Pollution Formation and Control

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1. Introduction

European Glass Industry produces about 30 million tonnes per year of glass of different types and values, with container glass accounting for about 60 % and flat glass for more than 20 % of the total production.(1)

The environmental impact of the sector is considered significant, in particular for the emissions to air deriving from the melting process which requires high temperatures and intensive use of energy.

The use of fossil fuel for the melting process is responsible of high levels of carbon dioxide (CO_2) emissions which represent the main discharge to the atmosphere, with levels that vary significantly with the type of glass produced, from 500 to 1400 kg CO_2/tonne of melted glass.

The main components of atmospheric emissions from the glass melting process are the following:

Nitrogen Oxides ($NO + NO_2$)	50 – 80 % of the total (excluding CO_2)
Sulphur Oxides ($SO_2 + SO_3$)	20 – 40 % of the total (excluding CO_2)
Particulate matter	4 – 6 % of the total (excluding CO_2)
Gaseous Chlorides	about 1 % of the total (excluding CO_2)
Gaseous Fluorides	about 0.2 % of the total (excluding CO_2)

While the emissions caused by the melting process are quite similar for each sector of the Glass Industry, downstream activities can represent a much different impact on the environment, based on the type of glass produced.

A summary of the most significant air emissions for each glass sector is presented in Table 1.

Table 1 – Emissions to air for the different sectors of the Glass Industry

SECTOR/ACTIVITY	AIR POLLUTANTS
Container Glass	
Storage and handling of raw materials	Particulate matter
Melting process	Particulate matter, NOx, SOx, HF, HCl, metals
Hot surface treatments	Particulate matter, inorganic and organic tin compounds, HCl, SOx
Flat Glass	
Storage and handling of raw materials	Particulate matter
Melting process	Particulate matter, NOx, SOx, HF, HCl, metals (in the case of tinted glass)
Hot surface treatment	SOx
Continuous Glass Filament	
Storage and handling of raw materials	Particulate matter
Melting process	Particulate matter, NOx, SOx, HF, HCl
Coating applications	Particulate matter, formaldehyde, ammonia, VOCs (based on the product type)
Glass Wool	
Storage and handling of raw materials	Particulate matter
Melting process	Particulate matter, NOx, SOx, HF, HCl, metals
Coating applications	Particulate matter, formaldehyde, ammonia, phenols, VOCs
Domestic Glass	
Storage and handling of raw materials	Particulate matter
Melting process	Particulate matter, NOx, SOx, HF, HCl, metals
Special Glass	
Storage and handling of raw materials	Particulate matter
Melting process	Particulate matter, NOx, SOx, HF, HCl, metals
Surface treatments	Particulate matter, HF (for lead crystal glass, artistic, etc.)

2. Emissions to air – Origins and associated phenomena

The melting process, being the main source of emissions to air, affects the quantity of air pollutants, while the batch composition and the choice of fuel is responsible for both quality and quantity of the emissions.

a) Particulates

It is well known that the presence of volatile components in the batch composition causes the formation of particulate emissions. For soda-lime glasses, about 95 % of the chemical composition of particulate matter is represented by sodium, potassium and calcium sulphates, while Na, K and Ca borates are the components of particulate emissions from borosilicate glasses. For a defined batch composition, there are several conditions that can affect the amount of emissions to air.

The following tables show the results of some measurements carried out in different operating conditions of the melting furnace, producing the same type of glass:

Table 2 – Influence of different melting parameters on the concentration and/or mass flow of particulate emissions

	Condition 1	**Condition 2**	**Note**
End Port Furnace – Green Container Glass			
	Cullet 40 %	Cullet 80 %	
Particulate (mg/Nm^3 8 % O_2)	230	127	Furnace maximum temperature decreased by 42 °C
End Port Furnace – Clear Container Glass			
	Cullet 30 %	Cullet 80 %	
Particulate (mg/Nm^3 8 % O_2)	336	203	Furnace maximum temperature decreased by 62 °C
Side Port Furnace – Clear Flat Glass			
	Reduced ratio Air : natural gas	Increased ratio Air : natural gas	
Particulate (mg/Nm^3 8 % O_2)	217	190	At standard operating conditions, particulate: 182 mg/Nm^3
End Port Furnace – Clear Container Glass			
	Specific pull rate 2.73 t/m^2. day	Specific pull rate 1.75 t/m^2. day	
Particulate (kg/h)	5.27	4.22	Furnace temperature maintained constant for the test

The data presented in Table 2 show how some parameters (i.e. cullet percentage, fuel/air ratio, specific pull rate) can influence the emissions of particulate from the melting furnace, with significant variations of particulate concentration or mass flow.
The quality of raw materials determines the chemical composition of particulate emissions to air. For soda-lime glasses, the use of cullet can be responsible of the presence of heavy metals in the particulate, increasing the environmental impact of

the glass melting process. The influence of cullet on the presence of Lead in particulate emissions is shown in Table 3.

Table 3 – Influence of the quality of cullet on the chemical composition of particulate emissions (2)

End Port Furnace – Green Container Glass with 70 % cullet			
Lead in the glass	**Lead emitted as particulate**		
ppm Pb	Pb (mg/Nm^3 at 8 % O_2)	Pb (kg/h)	Note
155	8.80	0.076	Pb exceeds the limit value of 5 mg/Nm^3 at 8 % O_2
225	13.5	0.119	
310	17.4	0.156	

b) Nitrogen Oxides (NOx)

The origin of nitrogen oxides is related to the oxidation, at high temperature, of nitrogen present in the air used for combustion and to the use of nitrates in the batch composition. While NOx emissions deriving from the decomposition of nitrates are easy to estimate, nitrogen oxides from combustion vary significantly with the type of furnace, fuel and with the parameters regulating the combustion process: type of burner, excess air, air temperature, etc.

Typical values of NOx emissions, for different types of furnace are presented in Table 4. The data reported refer to container glass production, only.

Table 4. Typical NOx emission values for different type of container glass furnaces

Type of furnace	**NOx emissions**			
	mg/Nm^3		***Kg/Ton. melted glass***	
	Average value	Standard deviation	Average value	Standard deviation
UNIT MELTER	680	270	1.59	0.38
END PORT	1161	506	2.21	0.99
SIDE PORT	2339	317	3.61	0.31

Note: The values refer to furnaces not implemented with specific primary measures or De-NOX secondary measures.

The data presented in Table 4 show a wide range of NOx concentrations that can be measured for container glass furnaces operating in different conditions of excess air, specific pull rate, furnace temperature, combustion air temperature, etc.

An example of the influence of excess air on the formation of nitrogen oxides and other gaseous emissions is shown in Table 5.

Table 5. Influence of excess air on NOx and other gaseous emissions for a flat glass furnace gas fired.

	NOx	**SOx**	**HCl**	**HF**
Furnace Conditions	***mg/Nm^3 at 8 % O_2***	***mg/Nm^3 at 8 % O_2***	***mg/Nm^3 at 8 % O_2***	***mg/Nm^3 at 8 % O_2***
Normal operating conditions	1779	561	19.3	3.92
Sub-stoichiometric ratio gas /air	1465	690	58.3	9.52
Over-stoichiometric ratio gas/air	2008	461	21.9	3.45

c) Sulphur Oxides (SOx)and other gaseous pollutants (HCl, HF)

The source of sulphur oxides emissions is represented by the use of fuel oil containing sulphur and/or the raw materials in the batch composition. Sodium and calcium sulphates are the most common refining agents for soda-lime glass; slag and pyrite are among the raw materials used in the production of coloured glass.

All these substances decompose and oxidise during melting, originating sulphur oxides (SO_2 + SO_3) emissions.

Impurities contained in the raw materials or, in a limited number of cases, the intentional use of substances necessary for refining the glass (i.e. fluorspar, sodium chloride, etc.) are responsible for the emission of gaseous chlorides and fluorides (HCl, HF).

In addition, the use of recycled cullet represents a source of “unwanted “ components that, in part, are released during the melting process as gaseous emissions. Some examples concerning the mass balance for Sulphur, Chlorides and Fluorides are given in Table 6.

Table 6. Contribution of recycled cullet and raw materials to gaseous emissions for a container glass furnace (2)

	Furnace Input		**Furnace Output**		
Substance	***Recycled cullet***	***Raw materials***	***Glass***	***Emissions to air***	
	Kg/h	Kg/h	Kg/h	Kg/h	mg/Nm^3 at 8 % O_2
Sulphur as SO_2	6.25	12.10	3.40	13.6	837
Chlorides, as HCl	1.59	0.50	1.63	0.46	27.9
Fluorides, as HF	0.51	0.018	0.38	0.14	8.80

From the data presented in Table 6, it is evident that the quality of recycled cullet is critical for the control of gaseous emissions, in particular SOx, HCl, HF.

3. Definition of Best Available Techniques for the Glass Industry

Glass Industry is very diverse, each sector shows significantly different characteristics, the most important being:

1. Type of glass and raw materials used in the batch composition;
2. Quality standard required for the final product;
3. Type and size of the furnace used for the melting process;
4. Type of fuel used for combustion;
5. Average life of the melting furnace.

The definition of Best Available Techniques for the Glass Industry must take into consideration these differences, as it has been done in the BREF document, were BAT have been established for each sector.

The techniques presented in the BREF document are available for a possible application to the Glass Industry, however a careful evaluation is necessary in order to identify the sector of applicability and the achievable emission levels. In fact, the applicability and the performance of a selected technique can be strongly influenced by several factors (see above list) and the level of performance can vary significantly when applied on a new or existing furnace.

Based on the definition given by the European Directive 96/61/EC concerning the term “available”, the following summary presents the applicability, advantages and disadvantages of the Best Available Techniques identified for the Glass Industry.

Table 7. Summary of the selected BAT for the Glass Industry

a. Particulate

BAT	Applicability	Advantages	Disadvantages
Primary measures			
Modification of batch composition	Depends on the type and quality of glass required	No need for modification of production cycle	Limited removal efficiency. Possible increase of energy consumption
Electric melting	For furnaces with limited capacity, generally < 70 t/day Requires complete rebuilt of the furnace		Lack of flexibility of the furnace and limited life. Use of electric energy with indirect emissions.
Secondary measures			
Electrostatic precipitator	More viable for large volumes of waste gas	Limited pressure drop. Suitable for operating at high temperatures, about 400 °C.	Removal efficiency varies with temperature, humidity, waste gas volume. Use of electric energy with in direct emissions. Production of solid waste
Bag filter	More viable for limited waste gas volumes	High removal efficiency	Requires cooling of waste gas. High pressure drop. Use of electric energy with indirect emissions. Production of solid waste.
Wet scrubbers	Not suitable for large waste gas volumes. For special applications only	When applied on all electric furnaces could be cost efficient and easy to operate	Production of liquid waste. Low removal efficiency for particulate < 1 μm

b. Nitrogen Oxides (NOx)

BAT	Applicability	Advantages	Disadvantages
Primary measures			
Modification and control of combustion	Suitable for all type of conventional furnaces. Limited implementation on existing furnaces. Complete implementation at furnace rebuilt	Possible energy saving	May cause carbon monoxide emissions No effects on NOx from batch composition
FENIX process	At present, applied only on flat glass oil fired furnaces. Implementation at furnace rebuilt	Possible energy saving	No effects on NOx from batch composition
Furnaces with special design for low NOx emissions (Flex melter, LoNOx, etc.)	Limited furnace capacity. Only for some glass types. Require complete furnace rebuilt	Possible energy saving	
Oxyfuel combustion	Limited efficiency when implemented on existing furnaces. Full application at furnace rebuilt.	Possible energy saving	Indirect emissions from electric energy use for the oxygen production. No effects on NOx from batch composition
Electric melting	For furnaces with limited capacity, generally < 70 t/day Requires complete rebuilt of the furnace		Lack of flexibility of the furnace and limited life. Use of electric energy with indirect emissions. No effects on NOx from batch composition
Secondary measures			
Reburning and 3R process	Applicable on regenerative furnaces		Increased energy consumption from injection of fuel. Possible damage on refractory materials.
Selective Non-catalytic Reduction (SNCR)	Applicable only on recuperative furnaces and particular type of regenerative furnaces		Possible NH_3 emissions. Environmental impact from ammonia storage
Selective Catalytic Reduction (SCR)	Not implemented for borosilicate and domestic glass. Limited number of applications		Possible NH_3 emissions. Environmental impact from ammonia storage Production of solid waste from replacement of catalyst.

c. Sulphur Oxides, Gaseous Chlorides and Fluorides (HCl, HF)

BAT	Applicability	Advantages	Disadvantages
Primary measures			
Improvement of the quality of raw materials and recycled cullet	Difficult availability of pure raw materials		
Fuel selection	Difficult availability of natural gas in some geographic areas. Limited selection of fuel oil on the market		Possible increase of nitrogen oxides emissions
Secondary measures			
Waste gas scrubbing with alkaline reagents	Only associated with a filtration system for particulates	In several cases, filter dust can be recycled into the batch composition, replacing a raw material	High levels of particulate (solid waste). Consumption of minerals (calcium hydroxide, sodium bicarbonate, etc)

When evaluating a selected BAT, all the different environmental aspects should be taken into consideration, in particular:

1. Achievable environmental performance
2. Indirect emissions associated with the application of the selected BAT (i.e. use of electric energy)
3. Use of natural resources (minerals, water, etc.)
4. Use of substances associated to a significant environmental impact (i.e. ammonia)
5. Production of solid and/or liquid waste, with the possibility to recycle

The result of the evaluation process should bring to the selection of a BAT that is technically and economically viable for the specific industrial site.

4. Conclusions

The origin of pollution associated with the production cycle of the Glass Industry is affected by several different factors. Some of them could be controlled, preventing high levels of emissions, others require the application of specific techniques in order to minimize the environmental impact of the sector. Each identified solution is normally associated with advantages and disadvantages that require a careful evaluation, in order to achieve an overall protection of the environment at sustainable cost for the sector.

5. References

(1) Integrated Pollution Prevention and Control - Reference Document on Best Available Techniques in the Glass Manufacturing Industry, European Commission, October 2000,

2) Scalet B. M.: Impact of recycling of glass and filter dust on glass furnace emissions . Proceedings of the International Commission on Glass Annual Meeting, Amsterdam (The Netherlands) 2000.