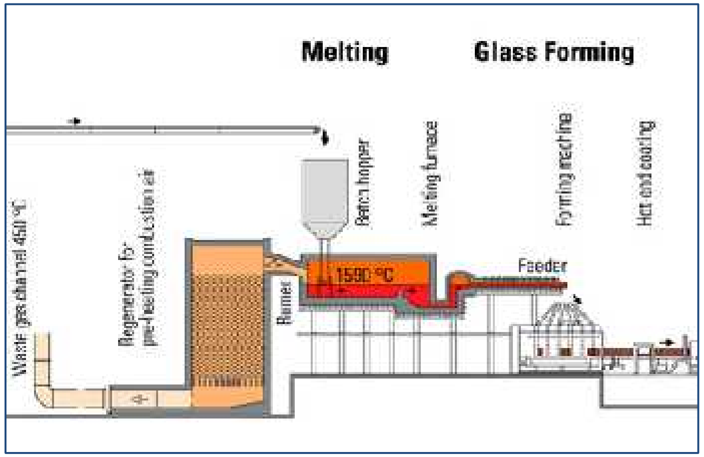
SSV Stazione Sperimentale del Vetro
The Glass Research Centre

CONCLUSIONI SULLE MIGLIORI TECNICHE DISPONIBILI (BAT) PER LA PRODUZIONE DEL VETRO AI SENSI DELLA DIRETTIVA 2010/75/UE

Nicola Favaro – Simone Tiozzo

IED- GLASS EMISSIONS



Batch composition

Raw materials handling, weighing → Dust

Melting

Combustion emissions → CO, CO_2, NOx, SOx

Carbonates decomposition → CO_2

Sulfate decomposition → SOx

Bath evaporation → Dust, HCl, HF, metals

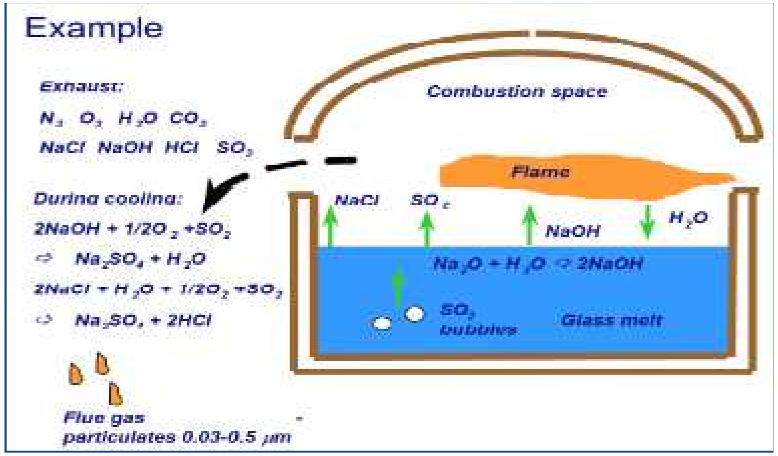
Waste gases condensation → Dust (sodium sulphate)

Secondary treatments

Hot end → Sn, HCl, SOx

Cold end → Organics compounds

DUST EMISSIONS – SOURCES



- **Sodium sulfate condensation (≈ 90%)**

  due to reaction between gaseous Na and

  NaOH volatilized from the melt with SO_2

  released by sulfate fining and fuel burning (Na_2SO_4, condensates below 1100° C, max below 884°C)

  Dust production is influenced by glass surface temperature (high T = high emissions), burner angle and turbulence (high turbulence and flames impinging on the melt = high emissions), H2O concentration in flue gases, soda-ash quality.

- **Batch carryover (≈ 5%)**

  due to fine particles or dolomite decrepitation (“explosion” of grains due to internal pressure buildup during calcination.

  Batch carryover is influenced by burner angle and turbulence, batch grain size distribution, batch humidity (< 1-3 %), dolomite quality, doghouse design.

- **Fuel combustion solid residues (≈ 5%)**

  Due to inorganic matter contents (ashes, metals like V and Ni, etc) in fuel oil. Natural gas, on the contrary, burns without significant solid byproducts.

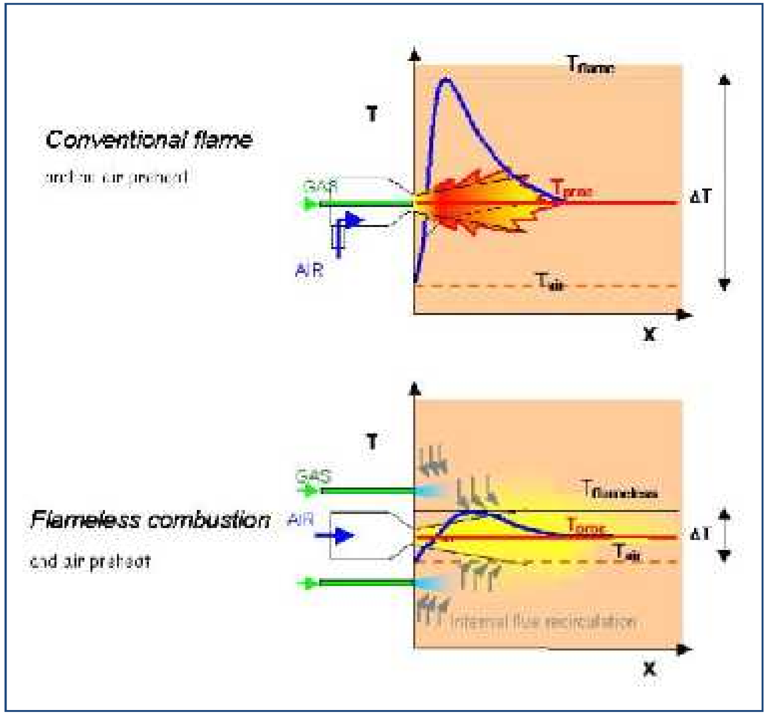
NO_X EMISSIONS – SOURCES

- **Thermal NO_x**:

  more than 95% of the NO_x is produced by direct oxidation at high temperature of nitrogen coming from air. Many reactions are possible starting from T > 1300°C, while the products are mainly NO (90 ÷ 95% of the total) and NO_2; N_2O is not formed.

  The conditions favouring NOx formation are:

  - High temperature in the combustion atmosphere and in the flame
  - Good mixing between N_2 and O_2
  - High amounts of N_2 in contact with over-stoichiometric combustion O_2



NO$_X$ EMISSIONS – SOURCES

- **Batch Nitrates**:

  high quality flint glasses (containers for perfumes or spirits, tableware) require strong oxidation; the use of $NaNO_3$ is practically unavoidable.

- **Nitrogen compounds in fuel**:

  this contribution is usually very small or negligible, but some natural gases can contain concentrations of N_2 as high as 13 ÷ 15% (e.g. gas from the Netherlands).

SO_X EMISSIONS – SOURCES

- **Sulfates in the batch**

  In a common soda-lime glass furnace, sodium sulfate is usually the main fining and oxidizing agent, and is present in the batch formulation as “pure” raw material and/or as main component of recycled filter dust.

  Sulfate fining alone generates approximately 200 ÷ 800 mg/Nm^3 of SO_x (complex dependence) for a specific production of around 0,2 ÷ 1,8 kg/ton_{glass}.

- **Sulfur as fuel impurity**

  Sulfur is present as impurity in heavy fuel oil at its elementary state, and combustion reactions oxidize it to SO_2 and, marginally, SO_3; Glass furnaces burning natural gas have on average an SO_x concentration in untreated flue gases of around 300 ÷ 800 mg/Nm^3, while the same furnaces burning 1% sulfur fuel oil might reach SO_x levels as high as 2000 mg/Nm^3 and above.

CRITICAL CONDITIONS FOR SO_X EMISSIONS

- **Color changes**: if the melt needs to be **oxidized** (e.g. changing to flint glass), a lot of **sulfates** must be **added** to the batch during the color change transitory, so a lot more SO_2 will be temporarily emitted; if the final glass is more **reduced** (e.g changing to amber glass) than the starting one, it will be able to “dissolve” less SO_3, so it will temporarily **release excess SO_2** during the transitory.
- **Recuperator** and regenerator **cleaning activities**: if the fouling sulfate deposits are removed by **thermal washing**, i.e. are re-volatilized by temporarily increasing the flue gases temperature, a lot of SO_2 is released into the atmosphere; mechanical cleaning (e.g. with sandblasting techniques) is usually less critical.

In these cases SO_x concentrations in flue gases can reach peaks much higher than in “everyday” operating conditions, so if the normal SOx emission levels of the furnace are close to the imposed limits, during color changes or regenerator/recuperator cleaning activities the emissions from the stack may temporary not respect the limits.

HCl AND HF – SOURCES

- **Impurities in soda-ash**:
  the Solvay process features NaCl as reagent and CaCl2 as byproduct, so small amounts (usually 0,05 ÷ 0,15%) of chlorides can be found in soda-ash as impurities, depending on its grade.
- **Impurities in dolomite**:
  fluoride impurities are sometimes found in dolomite.
- **Cullet contamination**:
  external cullet coming from household waste collection is often mixed with plastic bottles, labels, caps, stoppers etc, some of which might contain chlorinated compounds (e.g. PVC). Moreover, cyclic remelting of waste glass can lead to contamination buildup in countries with high cullet recycling.
- **Hot end coating off gases**:
  hot end coating features chlorides as reagents, and coating hoods off gases are usually treated together with furnace flue gases.

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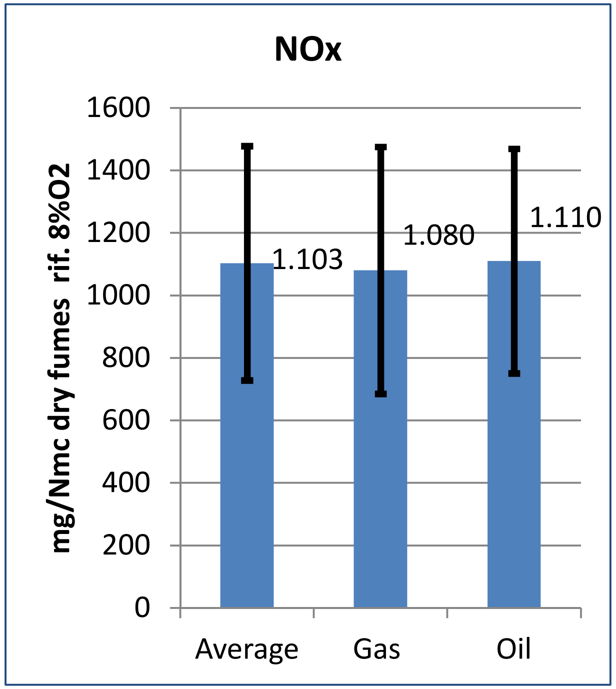
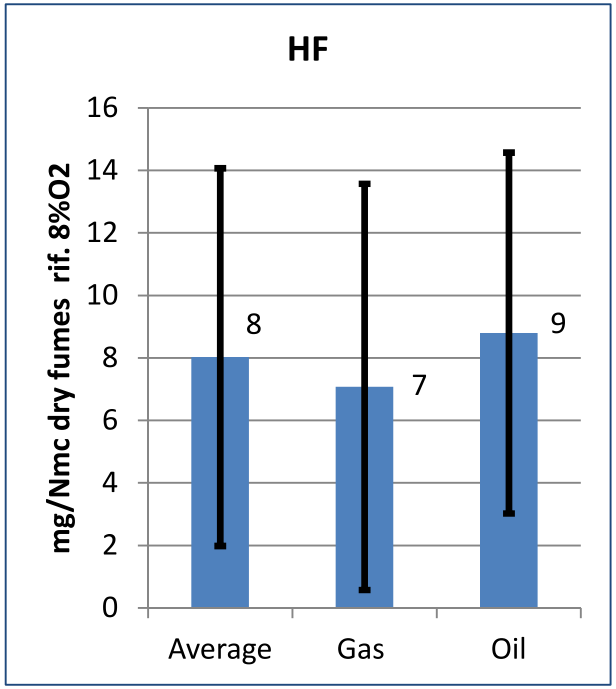
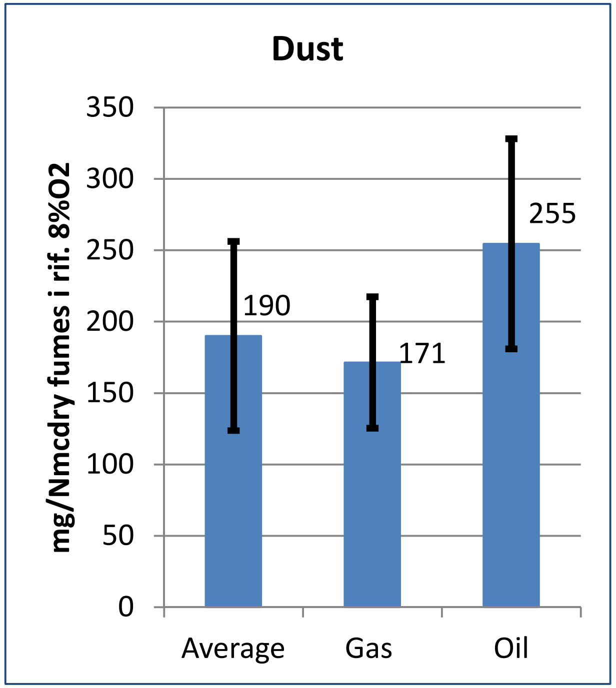
GLASS EMISSIONS

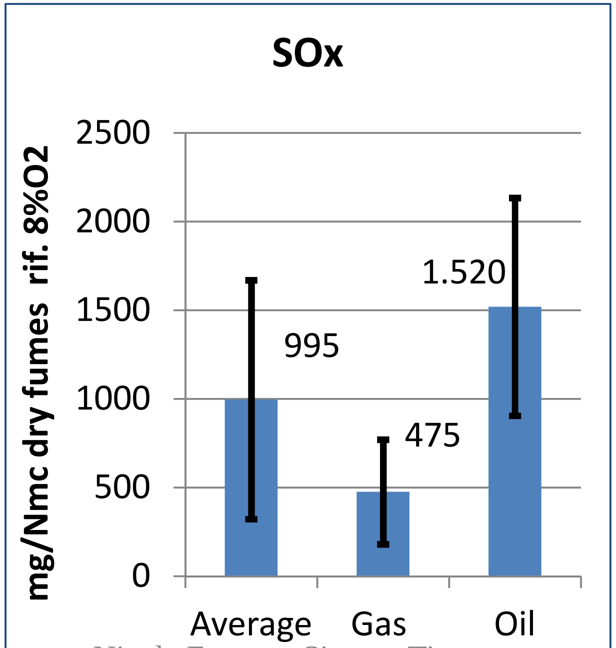
Example of glass raw emission from container glass productions

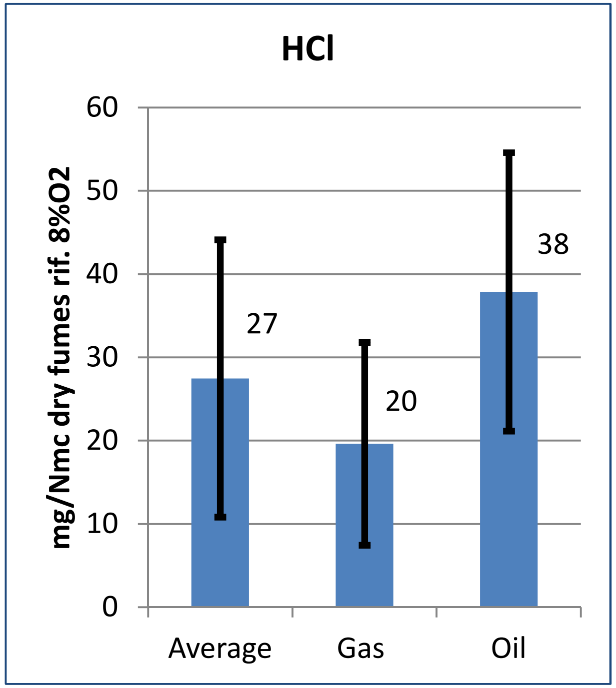
(SSV data)





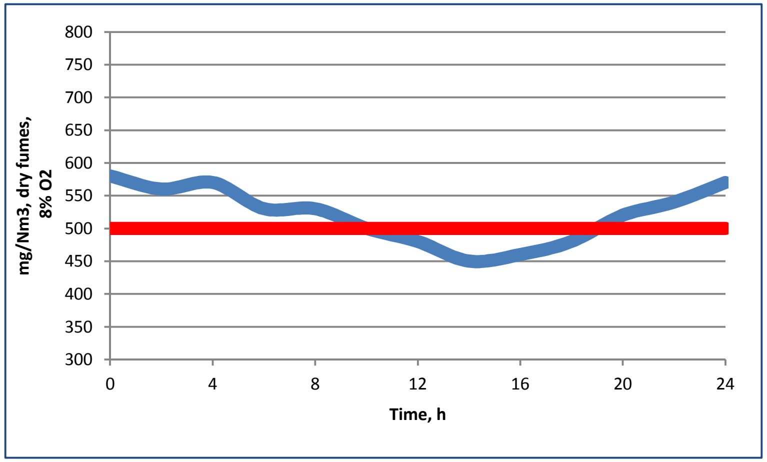






ELV – EMISSION LIMIT VALUES

- For **air-fuel** furnaces the ELV are expressed as **mg / Nm^3** dry fumes referred to a standard oxygen concentration of **8 %**;
- In case of **Oxy-fuel** fired furnaces, the limit is expressed as **kg / tonne of melted glass** (the expression of emission levels as mg/Nm^3 referred to a standard oxygen concentration is not applicable)
- In case of **Electric furnaces**, mg/Nm^3 or kg/tonne melted glass (the expression of emission levels as mg/Nm^3 referred to a standard oxygen concentration is not applicable)
- For discontinuous measurements BAT-AELs refer to the average value of three spot samples of at least 30 minutes each; for regenerative furnaces the measuring period should cover a minimum of two firing reversals of the regenerator chambers



- For continuous measurements BAT-AELs refer to daily average values

IED (INDUSTRIAL EMISSION DIRECTIVE)

The BAT-AEL for hollow glass are reported. All the data are expressed as dry fumes, 0°C, 1 atm and referred to 8 % O2

DUST	BAT	BAT-AEL mg/Nmc
All	EP – BF (no use of dangerous substances)	< 10 - 20

For tableware and special glass a ELV of < 1 – 10 applies to batch formulations containing significant amounts of constituents meeting the criteria as dangerous substances, in accordance with Regulation (EC) No 1272/2008 of the European Parliament and of the Council.

Selenium? Cobalt Oxide? Recycled dust?

IED (INDUSTRIAL EMISSION DIRECTIVE)

NOX	BAT	BAT-AEL mg/Nmc
Container glass	Primary techniques 1)	500 - 800
	SCR-SNCR	< 500
	Electric furnace	< 100
	Oxy fuel	< 0.5 – 0.8 Kg/tonne

1) The lower value refers to the use of special furnace designs, where applicable. These values should be reconsidered in the occasion of a normal or complete rebuild of the melting furnace.

When nitrates are used in the batch formulation and/or special oxidizing combustion conditions are applied for short campaigns in melting furnaces with a capacity of < 100 t/day, the applicable limit is 1000 mg/Nm3

IED (Industrial Emission Directive)

SOx	BAT	Combustion	BAT-AEL mg/Nmc
Container glass	Dry or Semi Dry Scrubber	Natural gas	< 200 - 500
		Fuel Oil	< 500 - 1200

1) For special types of colored glasses (e.g. reduced green glasses), concerns related to the achievable emission levels may require investigating the sulfur balance. Values reported in the table may be difficult to achieve depending on the rate of external cullet recycling and in combination with filter dust recycling.

2) The lower levels are associated with conditions where the reduction of SO_X is a high priority over a lower production of solid wastes, that is sulfate-rich filter dust.

3) The associated emission levels are related to the use of 1 % sulfur fuel oil in combination with secondary abatement techniques.

IED (Industrial Emission Directive)

HCl	BAT	BAT-AEL mg/Nmc
Container	Dry or Semi Dry Scrubber	< 10 - 20

The higher levels are associated with the simultaneous treatment of flue-gases from hot-end coating operations.

HF	BAT	BAT-AEL mg/Nmc
Container	Dry or Semi Dry Scrubber	< 1- 5

IED (Industrial Emission Directive)

Metals	BAT	BAT-AEL mg/Nmc
∑ (As, Co, Ni, Cd, Se, CrVI)	Dry or Semi Dry Scrubber	< 10 - 20
S (As, Co, Ni, Cd, Se, CrVI, Sb, Pb, CrIII, Cu, Mn, V, Sn)	Dry or Semi Dry Scrubber	< 1 - 5

1) The levels refer to the sum of metals present in the flue-gases in both solid and gaseous phases.
2) The lower levels are BAT-AELs when metal compounds are not intentionally used in the batch formulation
3) The upper levels are associated with the use of metals for coloring or de-coloring the glass, or when the flue-gases from the hot-end coating operations are treated together.
4) When high quality flint glass is produced, higher amounts of de-coloring Selenium are required, so higher values, up to 3 mg/Nm3, are reported.

IED (INDUSTRIAL EMISSION DIRECTIVE)

NH3	BAT	BAT-AEL mg/Nmc
all	SCR-SNCR	< 5 - 30

The higher levels are associated with higher inlet NO_X concentrations, higher reduction rates (ammonia slip) and the ageing of the catalyst.

CO	BAT	BAT-AEL mg/Nmc
all	Primary techniques	100

MONITORING

According to the BAT Conclusions document, the monitoring of emissions and/or other relevant process parameters must be performed on a regular basis, including:

- Continuous monitoring of critical process parameters to ensure process stability
- Regular monitoring of process parameters to prevent/reduce pollution, e.g. O2, fuel/air ratio.
- Continuous measurements of dust, NOx and SO2 emissions, or discontinuous measurements at least twice per year, associated with the control of surrogate parameters to ensure that the treatment system is working properly between measurements
- Continuous or regular periodic measurements of NH3 (SCR or SNCR)
- Continuous or regular periodic measurements of CO (primary measures for NO_x)
- Regular periodic measurements of emissions of HCl, HF, CO and metals

SPECIAL PROCEDURES

According to the BAT conclusions document, during normal operating conditions the waste gases treatment systems must work at optimal capacity and availability, in order to prevent or reduce emissions.

Special procedures can be defined for specific operating conditions, in particular:

- during start-up and shutdown operations
- during other special operations which could affect the proper functioning of the systems (e.g. regular and extra-ordinary maintenance work, cleaning operations of the furnace and/or of the waste gas treatment system, severe production change, etc)
- in case of insufficient waste gas flow rate or temperature, preventing the use of the system at full capacity.

ELV COMPLIANCE

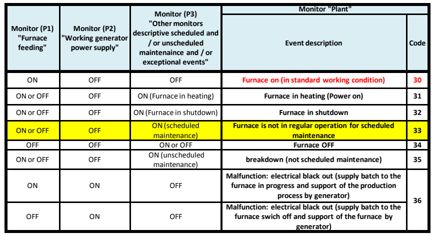
Regional Regulation

D.d.u.o. 20 dicembre 2010 – n.13310 e smi

Monitor (P1) "Furnace feeding"	Monitor (P2) "Working generator power supply"	Monitor (P3) "Other monitors descriptive scheduled and / or unscheduled maintenaince and / or exceptional events"	Monitor "Plant"	
			Event description	**Code**
ON	OFF	OFF	**Furnace on (in standard working condition)**	**30**
ON or OFF	OFF	ON (Furnace in heating)	**Furnace in heating (Power on)**	**31**
ON or OFF	OFF	ON (Furnace in shutdown)	**Furnace in shutdown**	**32**
ON or OFF	OFF	ON (scheduled maintenance)	**Furnace is not in regular operation for scheduled maintenance**	**33**
OFF	OFF	ON or OFF	**Furnace OFF**	**34**
ON or OFF	OFF	ON (unscheduled maintenance)	**breakdown (not scheduled maintenance)**	**35**
ON	ON	OFF	**Malfunction: electrical black out (supply batch to the furnace in progress and support of the production process by generator)**	**36**
OFF	ON	OFF	**Malfunction: electrical black out (supply batch to the furnace swich off and support of the furnace by generator)**	

Plant emissions are subjected to the control of the limit values if the system process is in a condition of **monitor’s code** equal to **30**

ORDINARY SCHEDULED MAINTENANCE EVENTS



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OFF	OFF	ON or OFF	Furnace OFF	34
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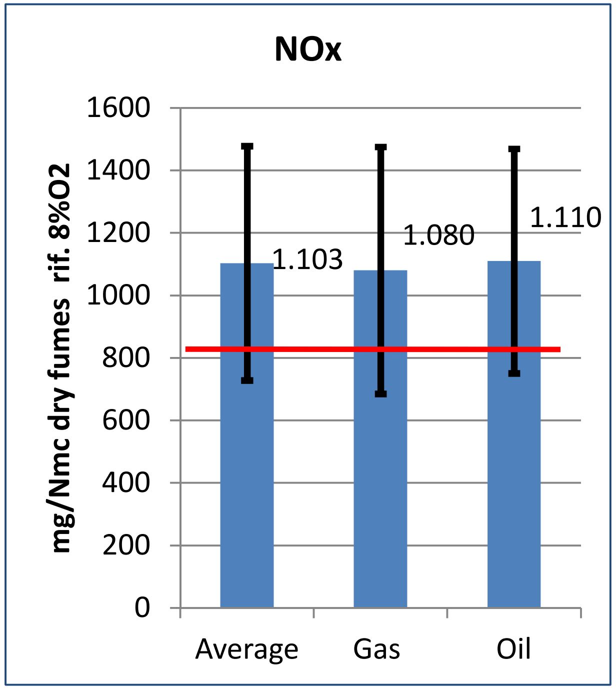
OFF	ON	OFF	Malfunction: electrical black out (supply batch to the furnace swich off and support of the furnace by generator)	

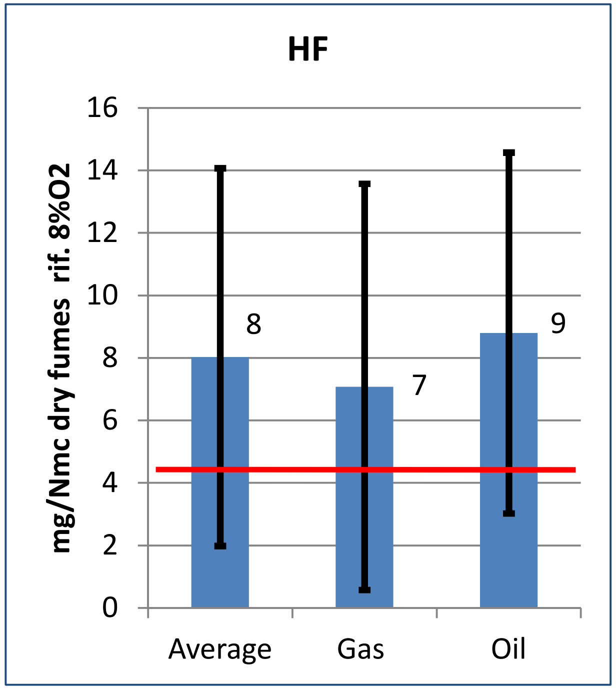
CODE 33	Maximum frequency		Duration (Days)		Duration (h/Day)		Total Hours/ year	
Cleaning of regenerator chambers and/or ducts annexes	min	max	min	max	min	max	min	max
➢ Manual cleaning	1	2	2	4	4	5	8	46
➢ Thermal cleaning	1	2	7	10	8	12	56	240
➢ Cleaning by compressed fluids / lances	1	2	1	3	3	5	3	30
➢ Countercurrent thermal cleaning	1	2	2	2,5	24	24	48	120
➢ Ducts cleaning	2	4	2	4	3	10	12	160
Furnace maintenance operation	12	24	1	1	2	8	24	192
Emissions treatment plant	1	1	5	15	24	24	120	360
Percentage referred to the year							**3,1%**	**13 %**

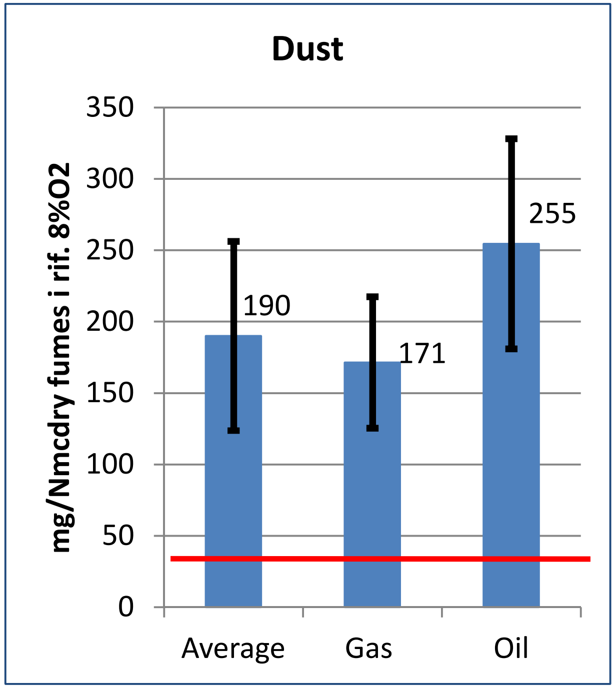
The emission data are not used for compliance assessment. If above the maximum permitted, the data are used for compliance. Special situations can be discussed with the authority during the Authorization update.

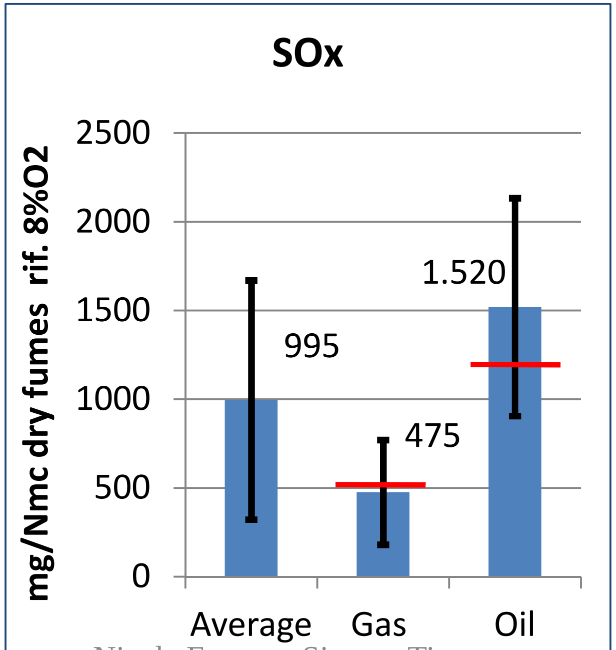
GLASS EMISSIONS

Example of glass emission from container glass productions (SSV data)









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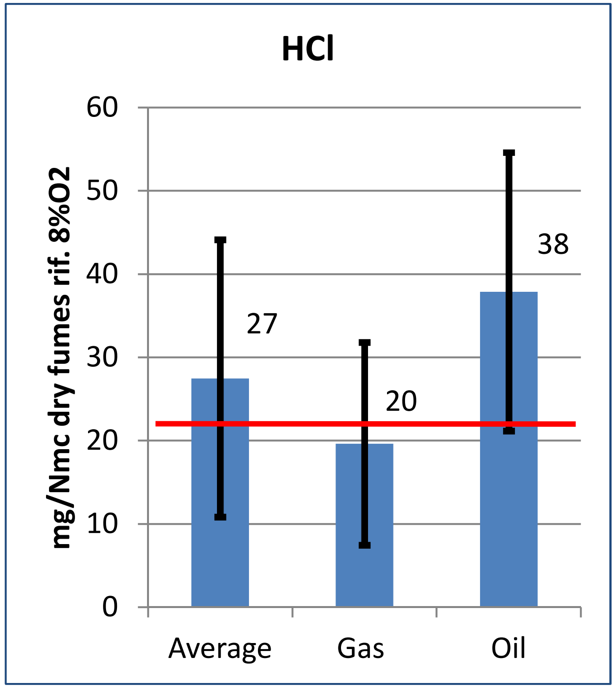
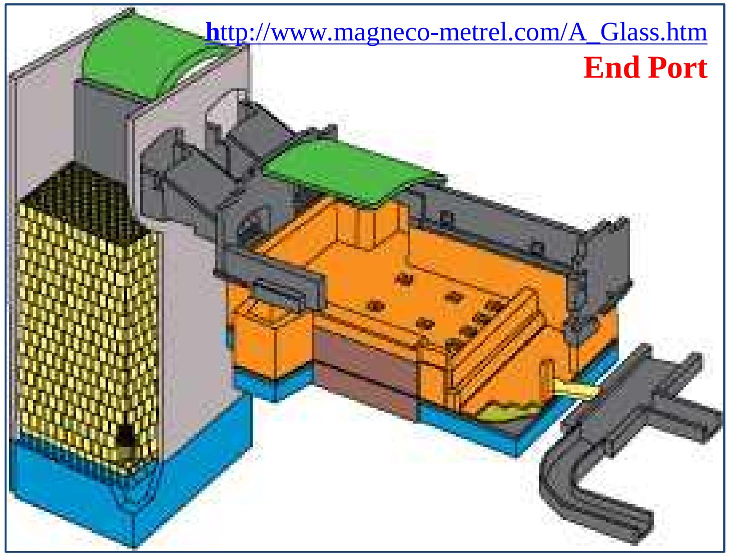


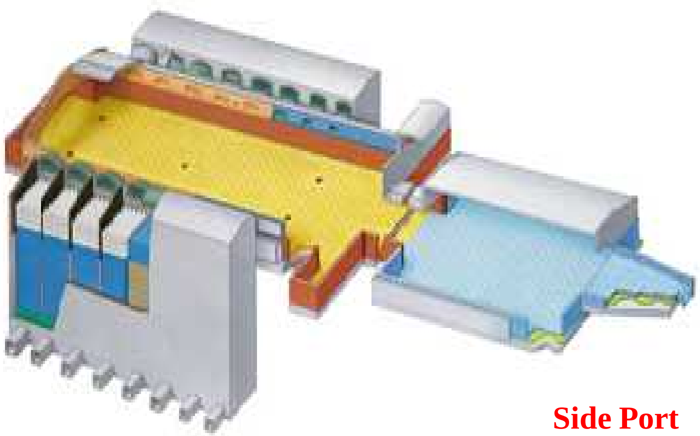
MAIN FACTORS AFFECTING GLASS EMISSIONS

- Combustion ratio
- Furnace ageing
- Emission treatment plants ageing
- Regenerative chambers cleaning
- Color changes
- Raw materials
- Cullet
- Secondary measures/technology applied
- Alkaline reagents use in the dry – semi dry scrubber
- Dust recovery



http://www.magneco-metrel.com/A_Glass.htm

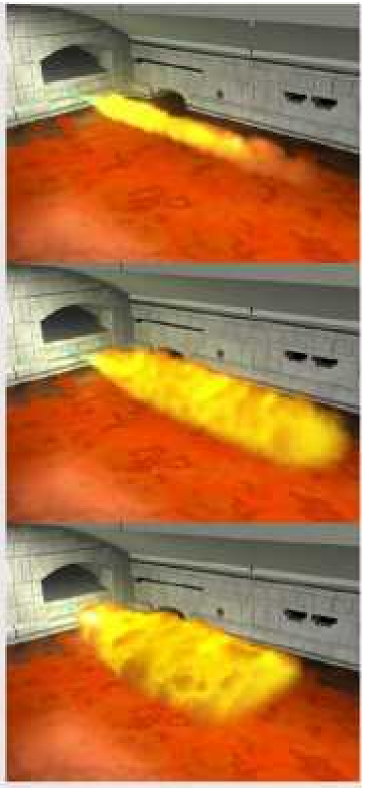
End Port



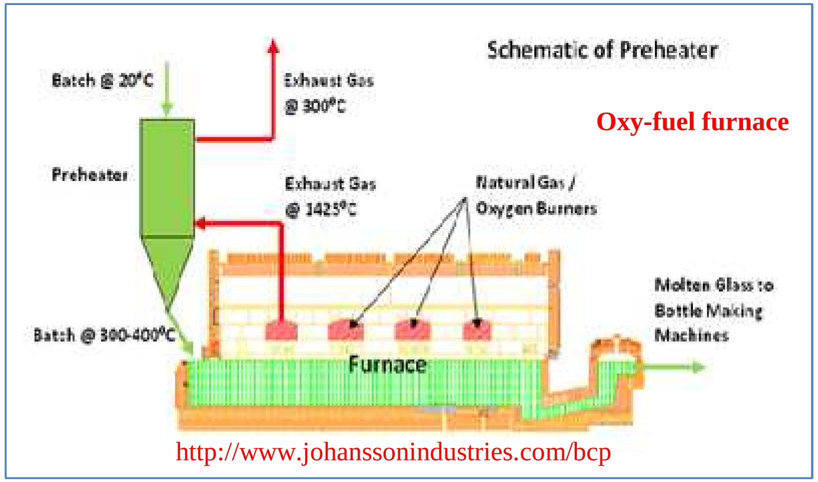
Side Port

http://www.sefpro.com/float.aspx

BAT – GENERIC PRIMARY MEASURES



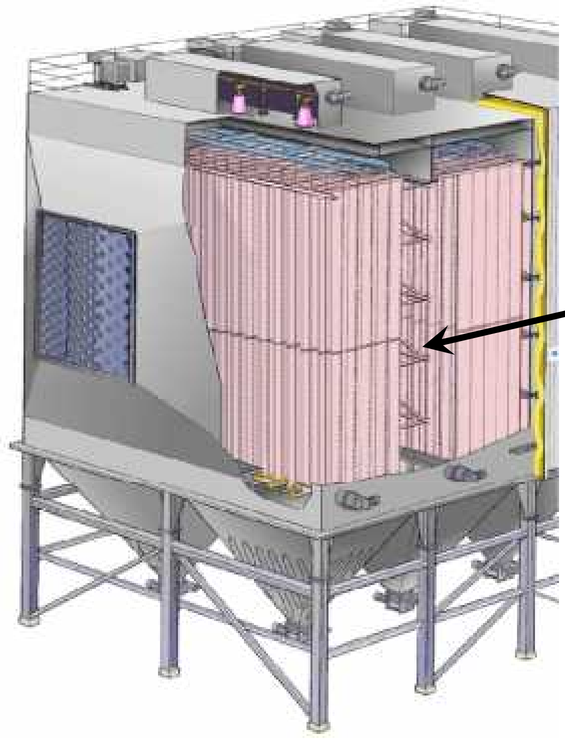
- Low NOX burners and flame optimization (NOx)
- Optimization of combustion ratio (NOx, CO, Energy)
- Reduction of infiltration of parasitic air (NOx, Energy)
- Refractory maintenance (Energy)
- Installation of cullet direct or indirect pre-heaters (Energy)
- Increase the use of cullet (Energy)
- Substitution of fuel (SOx)
- Oxy-combustion furnace (NOx)
- Electric furnace (NOx, Dust, SOx)



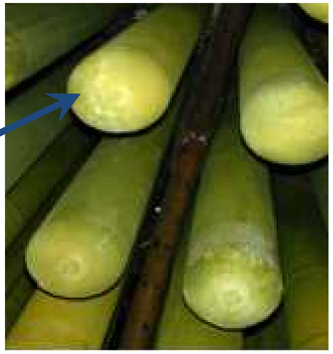
Oxy-fuel furnace

http://www.johanssonindustries.com/bcp

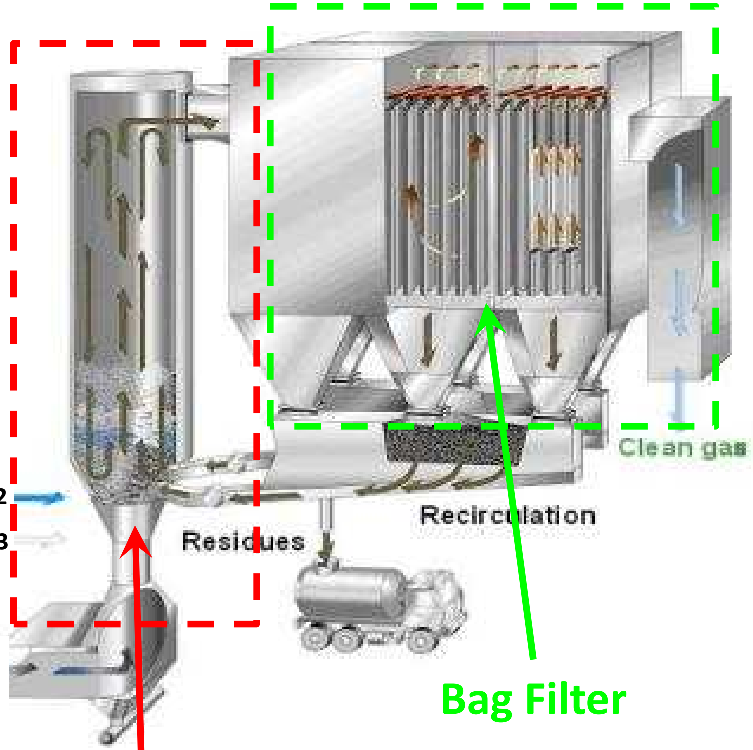
SECONDARY MEASURES FOR DUST



Multiple Fields Electrostatic Precipitator



Ceramic candles can be used as alternative



$Ca(OH)_2$
$NaHCO_3$
Na_2CO_3

Off gases

Bag Filter

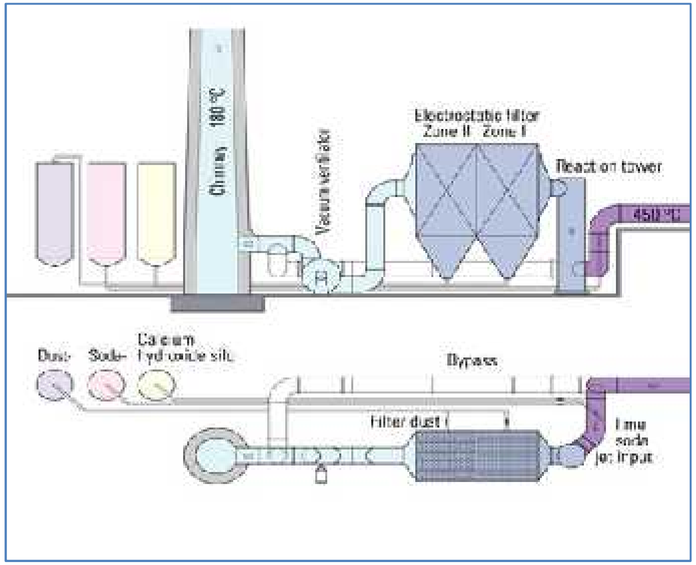
Acid gases scrubber

(SOx, HCl, HF abatement)

DUST – SECONDARY MEASURES COMPARISON

Technique	ESP	Bag Filter	Candles
Efficiency	95 ÷ 99 %	97 ÷ 99 %	≈ 99 %
Emission level	10 ÷ 20 mg/Nm^3	5 ÷ 10 mg/Nm^3	≈ 5 mg/Nm^3
Max temperature	420°C	200°C	400°C
Equipment size	Very large	Large	Large
Post-recuperator compatibility	Off gases need small cooling (heat exch.)	Off gases need strong cooling (heat exch.)	Off gases need small cooling (heat exch.)
SCR compatibility	YES: direct downstream installation possible	NO: too low T_{out}, would need off gas reheating	YES: catalyst directly embeddable in candles
Notes	Optimal for large pulls/furnaces; easily expansible; higher investment costs, but lower operating costs	Optimal for small furnaces; filter cake enhances metals retention; blinding risk; large induced pressure drop in off gases	Great performances but *young* technology; fragile candles; durability, cost and catalyst poisoning concerns; blinding risk

DRY AND SEMI DRY SCRUBBING



- The neutralizing reagent (“absorbent”) reacts with the SO_X species to form a solid particulate which is removed from the waste gas stream by an ESP or BF system.
- Removal of other acidic gases takes place, in particular of halides (HCl and HF); other volatile compounds, such as Se, condensate and adsorb on the particulate surfaces.
- Main absorbents: Ca(OH)2; NaHCO3, Na2CO3. Yields depend on the reagents, rate of dosage, temperature range, time of contact and recovery of dust (indicative yields on container glass - data SSV)

	$Ca(OH)_2$	$Ca(OH)_2$ high surface	$NaHCO_3$
SOx	30 %	45 %	60 %
HCl	75 %	80 %	40 %
HF	85 %	90 %	11 %

SO_X EMISSIONS – CROSS MEDIA EFFECTS

The scrubbing process produces a solid residue, that is recovered together with condensation products as filter dust; this material consists mainly of:

- Condensed Na_2SO_4 from SO_x reaction with NaOH volatilized
- $CaSO_4$ from SO_x solid state neutralization with injected $Ca(OH)_2$;
- Unreacted $Ca(OH)_2$ deriving from over-stoichiometric reagent dosage;
- Adsorbed volatile species containing Se, As, Pb, etc (< 1%).

Filter dust can be sometimes classified based on the metal concentration as dangerous. Special care need to be defined to handle properly the materials

Filter dust can be at least partially recycled into the furnace as sulfate bearing secondary raw material. Because of SeO_2 and PbO condensation over particles, filter dust contribution must be considered also when dosing Se as decolorizing agent and or to comply with Pb Regulation. Attention must however be paid to filter dust impact on glass quality, color, fining and viscosity of the melt.

PRELIMINARY COST ASSESSMENT

For a dry scrubber + ESP system treating fuel oil combustion flue gases of a container furnace (340 ton/day pull) having SO_x initial levels of 1800 ÷ 2000 mg/Nm^3, using $Ca(OH)_2$ as reagent with a sulfate abatement efficiency of 50% and final dust emissions of around 10 ÷ 20 mg/Nm^3, some cost data estimations are:

Investment costs ≈ 1,7 ÷ 3,1 M€

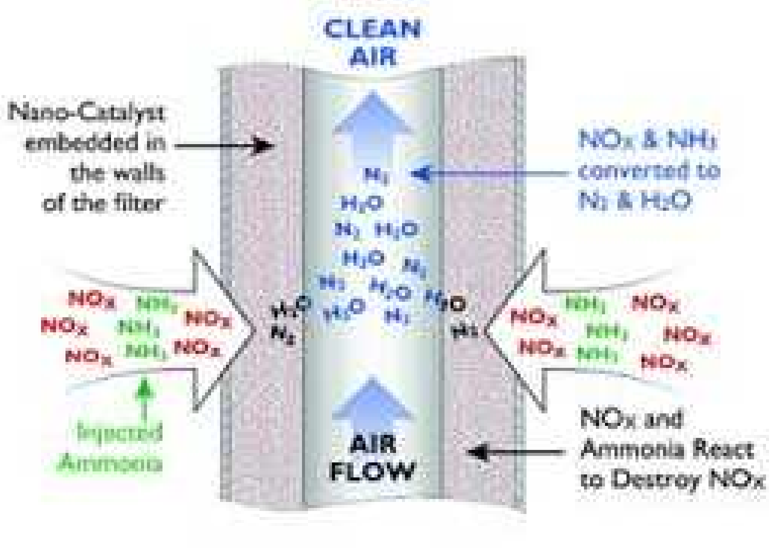
Operational costs ≈ 250 ÷ 600 k€/year, depending on reagent choice (high surface lime or $NaHCO_3$ additions increase considerably the costs) and on filter dust post-processing (landfill or recycling):

4 ÷ 6 €/ton$_{glass}$ for complete recycling of filter dust;

7 ÷ 10 €/ton$_{glass}$ for complete disposal in landfill and oil firing

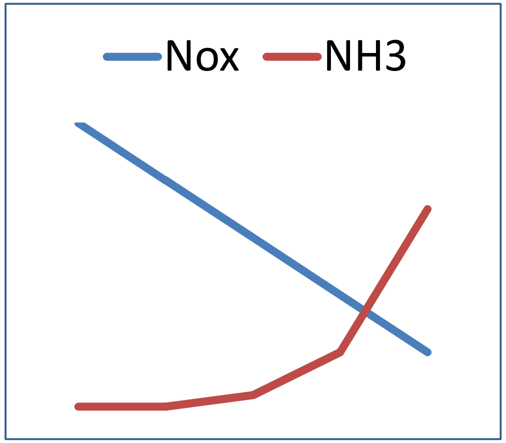
The systems required to operate the dry scrubbing determine a small increase in energy consumption of around 10 kWh/ton$_{glass}$

BAT – SECONDARY MEASURES
SCR



- SCR involves reacting NOX with ammonia in a catalytic bed (TiO_2 and V_2O_5) at an appropriate temperature.
- A water solution with 25 % ammonia is normally used, however also an aqueous solution of urea can be used.
- Most existing applications of the SCR technique within the European glass industry have achieved reductions in the range of 70 – 80 %, but 80 – 95 % could potentially be achieved (e.g. with a second layer of catalyst modules)

NO_X SECONDARY MEASURES – SCR



The over-stoichiometric dosage of ammonia, **above** the **1 : 1 ratio** with NOx is rather unusual, due to concerns of **ammonia slippage**, that is of emission of unreacted NH_3 from the stack.

If the flue gases are rich in SOx and their temperature is **below 330°C**, the catalyst can be **poisoned** by the side reaction:

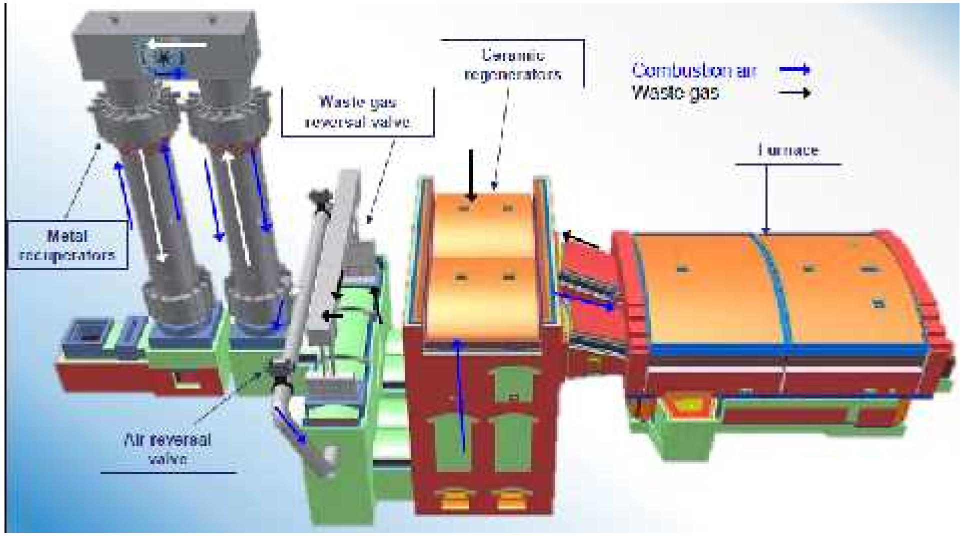
$$SO_3 + NH_3 + H_2O \rightarrow NH_4.HSO_4$$

Ammonium sulfate sticks to the catalyst and tends to trap dust particles, thus decreasing the chemically active surface and potentially clogging the system.

To avoid poisoning and extend the lifetime of the catalyst, the flue gases to be treated should have low SOx and dust content, and T > 330°C.

SNCR ?

- Centauro can be used as SNCR
- NH3 can be dosed after the regenerator at the appropriate range of temperature (700-800 °C)
- Test carried out in some plants have demonstrated good results in terms of yields



SCR RESULTS AND CROSS MEDIA EFFECTS

SCR involves also several cross media effects:

- The SCR system requires “clean” off gases to operate, so the simultaneous installation of SCRs with gas scrubbers and dust filters is mandatory.
- The usage of ammonia or urea as reagents requires special handling and stocking precautions, as well as dedicated facilities.
- The risk of ammonia slip must be accurately evaluated, and a periodic fine tuning of the dosage ratio may be necessary
- Every 3 to 5 years several cubic meters of spent catalyst have to be renewed and disposed of, involving costs and hot repair maintenance.
- The system requires a lot of space to be installed, and has quite high investment costs: 1300 ÷ 800 k€ for furnaces producing respectively 450 ÷ 200 ton/day; the operational cost are around 140 ÷ 80 k€/year (reagents + energy).

BAT – ENERGY EFFICENCY

According to the BAT conclusions document, the specific energy consumption can and should be reduced by using one or a combination of the following techniques:

- Process optimization (applicable)
- Regular maintenance of the melting furnace (applicable)
- Optimization of the furnace design (new plant)
- Application of combustion control techniques (applicable)
- Increase levels of cullet (applicable where available)
- Waste heat boiler for recovery (if economically sustainable)
- Batch and cullet preheating (if economically sustainable)

Thanks !