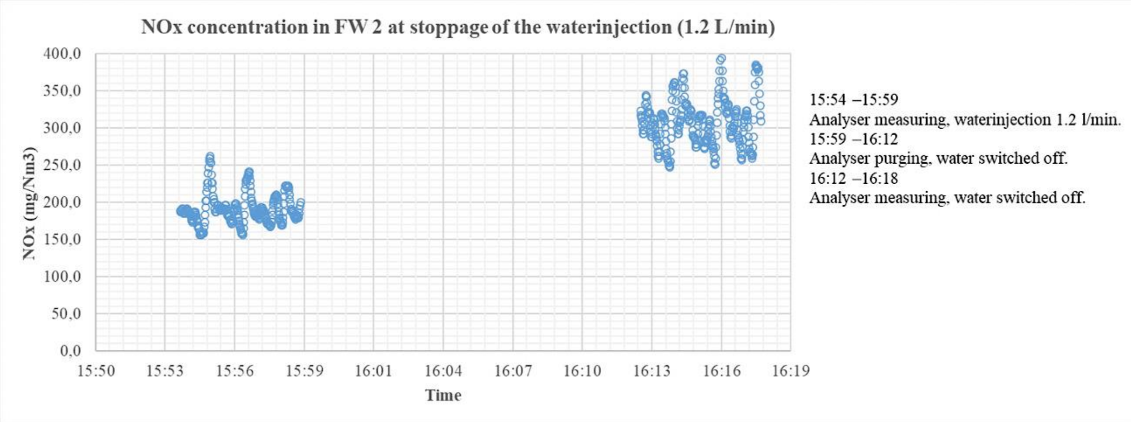
4.4 Results

1. NO_x generation

Over the 6 h period of the different trials, the NO_x levels in PH3 were reduced:

- by 9 % with the injection of water at a flow rate of 0,5 L/min, from 230 to 210 mg/Nm^3;
- by 30 % with the injection of water at a flow rate of 1 L/min over the period of the trial (6 h), from 155 to 110 mg/Nm^3 (in comparison, the level of reduction given by the model for this water flow rate was 43 %);
- by 38 % with the injection of water at a flow rate of 1.2 L/min, from 310 to 190 mg/Nm^3.

Figure 7 gives an example of the evolution of the NO_x measurements when the water injection is started and stopped at 1.2 L/min. A trial was done as well with the second type of nozzle which allows to get smaller droplets. For a water flow rate of 0.5 L/min, the NO_x reduction was increased from -9 % to -16 %.


NOx concentration in FW 2 at stoppage of the waterinjection (1.2 L/min)

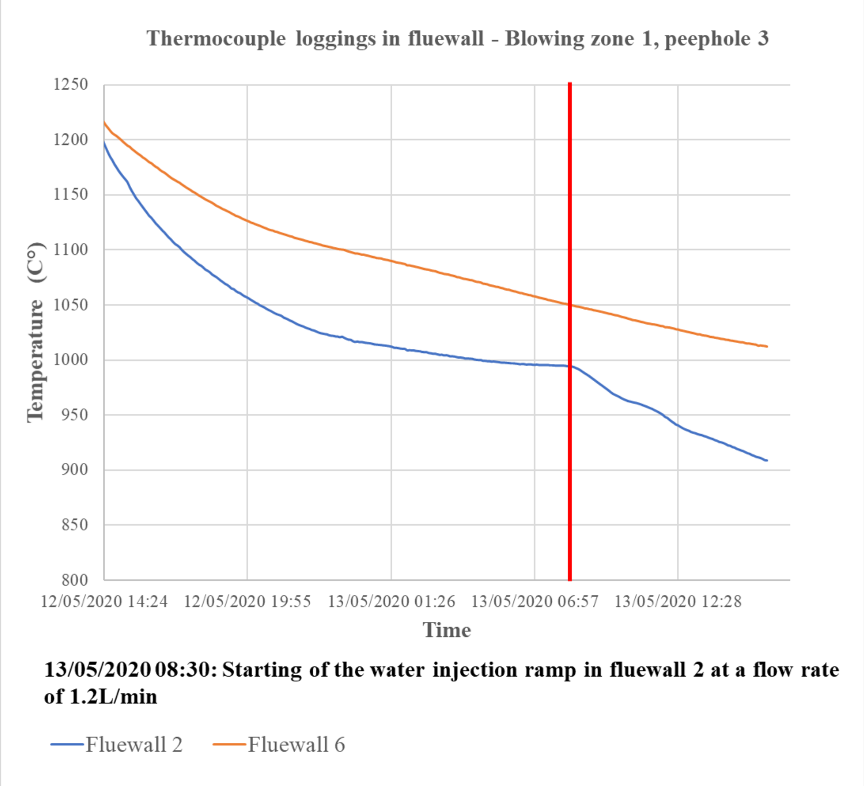
15:54 –15:59
Analyser measuring, waterinjection 1.2 l/min.
15:59 –16:12
Analyser purging, water switched off.
16:12 –16:18
Analyser measuring, water switched off.

Figure 7. Evolution of the NO_x measured in PH3 with or without water injection at 1.2 L/min.

2. Fume temperatures upstream HR3 and anode temperature

The fume temperatures were taken by putting a thermocouple in Blowing 1/peephole 3, upstream HR3 (Figure 8). The cooling rate of the fumes was increased with the water injection (Table 2).

Although it is uncertain if these cooling rates would have been maintained for the whole cycle, an approximation of the impact on the anode temperature can be calculated. If those values were to be projected in a 1D transient thermal transfer model, the anode temperatures would be decreased (Figure 9).


Thermocouple loggings in fluewall - Blowing zone 1, peephole 3

13/05/2020 08:30: Starting of the water injection ramp in fluewall 2 at a flow rate of 1.2L/min

Figure 8. Fume temperatures taken at a flow rate of 1.2 L/min

Table 2. Cooling rate of the fumes and anode temperatures in blowing zone 1

Water flow rate	**L/min**	**0**	**0.5**	**1**	**1.2**
Cooling rate of the fumes	**°C/h**	-6	-8.5	-10	-15.8
Average anode temperature at the end of BL1	**°C**	1084	1069	1061	1030

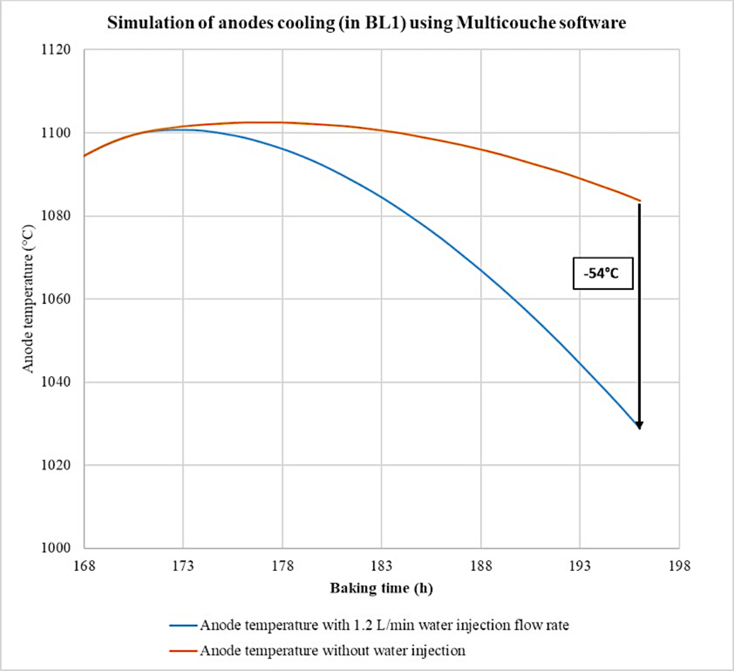


Figure 9. Evolution of anode temperature (in the middle of the anode) calculated by the 1D model for the fumes cooling rates observed with 1.2 L/min

3. Energy consumption

The burner power is highly influenced by the water injection (see Figure 10 for an example at 1 L/min). According to these observations, the water injection may help to reduce the gas consumption by 5.5 % in average for a water injection of 1 L/min. The same level of reduction was observed at 1.2 L/min, but the gas capacity was unchanged for 0.5 L/min. A longer-term trial is required to assess this reduction more precisely.

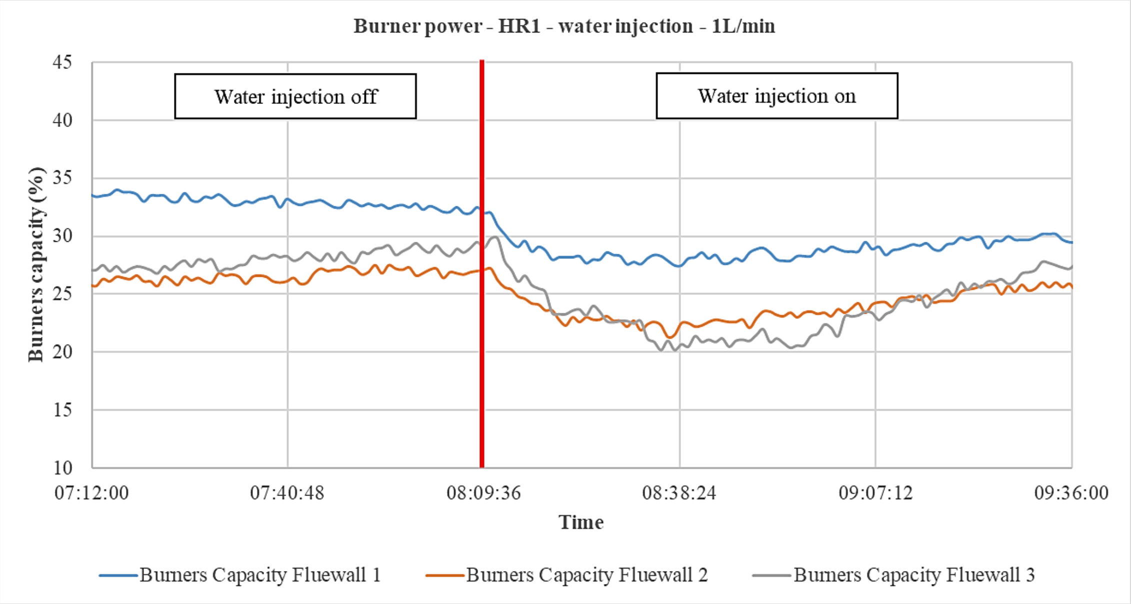
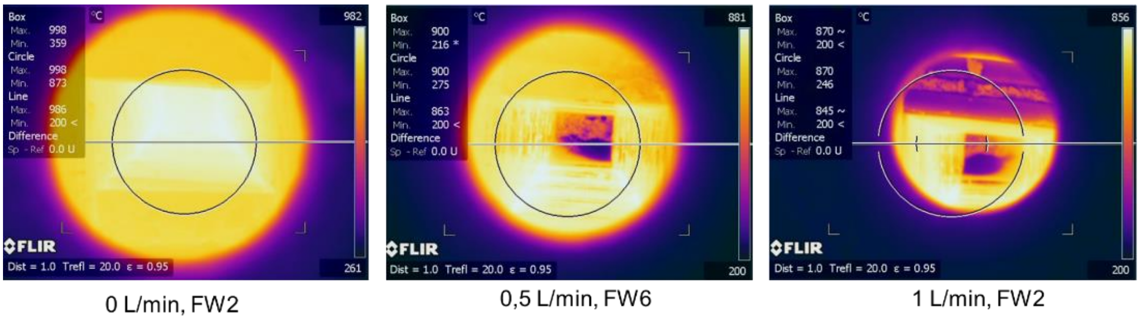


Figure 10. Evolution of burner capacity of the heating ramp 1 with the injection of water at 1 L/min

4. Refractory condition – Cold spots

Some pictures of the refractory temperature were taken with a thermal camera in the peephole where the water was injected. At the beginning of the trial, the temperature is homogeneous in the fluewall. After 6 hours of water injection at 0.5 L/min in fluewall 6, some cold spots could be observed at the bottom of the fluewall. When the water flow was set at 1 L/min, some cold spots could even be observed on the upper tie brick with temperatures as low as 200 °C (Figure 11).



0 L/min, FW2

0,5 L/min, FW6

1 L/min, FW2

Figure 11. Thermal picture taken through peephole 1, Blowing 1 after water injection for different flow rates

For all water injection flow rates, the fluewalls show signs of cold spots at the bottom of the flue wall; this indicates that the water droplets are too large to vaporize directly. Some trials have been carried out to try to mitigate this effect by changing the nozzle design and shifting the water injection from peephole 1 to peephole 2 in blowing 1. This showed interesting results with cold spots at minimum 500 °C instead of 200 °C previously.

5. Oxygen content and combustion efficiency (flooding risk)

No flooding effect (unburnt gas injection) could be observed during the trials. The O_2 content measured in PH3 did not vary with the injection of water in the blowing zone. The fact that the O_2 is diluted by the injection of water seems to be counter-balanced by the lower burner capacity.

The CO content was stable as well, but some higher peeks could be observed when water was running at 1 L/min and 1.2 L/min. Such effect was not observed at 0.5 L/min. Figure 12 gives an example of the evolution of those metrics when the water is started or stopped with a flow rate of 1 L/min.

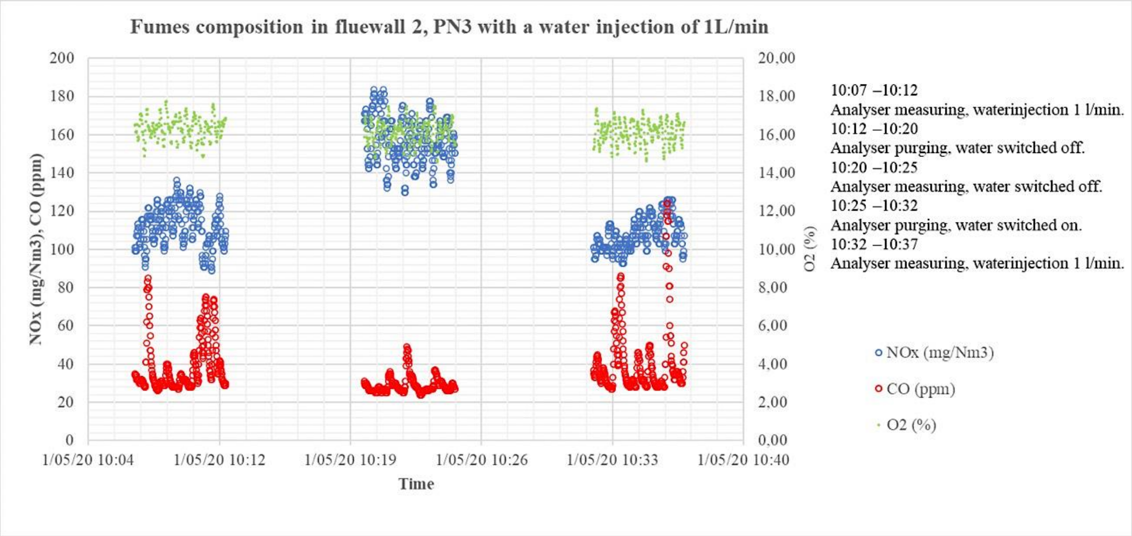


Figure 12. Measurements of fume composition in PH3 after 2 h of water injection at 1 L/min

6. Ramp use and nozzle condition

The ramp was used for approximately 30 hours of water injection, which is relatively short for this kind of application. The nozzles and the ramp were still in excellent condition after these trials.

7. Results Summary

The trials have enabled to confirm the promising benefits of water injection:

- NO_x: The NO_x concentration was reduced by up to 38 % when water was injected at a flow rate of 1.2 L/min in blowing zone 1.
- Anode cooling: 1.2 L/min injected into peephole 1, blowing zone 1 was shown to increase the fumes cooling gradients by 2.5, resulting in a reduction in anode temperature of approximately 54 °C.
- Gas Consumption: the study of the individual burner powers showed a decrease in overall gas burner power of about 6 % for water injection rates of 1 L/min and 1.2 L/min.
- Oxygen content: the injection of water in blowing zone 1 did not significantly affect the oxygen supplied to the forced combustion zone.

Table 3 sums up the results measured for different flow rates.

Table 3. Effect of water injection for different flow rates

	NO_x (%)	**Anode temperature in BL1 (°C)**	**Energy consumption (%)**	**O_2**	**CO**	**Cold spot temperature (°C)**
Nozzle 1, 0.5 L/min, peephole 1	-9	-15	/	no impact	no impact	275
Nozzle 1, 1.0 L/min, peephole 1	-30	-23	-5,50	no impact	occasional peaks	<200
Nozzle 1, 1.2 L/min, peephole 1	-38	-54	-5,50	no impact	occasional peaks	<200
Nozzle 1, 1.0 L/min, peephole 2	-30	-	-6,50	no impact	occasionalp peaks	335
Nozzle 2, 0.5 L/m, peephole 1	-16	-	-6	no impact	no impact	490

5. Conclusions

The trials carried out in Aluchemie with the injection of water in Blowing 1 have confirmed the benefits regarding the reduction of NO_x generation with reductions up to 38 %. The NO_x concentration decreases as the water flow rate increases in the studied range (0.5 to 1.2 L/min) without reaching a thershold effect. The design of the nozzle affects the percentage of NO_x generation, and the finer the droplets, the lower the NO_x.

The trial has also shown that the water injection enables the cooling of the fumes more efficiently during blowing, thus to improving the anode cooling efficieny, with expectations of up to 54 °C anode temperature decrease at the end of the first blowing section.

Trials also showed that a reduction in gas consumption by 5.5 % can be expected for a water flow rate ≥ 1 L/min. The change of nozzle type only slightly improved this reduction. Water injection has no impact on the percentage of oxygen supply to the preheating zone and doesn't impact the combustion in this area but some peeks of high CO values could be observed for higher water flow rates.

The thermal camera pictures show that water injection creates cold spots on the fluewall and on some tie-bricks: this could affect the refractory condition on the long term. Some further trials should be carried out on a longer term to evaluate this impact more precisely and identify possible mitigations.

6. References

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