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TNO report
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**Inventory of SO₂ emissions and emission reduction
potential in the Netherlands glass industry.**

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Preface

On the request of InfoMil-SenterNovem, a study on SO_x emissions of glass furnaces in the Netherlands has been performed by TNO in co-operation with the Vereniging van Nederlandse Glasfabrikanten (VNG). The study formally started on December 1., 2006 after a start-meeting with participation of representatives of permitting authorities for the Dutch glass manufacturers (Provinces of Groningen, Zuid-Holland, Noord-Brabant and Gelderland were represented), representatives of a few glass companies (OI-Europe, REXAM Glass and Glaverbel), a representative of VROM, two representatives from InfoMil and one from TNO.

The requested study includes two parts:

Part 1: Inventory of current SO₂ emissions by Dutch glass furnaces in 2005 plus historical development (1990-2005) in specific emissions and applied SO₂-emission reduction techniques plus observed bottlenecks in emission reduction;

Part 2: Potential of further SO₂ emission reduction by the Dutch glass industry by primary and secondary measures up to the year 2010 and the associated costs (costs of SO₂ emission reduction per kg SO₂ emission reduced and per ton molten glass).

The results of part 1 are presented in this report.

This report is separated in these two parts.

Summary

SO₂ emissions Netherlands glass industry

An inventory of the SO_x emissions per glass furnace has been made to assess the current SO_x emissions of the Netherlands glass industry. The total SO_x-gas emissions by the container glass, float glass, glass fibre, glass wool, special glass and tableware glass sector is in total 1350-1400 tons (SO₂)/year in 2005/2006.

Almost all furnaces are natural gas fired (92 % of the Netherlands glass melt production is fired with natural gas). About 600 tons/year of SO₂ is already removed by application of scrubbers combined with filters (without scrubbers the total SO₂ emissions in the glass industry in the Netherlands would be about 2000 tons SO₂ per year).

In the period 1992-2005, the total SO_x emissions of these glass industry sectors decreased from 2710 down to about 1380 tons/year, despite the 38 % production growth in that period. The specific SO_x emissions decreased in the same period from 2.38 kg per ton molten glass down to 0.875 kg/ton glass melt.

About 60 % of the Netherlands glass production (based on molten glass mass) applies air pollution control systems. In most cases the SO_x abatement is combined with filters. Dry scrubbers plus bag filters or electrostatic filters are the most used systems, but also semi-dry and wet scrubbers are applied. The selected type for air pollution control system and kind of absorption agent depends on the main pollutant to be removed (HF, HCl, SO_x, dust) and the regulations in the framework of the NER and permit obligations.

Most SO_x emission reduction is realized by conversion from oil-firing to natural gas fired (800 tons SO_x reduction by conversion to natural gas firing of the total 2710 tons of SO_x emission in 1992). The application of scrubbers contributed to about 600 tons SO_x emission reduction between 1992 and 2005. The optimization of the use of sulfate raw materials has given a few hundreds of SO_x emission reduction (100-300 tons) per year.

Applied abatement technologies

The dry scrubbers, based on hydrated lime: Ca(OH)₂ powder injection, show SO_x removal efficiencies of about 15-30 % for the hydrated lime quantities injected in the dry-

scrubbers in the Netherlands glass industry. Improved removal can be achieved by the use of more absorption agent, but this will result in higher disposal loads and costs of this disposal. The use of $\text{Ca}(\text{OH})_2$ powder and dry scrubbing systems or other lime based scrubbing methods were often chosen to remove HF emissions.

Dry scrubbers based on sodium bicarbonate injection show a significantly higher SO_2 removal efficiency (> 50 %). Thus, the air pollution control systems installed in the past may not always be the most optimum choice for SO_x removal only. Higher absorption rates seem possible by an increase of the injected amount of absorbing material, but this consequently leads to increased levels of filter dust disposal.

Semi-wet scrubbers show SO_x -removal efficiencies of more than 50 %, depending on injection rate of the soda or lime solution. Wet scrubbers gave efficiencies above 90 %.

Secondary waste

The largest problem encountered by the application of scrubbers is the amount of residue (filter dust, or waste water sludge) to be disposed. In 2005-2006, this was about 4100 tons (dry)/year. Increasing SO_x removal efficiencies by application of more scrubbers or more absorption reactant (soda, sodium bicarbonate, lime, hydrated lime) would increase this amount. The removal costs of filter dust are about 15 to 20 % (on average) of the total air pollution costs. This ratio might increase in future.

Internal filter dust recycling is limited in most cases, because of operational problems in several cases during filter dust recycling (damage to furnace construction) or due to the limited sulfur solubility in some glass types, which limits the sulfate digestion by the glass.

The selection of a certain system and absorption agent to reduce pollutant emissions depends on many factors, such as:

- The most important pollutant to be removed, for instance in case of HF emissions, lime based scrubber systems are to be preferred as being the most effective for these species, but this method often appears to be less effective for SO_x removal, compared to soda or sodium bicarbonate based scrubbing, which is less efficient for HF removal.

- Also the nature of the filter dust or filter residue, dependent on type of absorption agent and the possibility to recycle or re-use this filter residue is an important parameter for the scrubbing system and absorption agent to be selected.

An integral approach appears to be necessary when an air pollution control system or primary measures have to be selected for a glass melting furnace emitting several different types of gases. Selection of a system not only depends on the most optimum SO_x removal method. Cross media effects, energy consumption aspects of this system, secondary waste or secondary emissions or adverse impact on the emissions of a certain species when abating another species (SO_x versus NO_x for instance when changing the fuel type) should be taken into account.

The implementation of low temperature scrubbers and filters (bag filters) limit or constrain the application of SCR DeNO_x equipment, because of the low temperatures of the flue gases leaving the filters being too low for SCR systems based on ammonia injection.

An amount of about 4000 tons of secondary waste that cannot be recycled in the glass melting process is generated in 2005 in the Netherlands,. This waste is filter dust or sewage sludge from wet scrubbers. This waste cannot be recycled internally (in glass furnaces), because of several reasons: a). carry-over in the furnace, b). damage to the furnace refractories by carry-over or c).accumulation of components (like alkali vapors) in the flue gases, making flue gases reactive and corrosive, d). handling problems or e). accumulation of certain chemical elements in the furnace system, when recycling filter dust in the glass furnace.

Potential Air Pollution Control of SO_x

In 2007, about 70 % of the Netherlands glass production is equipped with air pollution control. In the case that all larger (container glass, float glass) furnaces (production levels above 250 tons molten glass per day) in the Netherlands apply scrubbers in 2010, the total emission of SO₂ in 2010 is estimated on 1150 tons per year, taking into account an

expected increase of the total glass production of 4-5 % compared to 2005. In that case, more than 90 % of the Dutch glass production is equipped with scrubbers and filters. Most filters are bagfilters and the applied scrubber systems are mostly based on dry scrubbing, but also wet and semi-wet scrubbers and electrostatic precipitators are used in the Netherlands glass industry. However, in this scenario it is assumed that mainly dry scrubbers are used often applying hydrated lime absorption agents.

Further SO₂ emission reduction potential

A further reduction down to ±950-1000 tons SO₂ emission per year may be possible by improving the efficiency of the (dry) scrubbers, for instance by using sodium bicarbonate or trona soda instead of hydrated lime or changing to more reactive hydrated lime qualities, probably without increasing the waste disposal.

A further reduction of the SO₂ emissions by increasing the ratio of absorption agent versus the amount of pollutant gas in the flue gases will consequently lead to an increasing amount of filter dust residue to be discharged and this will increase the amount of secondary waste that has to be disposed. The improvement of scrubber efficiency for SO₂ removal (by changing the absorption agent or process conditions) needs further investigations and the effect on HF emissions needs to be studied when changing from lime based absorption agents to other absorbents.

The specific SO₂ emissions are on average about 0.55-0.7 kg SO₂/ton molten glass by 2010.

Typical costs for emission reduction

The costs for combined dust and SO₂ removal is about 3 – 4.5 Euro per ton molten glass for dry scrubbers, but these costs can increase considerably to more than 10 Euro per ton for semi-wet or wet scrubbers.

Typical costs per kg SO₂ removal is 0.8-1.25 Euro/kg SO₂, but these costs are derived from the costs of combined particulate and SO_x emission reduction: Subtracting from the total costs, the costs for particulate removal with a weighting factor for SO_x of 0.5 compared to a factor 10 for dust removal (1 kg of dust removal is assumed to be 20x

relevant than 1 kg SO_x (calculated as SO₂). For other ratios of weighing factors, calculated SO_x removal costs may change significantly.

Other emission aspects

In the Netherlands, most furnaces are equipped with bag filters operating below 160-190 °C. The application of SCR for these de-dusted flue gases is questionable or needs reheating of the flue gases, because of the relatively low temperature level downstream the bag filters (160-200°C). SCR (DeNO_x) systems for glass furnaces generally need to operate with flue gas temperatures above 330°C, because of residual SO₂ in the flue gases.

TNO Science and Industry

TNO report

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Inventory of SO₂ emissions and emission reduction potential in the Netherlands glass industry.
Part 1: SO_x emissions in the Netherlands Glass industry, situation anno 2005/2006.

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Summary part I

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Figures and tables in this report, part I:

- Figure I.1* *Location Netherlands glass production plants*
- Figure I.2* *Development of glass production in the glass industry in the Netherlands in period 1992-2005*
- Figure I.3* *Development of mass averaged specific emissions (expressed in kg emission per ton molten glass) in glass industry in the Netherlands (includes: container glass, tableware, float glass, insulation wool, fibre glass, lighting glasses).*
- Figure I.4* *Schematic drawing of a dry-scrubber plus electrostatic precipitator system*
- Figure I.5* *Total SO₂ emission by the glass furnaces of the Dutch glass industry in period 1992-2005 and the development of the production volume (molten glass)*
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- Table I.1* *Figures and data Netherlands Glass Industry 2005*
- Table I.2* *Factors determining the SO_x emissions of glass furnaces*
- Table I.3* *Situation air pollution control NL glass industry in 2005*

Preface of part I

On the request of InfoMil-SenterNovem, a study on SO_x emissions of glass furnaces in the Netherlands has been performed by TNO in co-operation with the Vereniging van Nederlandse Glasfabrikanten (VNG). The study formally started on December 1., 2006 after a start-meeting with participation of representatives of permitting authorities for the Dutch glass manufacturers (Provinces of Groningen, Zuid-Holland, Noord-Brabant and Gelderland were represented), representatives of a few glass companies (OI-Europe, REXAM Glass and Glaverbel), a representative of VROM, two representatives from InfoMil and one from TNO.

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Part II: Potential of further SO₂ emission reduction by the Dutch glass industry by primary and secondary measures up to the year 2010 and the associated costs (costs of SO₂ emission reduction per kg SO₂ emission reduced and per ton molten glass).

The results of part I are presented in this report.

Because of confidentiality reasons, this report will not present detailed or site-specific data nor results per specific furnace, but total or average emission and cost values and general conclusions.

The study is focused on glass melting processes with more than 20 tons molten glass per day (IPPC threshold) and includes the glass furnaces of the following companies:

- OI-Europe: installations for production of container glass production in Schiedam, Leerdam and Maastricht;
- Libbey Glass: installations for tableware glass production in Leerdam;
- REXAM Glass: installations for container glass production in Dongen and Moerdijk;

- Saint Gobain Isover and Vetrotex Benelux: installations for glass wool (insulation) and fleece production in Etten Leur;
- Glaverbel Nederland: installation for float (flat) glass production in Tiel;
- PPG Industries Fibre Glass: installations for fiberglass production in Hoogezand;
- Philips Lighting: installations for lighting glass production in Roosendaal and Winschoten.

Information for this study has been collected by TNO, using a questionnaire (per furnace), see annex I.1. The questionnaires are completed by each company. Extra information and data are obtained from additional visits to some factories. This information includes: emissions and production in 2005 or 2006 per furnace, currently applied air pollution control (APC) equipment, capital and operational costs for APC and future plans of production and air pollution control by primary and/or secondary measures.

Annex I.2 gives some background information on the sources of emissions in glass melting processes and annex I.3 shows the effect of some primary measures applied in glass furnaces on several emissions.

I.1. Introduction

The objective of this report is to:

- a). present an inventory of SO₂ emissions* by the glass furnaces of the Dutch (Netherlands) glass industry anno 2005 and
- b). to show the developments in the production volume and SO₂ emissions in the period 1990-2005.

The applied technologies for SO₂ emission reduction in the Dutch glass industry are described and an inventory of the observed results (emission reduction levels), associated costs and observed bottlenecks or encountered problems are given. Especially, the relations between SO₂ emission abatement compared to reduction of other relevant emissions such as fine dust (dust in general, PM10, PM 2.5) and NO_x is discussed. Problems such as: disposal of filter dust residue or removal/disposal of scrubbing sludge are identified and quantified.

The second part of the study aims to obtain an estimate of the future course of the SO₂ emissions by the Dutch glass industry, based on current plans of applying SO₂ emission reducing methods between 2005 and 2010 and the potential of even further reduction of SO_x emissions, plus the associated costs, expressed in costs per ton molten glass or costs per unit mass of reduced SO₂ emissions. In the second chapter of this report (I.2), an overview of the glass industry in the Netherlands (anno 2005) will be presented with production data, types of applied furnaces and glass types plus the locations of the plants.

** Sulfur compounds in the flue gases of glass furnaces are: SO₂ gas, SO₃ gas, sulfuric acid and sulfate dust components. The gaseous part is called SO_x, the total SO_x emission is given as SO₂ and expressed in mg/Nm³ or kg per ton molten glass. In the glass industry the emission concentrations [1] are generally based on flue gas volumes at 273 K, 1013 mbar at dry conditions with 8 vol. % O₂.*

In chapter I.3, the specific emissions of SO_x, NO_x and dust in the past 15 years are given and the total emission of SO_x by de glass industry in the Netherlands (*excluding stonewool, water glass and enamel/ glazing frittes, the companies in these sectors are not members of the Vereniging van Nederlandse Glasfabrikanten*)** in 2005 will be shown.

Chapter I.4 gives an overview of the applied SO_x emission reduction techniques, often in combination with dust separation (filtration) and the amount of residue (filter dust or waste water sludge) to be disposed.

Chapter I.4 summarizes the main conclusions of part I.

In the second phase of this study (next report), the course of SO₂ emissions estimated until 2010 will be predicted, based on planned SO₂-emission reduction systems and production growth and the potential of additional SO₂ emission reduction methods will be studied. The costs per ton molten glass and per kg reduced SO₂ emissions will be estimated for the different cases.

*** The SO_x emissions of water glass furnaces can be neglected (only natural gas firing, no sulfur raw materials) and the SO_x emissions of the fritte furnaces are very low compared to the rest of the glass industry.*

I.2. Glass industry in the Netherlands

The glass industry, all over the world and also in the Netherlands, can be divided in several sub-sectors. The common factor is the application of a high temperature melting process, to convert well-mixed raw materials (batch) such as a mixture of sand, soda, limestone, dolomite, boron raw materials (boron is used in fiber or wool glass production), alumina-raw material (feldspars or slags) and colorants or fining agents (additives in batch to aid the removal of gas bubbles from the viscous melt) into a homogeneous mass: the glass melt [2]. Subsequently the glass melt (1100-1500 °C) is used to form products. The type of forming process depends on the type of glass product, but this process step is hardly associated with SO_x emissions. The melting processes take place in large furnaces, with production rates of 20 up to more than 500 tons molten glass per day. Today, many furnaces, especially in the container glass sector apply recycled cullet in the batch: cullet from own production reject (internal cullet) or from post-consumer sources (external cullet, sources are: collection banks, industrial glass).

The furnaces are mostly heated by firing natural gas with preheated air and maximum temperatures in the combustion space can be as high as 2000 °C. In few cases, electrodes are used to add extra energy (from 3 to even more than 10 % of the total energy demand) to the melt, so-called electric boosting. In the past, several furnaces applied fuel-oil, but today only one glass furnace in the Netherlands is still applying fuel-oil in combination with natural gas. This furnace still needs to apply fuel oil, because of production reasons: to achieve the required heat transfer and to avoid too high NO_x emissions. The existing furnace design is based on fuel-oil firing (the original float glass furnace was design for fuel-oil firing). For natural gas firing, major modifications (only possible for a complete new furnace) have to be applied similar to other natural gas fired float glass furnaces. These modifications include changes in the combustion chamber design, changes in burner port dimensions (larger burner ports) to reduce air velocities and adaptations of the burners/burner positions to be able to create flames with high radiative heat transfer rates.

Figure I.1 shows the locations of the Dutch glass industry installations. There are 10 production locations in the Netherlands. One of these locations includes a tableware and a container glass plant (Leerdam). There are 25 glass furnaces, 23 of these furnaces

continuously melt glass, only two of these 25 furnaces melt glass in shorter production campaigns. Table I.1 gives an overview of the production and total emission of the glass industry in the Netherlands in 2005. For one furnace the data of 2006 have been used, representing, for this furnace, the normal production situation. During extended time intervals the production conditions and emissions of this furnace appeared to be unstable and therefore the emission levels of 2005 are not representative for normal production conditions. Therefore data from a period in 2006 with 'normal' process conditions for this furnace have been collected and are used in this study.



Figure I.1 Location Netherlands glass production plants

*Bold printed are the production plants of concern of the VNG (Vereniging van Nederlandse Glasfabrikanten)

Table 1 Netherlands glass industry		2005 figures
Total production	1.576.000 tons	molten glass
	1.355.000 tons	sold glass
Average tonnage	180	tons molten glass/day
Range	1 - 550	tons molten glass/day
Products	Number of furnaces	% of production (based on mass molten glass)
container glass	12	74 to 76
float glass	1	11 to 12
fiber & insulation wool	4	these 12 furnaces together 13 %
special glass & tableware	8	
Types of furnaces		fuel
recuperative - air-gas fired	10	gas
oxygen-gas fired	5	gas
end port gas fired regenerative*	9	gas
cross fired regenerative	1	mixed fuel
* few furnaces equipped with electrodes		
SO ₂ emission	1350-1400	tons/year
NO _x emission	2900-3000	tons/year
dust emission	110-120	tons/year

Table I.1

The lifetime of a furnace is typically 6 up to 15 years (this means a campaign period with a continuous glass production without any cold repair), depending on the glass compositions and specific pull (pull per square meter glass melt surface area). Table I.1 shows production data of the Dutch glass industry anno 2005. This table also shows the totals SO₂, NO_x and dust emissions of all the Dutch glass furnaces (excluding enamel or glazing fritte, water glass production) in 2005. The total emissions of SO_x from water glass and frit production are much lower than in the rest of the glass industry.

The sub-sectors represented in the Netherlands glass industry are:

I.2.1 Container glass

There are 12 container glass furnaces in the Netherlands, the container glass sector is the largest and produces about 75 % of the glass in the Netherlands (75 % based on total mass of molten glass). Typical container glass furnace lifetimes (continuous production)

are 10-12 years, before a small cold repair is necessary. (A cold repair takes place by discharging the glass melt from the furnace by a draining system, cooling down the furnace plus the heat exchangers (regenerators or recuperators) and rebuilding a large part of the furnace, often the melting tank and throat is completely rebuilt and often also the crown or regenerators are renewed.) Between two cold repairs, the glass furnace continuously produces glass melt over 10-12 years.

The batch may contain 15 % (for ultra white glass) up to more than 90 % cullet (green glass production). Sodium sulfate is added to the batch as a fining agent and cannot be replaced by non-sulfate raw materials. Sometimes, sulfate filter dust can be used as a fining agent. Most container glass companies optimized the sulfate addition (tried to reduce the sulfate use) to the batch. Too low sulfate contents in the batch recipe, however, will lead to severe production problems (bubbles and seeds in the products).

Today, all container glass furnaces use only natural gas as fuel. There are two types of glass furnaces applied in this sector in the Netherlands:

- End-port fired furnaces: preheating air by regenerators positioned at the end of the melting tank. The air is preheated by regenerator chambers filled with a checker of refractory bricks. These checkers are heated by the flue gases during a short period of typically 20-25 minutes. After this period, air is preheated in the same chamber. Regenerative furnaces are always equipped with two regenerators, alternating air preheating or flue gas heat absorption by the checkers. Thus, every 20-25 minutes this process is reversed. Air preheat temperatures up to 1300 °C are achieved. Due to this type of air preheating, the desired furnace and glass melt temperatures can be reached and because of this heat regeneration the energy consumption is limited to about 3.5-5 MJ/kg molten glass. Without regenerative air preheating, the energy consumption could be twice or more.

In regenerative furnaces about 30-35 % of the energy input is lost by the hot flue gases exiting the regenerators at 450-550 °C (sometimes 600 °C) [2].

Typical NO_x emission levels in modern end-port fired container glass furnaces are 1.1-1.8 kg/ton molten glass. In glass furnace flue gases flowing through the

chimney, most of the NO_x is in the NO form (about 90 %), the rest is mainly NO₂ [3, 4].

- Oxygen-fired furnaces: instead of preheated air, on-site generated (air separation) oxygen or oxygen supplied by special trucks is used to fire natural gas in the combustion space above the glass melt in oxygen-fired glass furnaces. The use of oxygen instead of air may result in energy savings due to the fact that the nitrogen in the air is not heated any more and does not contribute to the flue gas heat losses. Depending on the air separation process [5], the oxygen may still contain a few percent of argon and nitrogen gas (so-called VSA or VPSA oxygen by using zeolyte absorption processes contains 90-93 % oxygen) or almost no other gases than oxygen (98-99.8 % purity by cryogenic distillation). The main driving force for applying oxygen instead of preheated air is to reduce the specific NO_x emissions in glass furnaces [6]. Oxygen supply, however involves extra costs and electric energy to produce this oxygen and the application of oxygen firing is not always economical beneficial. The economic and technical feasibility of oxygen firing depends on the individual circumstances per furnace. Total energy consumption (including the primary energy required to generate the oxygen) is comparable or slightly higher (0-10 %) compared to end-port fired container glass furnaces. According to an energy efficiency benchmark study of TNO, based on energy consumption data of 2003, the average specific energy consumption, including primary energy equivalent for oxygen generation, of the average Dutch oxygen-fired container glass furnaces was 12 to 15 % higher compared to the average Dutch end-port fired regenerative furnace both for 50 % recycled glass in the batch. Without taking the energy consumption of the oxygen production into account, the average energy consumption of the oxygen-fired furnaces is about 4 to 8 % lower than the energy consumption of end-port fired furnaces per ton molten glass.

Most oxygen-fired furnaces can achieve NO_x emission levels below 1 kg/ton molten glass. Part of this NO_x emission of oxygen-natural gas fired furnaces in the Netherlands is caused by the nitrogen contents in the Groningen natural gas (10-14 % N₂) quality used by all the Dutch glass furnaces.

The SO_x emission (before scrubbing) depends on the glass type. For some glass products higher concentrations of sulfate in the batch are necessary to oxidize the glass (sulfates are fining agents and oxidizing agents), especially in tableware, float glass and ultra-white container glass production. The oxidation state, depending on the level of added sulfates (or sometimes nitrates) and organic compounds in the cullet (contaminants in post-consumer cullet) determines the glass color, which needs to obey strict specifications. Recycled cullet also contains dissolved sulfate. Since all container glass furnaces are fired with natural gas with negligible sulfur content, the SO_x emission depends on the total sulfur input through batch charging, cullet and recycled filter dust on one hand side and on the other side the sulfur solubility (glass color dependent) of the glass and the formation of sodium sulfate dust in the flue gas. Therefore, the different glass types and colors (ultra-flint=white, flint, green, feuille-morte, light amber, dark amber=dark brown) and cullet ratios in the batch will consequently lead to a broad range of SO_x emission levels.

In 2005, 7 of the 12 Dutch container glass furnaces applied Ca(OH)₂ or sodium bicarbonate absorption systems (“dry scrubbers”) to eliminate part of the SO_x (SO₂ and SO₃) from the flue gases. For several furnaces dry Ca(OH)₂ based scrubbers have been chosen to reduce HF emissions as first priority. Lime based scrubbers are often more efficient towards HF removal than soda based scrubbers.

I.2.2 Float glass

The float glass sector in the Netherlands is relatively small and is only represented by one glass furnace. Float glass is a flat glass product formed by pouring the molten glass continuously on a bath of molten tin, forming a smooth thin sheet or ribbon of glass. The products are used for windows, greenhouses, mirrors, automotive glass (windshields, car windows).

The only float glass furnace in the Netherlands is the largest glass furnace in the country. Today, furnace lifetimes of 14-16 years are common in the float glass sector with a continuous glass melt production covering a period of these 14-16 years. About 10-12 % of the primary glass melt production in the Netherlands is flat glass.

Almost all float glass furnaces worldwide are cross-fired regenerative furnaces. The regenerators are positioned at both sides of the furnace and each regenerator connects to the furnace by 6 or 7 ports supplying preheated air to the combustion chamber or enabling the exit of the exhaust gases through the same ports from the furnace. Natural gas and fuel-oil with 0.9-1 % sulfur is applied as fuel in the Netherlands. Due to the higher glass quality level, compared to container glass production, the average residence times of the glass melt in the furnace (55-70 hours) are about 2-2.5 times the residence times in container glass melting tanks (24 hours). The fraction of recycled glass in the batch (20-30 %) is much lower than in container glass furnaces. The consequence is a higher energy consumption (about 50 % more) and a larger volume of flue gas per ton molten float glass compared to container glass furnaces. Thus, for the same concentrations of NO_x or SO_x in the flue gases, the specific emissions will increase due to the large flue gas volume flow per unit mass of glass melt..

Because of the high quality demand of the customers (automotive industries, mirrors, buildings), the presence of fine seeds (small bubbles < 0.3-0.4 mm) and blisters (large bubbles) is critical and therefore the sodium sulfate addition to the batch is crucial for glass quality and production efficiency. (sodium sulfate addition is necessary to remove gas bubbles from the molten glass by the so-called fining process)

Depending on the furnace design, especially the combustion chamber dimensions, heat transfer from natural gas flames is not always sufficient for the required heat demand [2] enabling melting of the batch. High-luminescent fuel-oil flames (more soot and higher emission coefficient of flames and intense radiative emission heat transfer) are often necessary to obtain the required production rate (pull) and to lower the exhaust gas temperatures. Natural gas flames produce less SO₂, but due to the poor heat radiation (less soot formation in the flame) the cooling rate in the flames is much lower than in fuel-oil flames. Natural gas combustion in glass furnaces generally leads to high thermal NO_x formation [2] compared to fuel-oil fired glass furnaces. Apart from the different NO_x and SO_x emission levels comparing fuel-oil with natural gas combustion in glass furnaces, the energy efficiency appears to be also influenced by the type of fuel. The oil-fired glass furnaces generally show lower (3-7 %) energy consumption levels. The CO₂

emissions of fuel-oil fired furnaces, of course are higher because of the higher carbon / hydrogen ratio in fuel oil compared to gas.

The high production rate, relatively large amount of sulfates in the batch and the use of fuel-oil required for heat transfer in the furnace consequently give the only Dutch float glass furnace a relatively high SO_x emission level. But, since 1996 the furnace is equipped with a semi-wet scrubber (injection of soda-solution in the flue gas prior to a reaction/scrubbing tower and a bag filter), and a large quantity of the SO_x is captured as sodium sulfite and sodium sulfate dust in the applied bag filters. Experiences with recycling of this filter dust showed very strong attack of the furnace due to NaCl in this dust and it caused also severe carry-over (dust formation in glass furnace) problems. Therefore, this filter dust recycling has been stopped and now the filter dust has to be disposed. The dust removal costs in case of transport to a disposal site outside the Netherlands (salt mines) amount to about 450 EURO per ton of this filter dust waste.

The level of acceptable residual SO_x emission levels determine the quantity of dust to be disposed or to be processed outside. A further decrease of the SO_x emissions to be achieved consequently will result in extra filter dust waste to be disposed or discharged. It has been observed that a change from fuel oil to natural gas, to lower SO_x concentrations in the flue gases, increases the NO_x emissions.

I.2.3 Fibre glass

In general most glass fibre furnaces, producing molten glass for continuous filament fibers are oxygen-gas fired furnaces or furnaces using metallic recuperators for combustion air preheating. In the last case, the air is preheated in a heat exchanger, exchanging heat from the exhaust gas through a steel separation wall to the combustion air. The combustion air temperature (500-750 °C) is much lower compared to regenerative furnaces (1150-1300 °C). Furnaces with a melt pull below 100-150 tons molten glass per day are often of the recuperative furnace type or oxygen fired furnace type. Capital costs for regenerators of such relatively small furnaces are too high.

For the production of E-glass fibers, some sulfate (sodium sulfate) is added to the batch for fining.

The initially oil-fired furnaces of PPG in Hoogezand are meanwhile converted to natural gas firing. One furnace is a recuperative air-natural gas fired furnace and the other an oxygen-gas fired furnace. The addition of sulfate to the batch has been minimized in recent years.

SO_x situation fibre glass sector

So far, the following measures between 1990 and 2005 have been taken by the Dutch fibre glass producer in order to reduce SO_x emissions:

1. Change from oil firing to gas firing at the end of the nineties;
2. Reduction of sulfate content in the batch;
3. Application of wet scrubbers by a company owned process (confidential, this method as applied in this factory is not available on the open market), the first installation started in 2000 and the second one in 2003. The wet scrubber uses water for quenching and a limestone suspension for acid neutralization. The wet scrubbers remove acid gases such as HF, SO₂, SO₃ from the flue gases. The SO₂-removal efficiency is more than 98 %.

These measures resulted in an SO₂ emission level of both furnaces of less than 1 tons per year. In 1999 the emission was still about 320 tons SO₂ per year.

Consequence however, is the generation of semi-wet sludge from the wet scrubber of about 1650 tons per year (dry material).

NO_x

Conversion of one of the fibre glass furnaces to oxygen firing (furnace 608 in the year 1995) resulted in a NO_x emission of this furnace of about 1 kg/ton compared to the recuperative furnace: 3 kg NO_x (calculated as NO₂) per ton molten glass. This measure: conversion to oxygen firing, applied to reduce NO_x emissions resulted in several serious technical and melting problems. Solving of all these problems took about 10 years of experimentation and technical development. Unexpected phenomena had to be investigated and several modifications in the process had to be applied.

Full conversion of all melter combustion systems to oxygen firing in continuous filament fiber production is envisaged before 2010.

I.2.4 Insulation wool and fleece glass

In the Saint Gobain Iover Benelux factory, two glass furnaces of the recuperative type are used to melt sodium borosilicate glass melts for wool and fibers (fibers to manufacture glass fleece). Both furnaces are firing natural gas and preheated air (about 500-600 °C). The air is preheated with steel recuperators.

The total sulfur input through the batches is very small. Only sulfur in recycled (mainly flat glass) cullet enters the furnace. The total emission is estimated on less than 1 tons of SO_x per year and is therefore not significant in this sector.

The flue gases are treated by an Electrostatic Precipitator, but without scrubber. Sometimes nitrates have to be applied in the batch to oxidize the organic contaminants in the cullet. This occasionally may lead to a temporarily increase of the NO_x emissions.

I.2.5 Tableware glass

Royal Leerdam, a tableware glass plant of Libbey Glass in Leerdam produces soda-lime-silica tableware and crystal glass (but crystal glass production is very small and is smaller than the IPPC threshold limit). There are no sulfates used in crystal glass ware production. Most soda-lime-silica tableware products from Leerdam are stemware (wine glasses, liquor glasses). The glass is molten in natural gas – preheated air, recuperative furnaces.

The glass type is soda-lime-silica glass, using sodium sulfate as a fining agent. Due to the lower temperatures in recuperative furnaces and high quality demands for wine glasses, the sodium sulfate refining agent input in the batch needs to be rather high compared to container glass production.

Two furnaces are equipped with filters to remove the primary flue gas dust (this dust consists of about 90 % sodium sulfate), one applied a bag filter and the other an Electrostatic Precipitator.

The 4 tableware furnaces are not equipped with DeSO_x (scrubbers or absorption towers).

The total SO_x emission of the tableware glass sector, expressed as SO₂, is between 30 and 35 tons/year (less than 3 % of the SO_x emissions of the glass industry).

I.2.6 Special glass

There are two special glass production plants, both of Philips Lighting, producing glass products for lighting purposes. One furnace, in Roosendaal, produces fluorescence lighting tubes made of soda-lime-silica glass. This is an oxygen-natural gas fired furnace without extra air pollution control (no scrubber or filter). Sulfate in the batch is used as a fining agent. There is no SO_x emission from the fuel, only from the sulfate in the batch. The total level of SO_x emission of this furnace is about 1 % of the total SO₂ emission of the Netherlands glass industry. Thus, it is a minor contributor to the glass industry SO_x emissions.

The production plant of Philips Lighting (special glass factory) in Winschoten includes 3 glass melting furnaces. All three furnaces are natural gas air fired recuperative type glass furnaces (air preheating by metallic heat exchangers). One furnace is equipped with an electrostatic precipitator. A large number of different glass types are molten in these furnaces. Production campaigns are often within a limited time frame. The SO_x emissions are very low, because most batches hardly contain sulfate. The contribution to the total SO_x emissions is estimated on less than 1 ton SO_x per year for all three furnaces together. Thus, this production presents a negligible SO_x source.

Thus, container glass, float glass and tableware glass production are responsible for more than 98 % of the SO_x emissions of the glass industry in the Netherlands in 2005. 4 glass furnaces in the Netherlands emit about 55 % of all SO_x emissions of the Dutch glass industry.

I.3. Development of specific emissions in the glass industry in the Netherlands

The flue gas SO₂, NO_x and particulate (fine dust) emissions of glass furnaces are strongly reduced since 1990, in order to meet the emission limits of these components as pre-described in the permits based on the NER (special regulation glass industry in 1994) and the 'oplegnotitie' of the 2004 revised NER (Netherlands Emission Regulations, Dutch version) [7].

Although the glass melt production in the Netherlands increased by 38 % from 1992 till 2005, the total emissions of all the glass furnaces in the Netherlands together have significantly been decreased. The estimated glass furnace emissions in 1992 were about 2710 tons SO₂ (± 5 %) and in 2005 about 1350-1400 tons SO₂ despite the higher glass production volume. The specific emissions, expressed in kg SO_x (as SO₂) per ton molten glass decreased from 2.28 kg/ton down to about 0.875 kg SO_x/ton molten glass.

SO_x

The following measures have lead to these reduced SO_x emission levels in the Dutch glass industry.

1). In 1992, still 6 glass furnaces fired fuel-oil with 0.9 to 1 % sulfur, in 2005 only one (large) furnace is still using fuel oil firing in combination with natural gas. At this moment (2005), 92 % of the fossil fuel used in the glass industry for firing glass furnaces is natural gas, fuel oil consumption is about 8 % of the total fuel input in the Dutch glass furnaces.

This conversion from fuel-oil to natural gas or replacement/closing of few oil-fired furnaces, resulted from the year 1992 to 2005 in about 800 tons SO₂ emission reduction/year.

2). The sulfate content in the batches of several glass furnaces has been optimized. In several glass furnaces the sulfate content is reduced. The effect of these batch modifications on SO_x emissions are not known, but probably resulted in a few hundred tons of SO_x emission reduction per year.

3). Since 1996, dry or semi-dry absorption methods have been applied upstream a bag filter (=doekenfilter) or ESP (Electrostatic Precipitator=E-filter), and since the year 2000

wet scrubbers are used for a few furnaces. The injection of lime-based chemicals (CaCO_3 or Ca(OH)_2 suspensions or powder) or soda based absorbents such as soda solution or sodium bicarbonate powder will convert these chemicals in sulfites, sulfates, chlorides and fluorides by absorbing respectively SO_2/SO_3 , HCl and HF .

Injection of lime based absorbents in dry scrubbing systems in the flue gases results in 15-30 % SO_x reduction. Soda-based absorbents can capture (depending on the amount of injected material) 90 % of the SO_x , but absorption levels of more than 50-60% by soda solution injection require strongly increasing amounts of overdose of absorbing reagents and consequently a strongly increase of the filter dust residue to be disposed. SO_3 is more reactive than SO_2 . Generally, more than 90 % of the SO_x in glass furnace flue gases is in the SO_2 form [4]. At this moment 60 % of the Netherlands glass production is equipped with scrubbers. Most scrubbers are combined with dust (particulate) filtration units. First, the absorbing material (powder, suspension or solution) is injected in the hot flue gas flow from the glass furnace (from regenerators or flue system) and during 10-20 seconds flue gas components react with the lime, Ca(OH)_2 or soda, forming solid reaction products. These dust particles, and the primary dust (carry-over of fine raw material particles or evaporation products from the glass melt) from the glass furnace are both captured by filters. Bag filters generally operate below 160-200 °C and electrostatic precipitators between 300-400 °C. Few furnaces are equipped with wet scrubbers without extra dust filtration downstream the scrubber.

In several cases, a surplus of filter dust or scrubbing sludge is generated and cannot be recycled in the batch, because of several glass quality and glass furnace operation /corrosion reasons given in one of the following chapters.

The SO_2 -absorption efficiency of most scrubbers could be improved by injecting larger quantities of absorbents or by changing the absorbent composition (e.g. a change from lime based chemical to soda based chemicals). The effect of the first possibility, is that the amount of filter dust residue to be disposed will increase. There may be an effect on the HF emissions when changing from lime-based absorbents (more efficient for HF removal) to soda-based scrubbing chemicals. In 2005, about 4100 tons flue gas cleaning residue had to be disposed by the glass industry in the Netherlands. An estimate of the SO_2 emission reduction, due to application scrubbers often in combination with filters in

the Dutch glass industry is 550-600 tons SO₂ per year. This value is calculated from the measured or estimated SO_x concentrations in the flue gases upstream and concentrations downstream the air pollution control system for all furnaces.

Table I.2

Table 2 Factors determining the SO_x emissions of glass furnaces	
FUEL	
Fuel consumption per ton glass	
Sulphur content in fuel	Example 125 kg fuel oil combustion /ton glass, oil with 1 % sulphur: extra emission 2.5 kg SO ₂ (from fuel)/ton glass but natural gas firing will not contribute to SO ₂ emissions
BATCH COMPOSITION	
Addition of salt cake for fining and oxidation	High quality glasses (perfume bottles, tableware, high quality float glass) require more sodium sulfate for fining (removal of bubbles from the glass) and consequently produce more SO ₂ emissions
	Reducing components in the batch (e.g. organic material in cullet) require extra sodium sulfate for oxidation of the batch, this will increase SO ₂ emissions (up to > 1 kg/ton molten glass): Fresh cullet (from collection banks) contain more organics than old cullet and therefore batch with fresh cullet needs more sulfate and gives more SO ₂ emissions than batches with aged cullet.
Use of different types of cullet (in availability of different types of cullet may depend on local conditions)	Recycling of cullet with higher concentration of SO ₃ in cullet compared to produced glass will contribute to extra SO ₂ emissions
	Example: Green glass from batch (30 %) plus pure green cullet (70 %): 0.7-1 kg SO ₂ /ton glass Green glass from batch with mixed cullet (amber, green, flint, float) may give up to: 1.5-2 kg SO ₂ /ton glass, because amber, flint and float glass contain more SO ₃ than green glass.
Filter dust recycling in batch	The re-introduction of sulfur containing filter dust will/may lead to accumulation of SO ₂ in the flue gases
Impurities of batch components	Some batch components like: calumite, furnace slags, colemanite, limestone, clay may contain sulfur as impurity and this will contribute to the SO _x flue gas emissions
GLASS COMPOSITION	
The SO ₃ content of the glass depends often on the colour of the glass and required redox state	SO ₃ contents in the different glass products can vary between 0.03 and 0.3 % for soda-lime-silica glasses For the same sulfur input in the batch, a lower retention in the glass leads to higher SO _x emissions
Amber glass contains sulphide	Part of the added sulfur via batch and recycled cullet will remain in the glass as sulfide, required to obtain an amber color
SCRUBBER	
Type of scrubber (wet, semi-wet, dry)	Dry scrubbers generally have a lower removal efficiency than wet or semi-wet scrubbers
Amount of scrubbing agent	The molar ratio of absorbing agent versus moles of 2xSO ₂ +HCl+HF is important
Type of scrubbing agent	Limestone/hydrated lime is effective for SO ₃ and HF but soda or sodium bicarbonate is more effective to remove HCl and SO ₂
Temperature of scrubber	In case of dry scrubbing with Ca(OH) ₂ , temperatures far above the dew point and below about 350 °C give a relatively poor scrubbing performance for SO ₂ removal
Residence time of flue gas in scrubber	Several seconds of contact between absorbing agent and flue gases are required
Composition of flue gas competitive reactions of SO ₂ with SO ₃ , HCl, HF	Lime based absorbing agents first react with HF
TYPE OF GLASS FURNACE	
In oxygen-fired furnaces the sulfur retention is generally lower than in the glass than in the case of air firing	For the same input of sulfur via raw materials and cullet, the SO ₂ emissions will be higher for oxygen-fired furnaces compared to air fired furnaces. Sometimes the sulfate addition in the batch can be decreased for oxygen-fired furnaces.
Furnaces with higher temperatures will cause more sulfur release from the glass melt	The SO _x emissions may depend on furnace temperatures

Table I.2 shows that the SO₂ emissions of glass furnaces not only depend on the type of fuel and glass type. The raw material batch composition plus type of applied fuel determines the input of sulfur species into the glass furnace. The same glass can be produced from different combinations of raw materials and different types of recycled glass (cullet). For instance green glass can be produced using up to 90 % cullet. This cullet can be green glass cullet, but can also be mixed colored cullet. The input of sulfur will be much higher in case of mixed cullet with large quantities of flint or float glass (in general, this glass contains more sulfate than green glass). Also the presence of sulfur impurities in raw materials will effect the SO_x emissions. Some glass products need extreme good fining and require high amounts of sodium sulfate (salt cake) in the batch to optimize the fining process (removal of fine gas bubbles from molten glass).

Another important parameter in the SO₂ release from the melt is the concentration of organic material in the post-consumer recycled glass (glass collected from municipal waste glass collection banks). In glass furnaces using large quantities of recycled cullet with organic contamination extra sodium sulfate is required for the oxidation of the reducing (organic) components in the cullet. Sulfate is necessary to neutralize the reducing power of the organic material (or amber glass) in the cullet.

The Figure I.2 shows the production development in the Netherlands glass industry from 1992 until 2005 and figure I.3 the specific emissions of NO_x, dust and SO_x.

NO_x (for sources of NO_x, see annex I.2)

The NO_x emission levels have also shown huge reductions from 5.24 kg NO_x per ton molten glass in 1992 down to 1.87 kg NO_x per ton glass melt in 2005. The estimated NO_x emission of all glass furnaces in the Netherlands glass industry (excluding water glass and frittes) in 1992 was 6000 tons NO_x/year and in 2005 it has been decreased to 3000 tons per year. This reduction is completely caused by the application of primary measures at air-firing systems and conversion of 5 furnaces to oxygen-gas firing. These modifications in combustion systems between 1992 and 2005 required also adjustments in other process parameters and many operational problems had to be solved.

In glass furnaces, a conversion from fuel-oil firing to natural gas firing will decrease the SO_x emissions by about 1150 mg/Nm³ flue gas, but due to the higher flame temperatures in natural gas firing, the thermal NO_x formation will increase. In the glass industry, natural gas firing instead of fuel oil firing will increase NO_x emissions.

Despite this effect, the total NO_x emissions could be decreased by about 50 % and the specific NO_x emissions by about 65 %. The most important measures in the period 1992-2005 have been:

- 1). Replacement of preheated air by oxygen. Most oxygen-natural gas fired soda-lime-silica glass furnaces (e.g. container glass) show NO_x emission levels of 1 kg NO_x/ton glass melt or lower. In 2005, about 21 % of the Dutch glass production is performed by oxygen-natural gas fired glass furnaces. Estimated emission reduction by this measure: 400 tons NO_x per year. The application of oxygen combustion may significantly increase melting costs, due to the costs (and energy consumption) of oxygen generation. This combustion technology in glass furnaces often required several adjustments in furnace operation in the Netherlands in the period 1994-2006 to overcome unexpected problems with glass quality (3 cases), foaming (3 cases) and refractory corrosion (3 cases).
- 2). Replacement of burners (such as the application of adjustable jet-burners or other burners enabling a change in injection velocity or angle of fuel into the combustion space) enabling the adjustment of flame length and low fuel injection velocities (delayed mixing between fuel and air or oxygen).
- 3). Reduction of air or oxygen excess. The NO_x emissions will decrease by a decrease of the air excess in the combustion process. However, the atmosphere above the molten glass should be mildly oxidized. Reduced furnace atmospheres may lead to glass defects, increased evaporation (dust emissions) and sulfate decomposition (increased SO_x emissions) and can damage the refractory materials in the regenerators. In several glass furnaces oxygen sensors in the exhaust gas flow measure the oxygen content of the combusted gases and the continuous oxygen content measurement is used to adjust the air or oxygen excess of the combustion process to the lowest acceptable level. In annex I.3, an illustrative and practical example is presented showing the effect of NO_x-emission reduction measures on the emissions of other components in glass furnaces. This

example, valid for the majority of glass furnaces, shows that the effect of some primary measures for emission reduction should be assessed in an integral way: some “BAT” methods seem to be very efficient to reduce certain emissions (e.g. NO_x), but may have an adverse effect considering other emissions (e.g. particulates, SO_x). Because, of the measures 2) and 3), in regenerative container glass furnaces, the NO_x emission levels decreased from typically 4 kg/ton down to 1.2-2 kg NO_x/ton molten glass.

Secondary measures for NO_x emission reduction, based on SCR (Selective Catalytic Reduction based on ammonia or ureum injection) are not applied in the Netherlands glass industry.

Dust/particulate emissions

Because of the installation of bag filters and electrostatic precipitators, particulate emissions decreased from about 330 ton per year down to 120 tons dust per year. Most dust is composed of sodium and calcium sulfates. In some glass furnaces, borate raw materials are used. Consequently, the flue gases contain gaseous boron components that can condense at lower temperatures than the chimney temperature and for the determination of dust concentration there is not unambiguously defined method available in this case. Sometimes, part of the boron emissions is included in the dust emission, but often a large part is emitted as gaseous species. Figure I.3 shows that the specific emissions of NO_x, SO₂ and particulate, all have been reduced between 1992 and 2005 by more than 50 % after application the above mentioned measures.

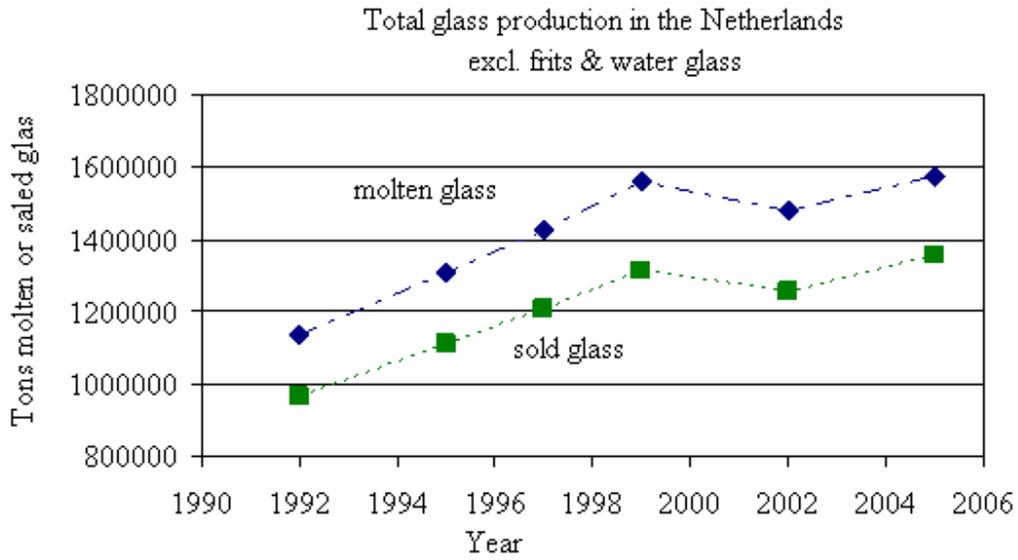


Figure I.2 Development of glass production in the glass industry in the Netherlands in the period 1992-2005

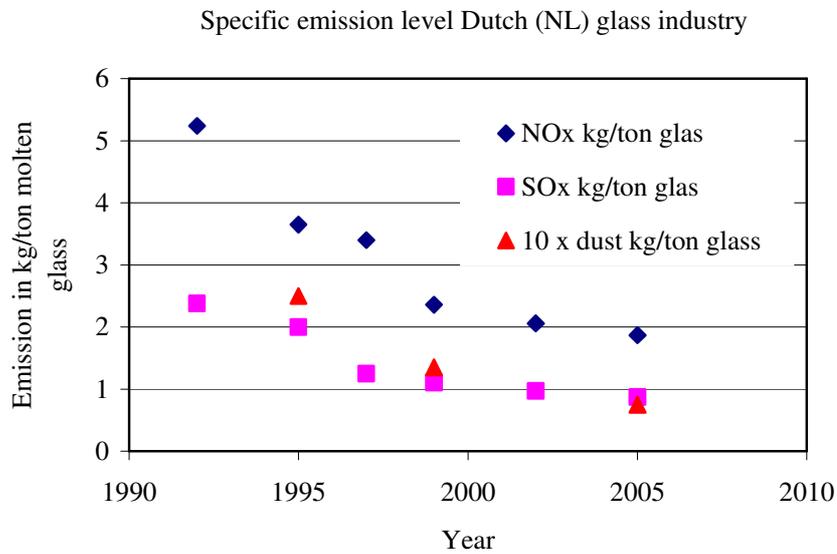


Figure I.3 Development of mass averaged specific emissions (expressed in kg emission per ton molten glass) in glass industry in the Netherlands (includes: container glass, tableware, float glass, insulation wool, fibre glass, lighting glasses). The values indicated on the vertical axis (kg/ton molten glass) have to be divided by a factor 10 for the dust data points.

I.4. Application of SO_x abatement techniques in the glass industry in the Netherlands

Since 1996, several glass furnaces have been equipped with air pollution control (APC) systems. Although in the German glass industry [8], most furnaces apply a so-called dry-scrubbing system (injection of absorbing powder such as Ca(OH)₂ in flue gas stream upstream of a filter) and electrostatic precipitation of primary dust (from glass furnace) and secondary dust (reaction product of scrubber), in the Netherlands glass industry several different systems are applied. Table I.3 shows the number of furnaces equipped with different types / combinations of APC anno 2005. At this moment, there are still 7 furnaces, mainly small furnaces that are not equipped with any scrubbing and/or filter system. About 3 or 4 extra APC's installations are planned to be installed between 2005 and 2010.

Table I.3 Situation NL glass industry 2005	Furnaces
Ca(OH) ₂ scrubber plus baghouse	4
Ca(OH) ₂ scrubber plus ESP	2
NaHCO ₃ scrubber plus ESP	1
Na ₂ CO ₃ semi-wet plus baghouse	1
Lime suspension wet scrubber	2
ESP only	6
Baghouse only	1
Oxy-Fuel	5
SCR	0
SNCR	0
3R	0
Furnaces without any secondary air pollution control	7

* ESP = Electrostatic Precipitator (E-filter)

In the Netherlands glass industry (2005 situation), 4 furnaces are equipped with a system for injection of hydrated lime (Ca(OH)₂) in dry form to absorb HF, SO₃ and part of the HCl and SO₂ content of the flue gases. A special quality hydrated lime, with high BET (reactive surface) is used. Temperatures of the flue gases are quenched, by addition of diluting air, to a level of about 200 °C. The scrubber is a tower or a small compartment

where powder is injected in the flue gas stream. The flue gas plus absorbing powder, injected and distributed in the flue gas, both flow into the bag filter, consisting of fabric filter modules (often Teflon based fabrics) [9]. A filter cake is deposited on the fabric surfaces and reaction between flue gas components and injected powder continues in the filter cake layer (residence time \ll 1 second). A flue gas fan is required to compensate for the pressure drop over the filter and filter cake. The filter cake is periodically removed from the bag filter / fabric and the modules can separately be cleaned by pressurized air. The collected filter cake is partly recycled in the scrubber, or in the glass furnace. In case of high levels of absorbent injection, not all filter dust can be recycled and has to be disposed.

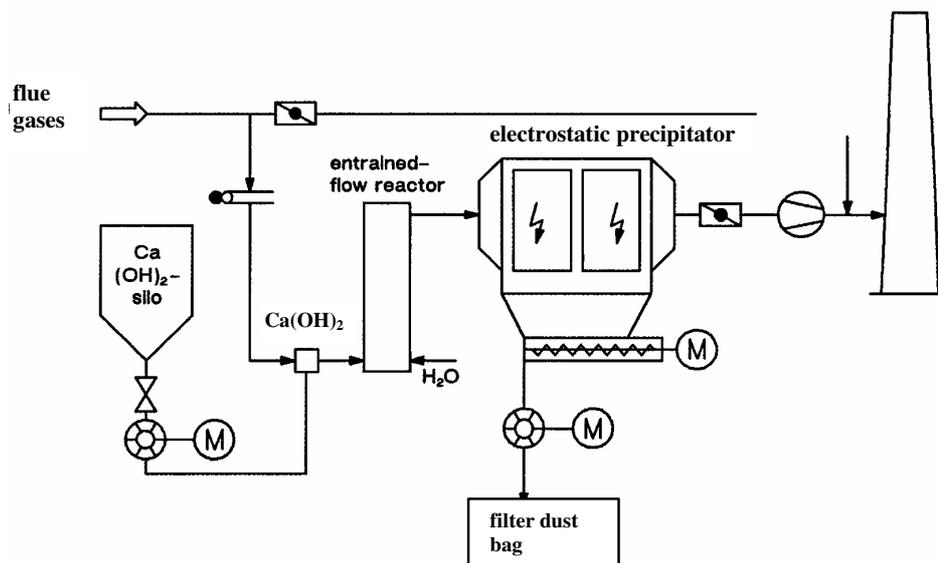


Figure I.4 Schematic drawing of a dry-scrubber plus electrostatic precipitator system (in several Dutch glass furnace situations, instead of an electrostatic precipitator, extra flue gas cooling in combination with a bag filter has been applied)

The lime or hydrated lime particles will react with HF (CaF₂ formation), SO₃ (CaSO₄ results in gypsum) formation and to less extent with HCl (CaCl₂) and SO₂ (CaSO₃ that can further oxidize into CaSO₄). Exact figures about the efficiency of SO_x removal are not known and depend on many parameters:

- kind of scrubbing system (filter cake, fluid bed, wet scrubber, dry scrubber, semi-dry scrubber, ionizing wet scrubber, filter bed, etcetera);
- temperature of scrubber and injection point of absorbing material;
- residence time of powder in flue gas;
- distribution of powder in flue gas stream;
- amount of injected absorbent per Nm^3 flue gas or molar ratio of absorbing medium versus SO_2 (or HCl , HF , SO_3 , boron gases) in non-cleaned gas;
- presence of HF and SO_3 in flue gas;
- type of absorbing material.

The estimated SO_x absorption by dry-scrubbing based on hydrated lime is expected to be about 15-30 % of the initial SO_x concentration in the flue gas and depends on many parameters. The residual dust in the flue gases downstream the bagfilter is in the range of 0.5-2 mg/Nm^3 .

Two glass furnaces in the Netherlands are equipped with a scrubbing unit, and downstream of the injection of $\text{Ca}(\text{OH})_2$ in combination with a reaction tower (to achieve complete mixing of the absorbing medium in the flue gas and to have sufficient residence time) an electrostatic precipitator (ESP), see figure I.4 is installed in order to collect the secondary and primary dust. The temperature in the reaction tower is typically just above 350 °C. The absorbing medium is injected for emission reduction (sometimes the optimum absorption agent for HF emission reduction is chosen), but also to reduce the acidity of the flue gases and sulfuric acid formation that may damage the ESP. The residence time of the flue gases in the reaction tower is about 15 to 20 seconds.

The ESP operates at temperature levels between 300-400 °C (above 400 °C, the steel can be attacked by chlorides, below 200 °C, corrosion by condensation of acids may occur). The residual dust emissions, measured are in the range of 3-20 mg/Nm^3 . The SO_2 emission reduction is about 15-30 %.

The filter dust contains sodium sulfate, calcium sulfate, calcium fluorides and few metals.

One furnace applied a scrubbing tower, using reactive sodium bicarbonate (NaHCO_3) powder as absorbing medium. Downstream this tower (residence time 15-20 seconds)

operating at about 250 °C an ESP is applied. The SO_x emission reduction is much more efficient compared to the situation of Ca(OH)₂ dry scrubbing. About 60 % of the SO₂ is removed from the flue gas. The particulate emissions are about 10-20 mg/Nm³. The particulates are mainly sodium sulfate.

Another glass furnace applies injection of a soda solution at a flue gas temperature level of 200 °C. The flue gases are quenched by ambient air and water to achieve this temperature (a flue gas – steam heat exchanger is used to decrease the flue gas temperature from 550 °C down to temperatures of about 300 °C and to produce steam).

The droplets of injected sodium carbonate solution will be dried in the flue gas and simultaneously react with flue gas components such as HCl, HF, SO₃, SO₂ and SeO₂ (if present). The estimated contact time between flue gas and aspirated soda solution is 10 to 15 seconds. Downstream the reaction unit, the flue gases with the primary dust particles plus the scrubbing reaction product and the non-reacted soda are filtered by a bag filter with high temperature resistant (180-220 °C) based fabric modules. The SO₂ removal efficiency depends strongly on the amount of injected soda solution per mass of SO₂ in the original flue gas. In this case, 50-60 % of the SO_x in the uncleaned flue gas is removed. A very high efficiency by addition of a larger quantity of soda-solution results in the collection of a much larger amount of filter dust. This filter dust contains also NaCl. This NaCl is very volatile in the glass furnace and attacks refractory materials (combustion space, regenerator refractory bricks), the filter dust is present in the form of a very fine powder prone to carry-over in the furnace when mixing this filter dust into the raw material batch. The recycling of filter dust into the raw material batch charged to the glass furnace is not always possible, because of corrosion problems and glass melt operation problems and has to be disposed or has to be treated externally. Thus, in that case a high SO₂ removal efficiency will cause high disposal costs and disposal problems. The dust contains sodium sulfate, sodium sulfite, sodium chloride, sodium fluorides, soda and some metals. The residual dust emission downstream the bag filter is in the order of 1 mg/Nm³.

Two glass furnaces, apply a system developed by the glass company themselves. Detailed information is restricted, because of confidentially reasons. The scrubbing is based on a

full wet scrubbing principle using water and limestone suspensions to cool the flue gases far below 100 °C and to absorb SO_x, boric components and HF from the flue gases. The water/suspension is separated from the flue gases by a special system. The efficiency for SO_x removal is more than 98 %. About 800 to 900 tons (based on dry mass) sewage sludge residue is produced per furnace per year. This residue has to be disposed and cannot be recycled in the batch.

There are 7 furnaces equipped with filters (6 ESP and 1 bag filter), but no scrubbing. The dust emissions are generally reduced down to less than 10 mg/Nm³ but the SO_x emissions are hardly affected by the application of only filters (without scrubbers).

There are 5 all-oxygen fired glass furnaces in operation in the Netherlands glass industry. One of these is equipped with a full-wet scrubber, another oxygen-fired furnace applies dry scrubber (Ca(OH)₂) in combination with a bag filter system and 3 oxy-fired glass furnaces are (still) not equipped with scrubbing units or filters.

In the Netherlands anno 2005, 7 glass furnaces, most of them producing less than 30-40 tons glass per day do not apply any APC.

Figure I.5 shows the total SO₂ emission by the Dutch glass industry since 1992.

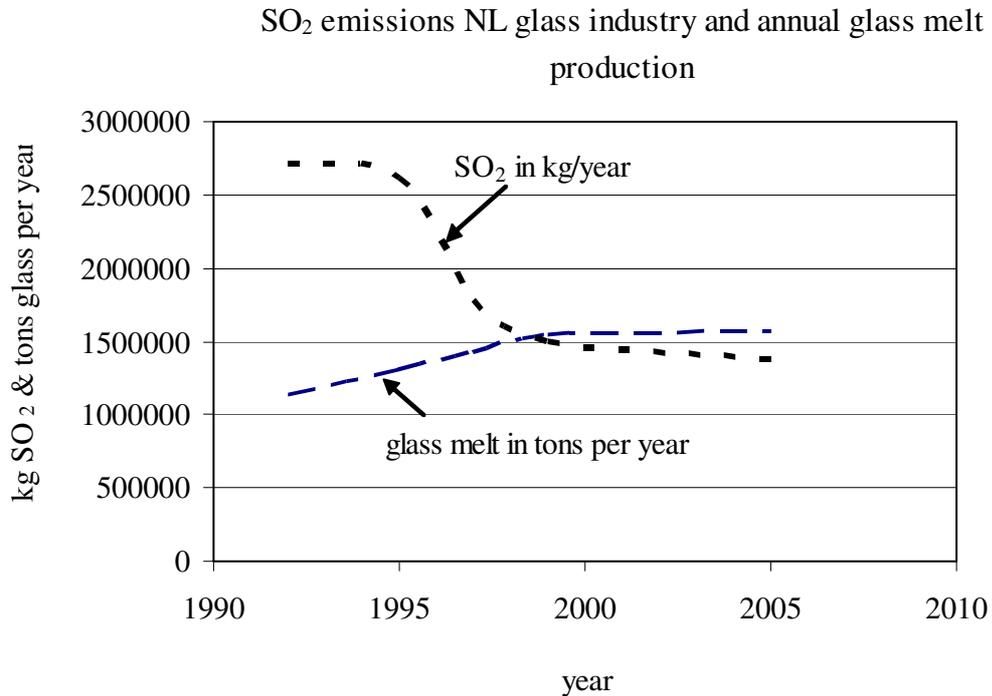


Figure I.5 Total SO₂ emission by the glass furnaces of the Dutch glass industry in the period 1992-2005 and the development of the production volume (molten glass)

The reduction of SO_x emissions in the period 1994-1999 is clearly shown. In this time period, few furnaces converted from fuel oil to natural gas combustion and 3 large furnaces installed scrubbers. The reduction from 1999 to 2005 is caused by 5 additional dry scrubbers plus two wet scrubbers. However, SO₂ removal efficiencies of the applied dry Ca(OH)₂ scrubbers are rather low (15-30 %).

The average estimated SO₂ removal efficiency in the Dutch glass industry:

- Dry scrubber based on Ca(OH)₂ : 22-23% (depends on amount of Ca(OH)₂ injection and temperature)
- Dry scrubber based on NaHCO₃: 55-60% (depends on amount NaHCO₃)
- Semi-wet based on soda-solution: 45-60 % (depends on amount soda)
- Wet scrubber based on lime suspension: > 99.5 % (company owned technology not available on market)

I.5. Conclusions

The total emissions of the glass industry (container glass, flat glass, tableware, fiber, insulation wool, lighting glass) have been decreased by more than 50 % in the period 1992-2005.

The SO_x emissions in 2005/2006 are 1380 tons SO₂/year and in 1992 this was 2710 tons despite the production growth from 1.14 million tons molten glass in 1992 up to 1.57 million tons glass melt in 2005. The specific SO_x emissions expressed in kg/ton molten glass reduced by 60%.

The total SO_x emission in the Netherlands (2002 figures) are 67 kton (expressed as SO₂), assuming in 2005 about the same level, the glass industry contributes 2.1 % to these national SO_x emissions.

About 800 tons SO_x emission reduction in the glass industry is achieved by a conversion from fuel-oil to natural gas firing on several glass furnaces in this period: 1992-2005. In 1992, 6 furnaces applied oil as main fuel. In 2005 one furnace partly uses fuel oil, which appears to be still necessary, because of the required process conditions for that particular case.

About 600 tons SO₂ emission reduction has been realized by application of scrubbers. This emission reduction, has lead to about 4100 tons filter dust to be removed or disposed per year.

A few hundred tons of SO_x emission reduction is probably caused by minimizing the addition of sodium sulfates in the batch.

The actual realized SO_x scrubbing efficiency for dry scrubbers based on Ca(OH)₂ injection in the flue gases is between 15-30 % for the molar ratios of absorbing agents used, the efficiency of the SO_x removal depends strongly on the amount of injected absorption agent. Semi-wet, wet or systems based on sodium bicarbonate show SO_x removal efficiencies of 45-60 % and more. An increase of the supply of absorption agent to the scrubbers will improve the removal efficiency, but the extra SO_x removal will not be proportional anymore (the removal efficiency curve as function of absorption agent quantity will start to become less steep above a certain addition level) with the extra added amount absorption agent and the amounts of generated filter dust residues will increase.

The choice of the installed system and applied absorption agent depends on many factors. For instance in some cases, the pollutant of primary concern was HF and therefore an effective scrubbing system for this gas species was applied. Lime based scrubbers are very effective for HF removal from flue gases, but dry lime-based scrubbers appear to be less effective for SO_x emission reduction compared to soda / sodium bicarbonate absorption agents. Depending on the main pollutants of concern, and the emission level to be reduced for a certain pollutant, according to the NER [13] a certain type of air pollution control system was selected in the past. In some cases the focus was on NO_x (oxygen firing, LowNO_x combustion) and in some other cases on dust or HF or HF or SO_x or a combination. The NER [13-bijzondere regeling productie van glas] for the glass industry offered the possibility to address in a first stage the NO_x abatement or at first dust/SO_x emission reduction. Therefore the chosen technology might not always be the most optimum method for SO_x abatement only. When selecting a certain air pollution control system and scrubbing agent, factors such as filter dust recycle possibilities, or other emissions (NO_x, HF, HCl, etcetera) to be reduced have to be taken into account as well.

The SO₂ emissions of a glass furnace not only depend on the type of fuel and type of glass but on many other factors (see table 2), such as glass quality demand, glass color, amount of types of recycled glass used and furnace type.

In 2005, 4 of the 25 furnaces contribute to 55 % of the SO_x emissions of the Dutch glass industry. Three of these four furnaces already apply scrubbers, but the quantity of the injected absorbing reactant is chosen to limit the generation of filter dust residue that cannot be recycled. Further SO_x emission reduction would require increasing overdoses of absorbing reagents.

Primary NO_x emission reduction by LowNO_x combustion process, by improved combustion control and by oxy-fuel firing showed a decrease of the specific NO_x emission levels from more than 5 kg NO_x per ton molten glass down to 1.87 kg/ton. Cross media/integral effect: Further reduction of NO_x emissions by combustion measures often will increase particulate and SO_x emissions, because lower oxygen contents in the

combustion atmosphere will lower NO_x formation but promotes sulfate decomposition in the batch. Secondary NO_x reduction is often associated with extra energy consumption or its application is limited (in case of SCR) in combination with high efficient dust filtration.

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Annexes part I

Annex I.1 Questionnaire per furnace for inventory SOx emissions glass industry

Questionnaire rookgasemissies per glasoven (SOx = SO ₂ +SO ₃)		Studie INFOMIL 2006	
gele velden 'verplicht' invullen			
Naam glasoven			
Soort glas en kleur			
Jaarlijkse productie		ton gesmolten glas	
Gem. scherven %		%	
Jaartal gegevens		bij voorkeur 2005	
Brandstofsoort		stookolie, aardgas, anders	
Zwavelgehalte olie (gemiddeld)		gew. %	
Jaarverbruik zwavelhoudende olie		ton	
SO ₃ in totaal in gemeng per ton glas		kg	
Verwachte productie oven 2006		ton gesmolten glas	
Verwachte productie oven 2008		ton gesmolten glas	
Verwachte productie oven 2010		ton gesmolten glas	
Installatiejaar scrubber			
Ruw rookgas (voor rookgasreiniger)			
SO ₂ voor rookgasreiniging		mg/sm _n ³	(273.15 K, 1013 mbar, 8 % O ₂ , droog)
stof voor rookgasreiniging		mg/sm _n ³	(273.15 K, 1013 mbar, 8 % O ₂ , droog)
NOx voor rookgasreiniging		mg/sm _n ³	(als NO ₂ : 273.15 K, 1013 mbar, 8 % O ₂ , droog)
Gereinigd rookgas (voor rookgasreiniger)			
SO ₂ na rookgasreiniging		mg/sm _n ³	(273.15 K, 1013 mbar, 8 % O ₂ , droog)
stof na rookgasreiniging		mg/sm _n ³	(273.15 K, 1013 mbar, 8 % O ₂ , droog)
NOx na rookgasreiniging		mg/sm _n ³	(als NO ₂ : 273.15 K, 1013 mbar, 8 % O ₂ , droog)
SO ₂ na rookgasreiniging		kg/ton glassmelt	
stof na rookgasreiniging		kg/ton glassmelt	
NOx na rookgasreiniging		kg/ton glassmelt	
Type rookgasreiniger			
jaar van opstart scrubber (plus eventueel filter)			Euro
scrubbertype		volledig droog, nat, semi-droog (droog filterstof)	Euro
scrubber additief		soda, soda-oplossing, natriumbicarbonaat, Ca(OH) ₂ , kalksuspensie etc.	Euro
temperatuur scrubber		°C	Euro
gemiddelde verblijftijd rookgas in scrubber		geschat in secondes	
filtertype		EP, doekfilter, anders...	Euro
			Euro
jaarverbruik Ca(OH) ₂		kg	
jaarverbruik scrubber Na ₂ CO ₃		kg	
jaarverbruik scrubber NaHCO ₃		kg	
jaarverbruik kalk		kg	
kosten scrubber (investering)		Euro	
kosten filter (investering, incl. leidingen)		Euro	
kosten rookgasmetingen (continu monitor)		Euro	
kosten per jaar voor onderhoud installatie (scrubber)		Euro	
kosten per jaar voor onderhoud installatie (filter)		Euro	
electriciteitsverbruik filter plus scrubber		kW	

Annex I.2 Sources of glass furnace emissions (see also literature reference 2)

Sulfur oxides (SO_x)

The most important causes of SO₂ emissions of glass melting furnaces are:

1). Sulfur in the fuels: fuel oils may contain up to 3 mass-% sulfur. In the Netherlands the glass industry uses only fuel-oils with less than 1 mass-% sulfur. The fuel oil consumption in the glass industry in the Netherlands decreased drastically. For firing of glass furnaces, mainly natural gas is used (> 95 %) in the glass industry in the Netherlands today.

2). Sulfates are used as so-called fining agents. The most important fining agent is sodium sulfate added to the batch (batch: the mix of raw materials charged to the furnaces).

Sodium sulfate dissolves in the molten glass and starts to decompose at high temperatures at which the glass melt viscosity is relatively low (10-100 Pas). The reaction:



produces the fining gases SO₂ and O₂. Especially the generated SO₂ gas diffuses from the molten glass into small bubbles. The absorption of SO₂ (and O₂) by the small bubbles consequently leads to bubble growth. Bubble ascension (buoyancy) rates in viscous melts are proportional to the square of the bubble diameter. Thus, the decomposition of sulfates in the melt and consequently bubble growth results in faster ascension of the originally fine bubbles to the surface of the melt. The surface bubbles will collapse and will emit the bubble gases into the furnace atmosphere: e.g. SO₂.

In case of reducing atmospheres (such as flames touching the surface of the glass melt or touching the freshly charges batch), sodium sulfate can decompose at the batch or glass melt surfaces, even before fining takes place. In order to compensate for these early sulfate losses, extra sodium sulfate may be required to ensure complete fining

(complete removal of bubbles from the glass). The fining process is one of the most essential process steps in glass melting operation. Glass products with bubbles or a certain level of bubbles is not accepted by the market, because of optical or mechanical strength or other reasons (formation of leaks at the mouth of bottles or jars by so-called Line over Finish).

Sulfates are sometimes added as an oxidant (see reaction equation), since it releases apart from SO₂ also O₂. The oxidation state of the glass (melt) is a very important property, determining many other properties such as: color of glass, UV absorption, temperature of fining, reboil sensitivity etcetera.

3). Recycled filter dust. Part of this dust is in sulfate form and acts similar to the sodium sulfate fining agent. The filter dust, however may also contain other components which are not always favorable for the glass quality or for the performance of the melting processes (e.g. NaCl in filter dust leads to refractory corrosion and furnace damages).

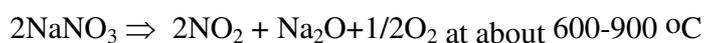
4). Sulfur in the raw materials as impurity. Some batch raw materials may contain sulfur impurities or are sulfur enriched. Sometimes, the impurity level is variable and hardly controllable. Examples of raw materials with sulfur: calumite (purified blast iron furnace slag), colemanite (a boron raw material for E-glass fibers), clays, limestone, recycled cullet, dolomite.

Kircher [4] found that about 4-11 % of the SO_x in the flue gases of glass furnaces consist of SO₃, about 89-96 % is SO₂ gas.

Nitrogen oxides (NO_x)

The main mechanisms of NO_x formation (NO_x represents all nitrogen oxide compounds, the NO_x emission is given in mg/Nm³ or kg/ton molten glass and calculated as NO₂) in glass furnaces are fourfold:

a. Nitrate decomposition (K NO₃ or NaNO₃) in the batch blanket: 600-900 °C



Part of this NO₂ dissociates into: NO + 1/2O₂

In the Netherlands nitrates are used in only a limited number of cases to oxidize the batch, especially when recycling waste glass or scrap fibers with organic coatings in the glass furnace.

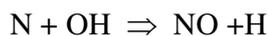
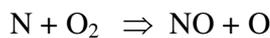
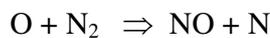
b. Fuel bound nitrogen (mainly HCN- components in oil, coal): nitrogen atoms bonded to organic molecules react with oxygen, forming NO_x

c. Prompt NO_x near flame zone (very rapid):

PROMPT NO_x is produced by the breakdown of CH portions of methane and other hydrocarbons in the fuel and their rapid subsequent combination with nitrogen in the air. Hydrocarbon radicals reacting first with molecular N₂, are forming amines & cyano in the flame front. These amines or cyano compounds will further oxidize and can form NO. Prompt NO formation is only important in the first parts of the flame, when hydrocarbon components are still present.

d. Thermal NO_x: according to the Zeldovich mechanism (strongly temperature dependent):

NO_x formation takes place when at same moment and position: O₂, N₂ and high temperature (T > 1700 K) co-exist. The main reactions forming so-called thermal NO:



For the situation of natural gas firing in glass furnaces, especially when using preheated air, mechanism d. (Thermal NO_x) is the dominating mechanism. Thus thermal NO_x is the main source of NO_x emissions in most glass furnaces. Thermal NO_x is promoted by the situation where at the same location in the combustion space at the same time, high temperatures, free nitrogen and free oxygen co-exist. Elimination or reduction of high flame temperatures (fast cooling by high heat transfer rate), a decrease of the oxygen concentration or elimination of nitrogen (oxygen instead of air firing) will drastically lower NO_x formation.

A delayed mixing of air and fuel will lead to combustion in oxygen lean zones and this will lead to soot formation (high carbon species) emitting heat radiation

(especially important in the wavelength range: 800-2500 nm) to the glass melt. Thus, soot formation leads to increased heat transfer by radiation and will also cause a fast cooling of the flame. This will reduce the formation of thermal NO_x.

New glass furnace burners [11] are developed since the eighties, with additional refinements in the nineties to enable reduced mixing between fuel and preheated air. Furnace design modifications have also been applied to allow flames to become longer (as a result of slower mixing rates). Since more than 90 % of the heat transfer from the combustion space to the glass melt takes place by radiation, this method of firing will also improve the glass melt heating process and energy efficiency of glass furnaces.

Thermal NO_x formation is also suppressed by applying only limited air excess. Only about 4-6 % more air, than required for complete combustion, is applied. A small excess of air is still necessary to ensure slightly oxidizing conditions above the batch and melt. Reduced conditions will affect the melt, will increase evaporation (extra dust formation), may damage refractory materials in the combustion chamber or regenerators of the glass furnaces and will enhance sulfate decomposition (increase SO_x emissions), see annex 3.

Particulate (dust)

The main sources of dust are:

1. Evaporation of volatile components from the glass melt [12]. At high temperatures the evaporation products (NaOH, HBO₂, NaCl, KOH, PbO, Pb(OH)₂) from the melt or batch are volatile and gaseous. During cooling of the flue gases containing these volatiles, chemical reactions and condensation may take place. This condensation may lead to formation of sub-micron sized droplets (above the melting temperature of a condensing species) or sub-micron sized particles. The most important example for container and float glass furnaces is the evaporation of NaOH by a reaction of water vapor (product of hydrocarbon combustion) with Na₂O (soda) in the molten glass at the glass melt surface [2, 12].

The evaporated NaOH is entrained in the combustion gases and reacts below 1050-1100 °C (in regenerators or recuperators) with SO_x to form sodium sulfate condensation products:



Very fine droplets of Na₂SO₄ (melting point 884 °C) or fine dust particles (0.03-0.5 micrometer sized) are formed in the cooling flue gases.

In most cases more than 85-90 % of the flue gas dust consists of material originating from evaporation products from batch and melt.

2. Entrainment of fine raw material particles by the combustion gases flowing above the freshly charged batch in the furnace. Often batch wetting is applied to avoid this entrainment. Most of these particles (> 10 micrometers) will be deposited in the flue gas system (top of regenerator or in recuperators). Generally, this 'dust' will hardly contribute to the particulate emissions of glass furnaces.
3. "Decrepitation" of de-composing carbonates such as dolomite. During heating of the batch in glass furnaces, carbonate raw materials may develop a high internal CO₂ pressure that eventually leads to bursting of the raw material grains into many small fragments (micro-explosion). These very fine fragments will be entrained by the combustion gases. Most of this fine material will be deposited in the flue gas system. In most cases, the primary dust consist only for a small part of precipitated dolomite of lime.
4. Fuel-oils contain metals (Na, Ni, V) and ash that can form particulate. But, also this source is minor for total dust emissions compared to the evaporation process (source 1).
5. Secondary dust is dust from caused by injection of absorbents in the flue gases and consists of scrubbing reaction products and non-reacted absorption medium.

Annex I.3 Mutual impact of combustion conditions on SO₂, particulate, NO_x emissions and CO content

Figure A1 shows the results of an experiment with the aim of lowering NO_x emissions by a decrease of the air excess in the combustion process carried out at an industrial container glass furnace in the Netherlands. The furnace is a full-scale end-port fired furnace with regenerators and using Groningen natural gas as fuel. The results are given as concentrations of CO, NO_x, SO₂ and dust in the exhaust gases of the furnace measured at the position before the exhaust gases enter the regenerator (at 1350-1500 °C). Downstream the measuring point the CO is almost completely converted in CO₂. Therefore, the CO emissions in the chimney are very low or nil. The figure shows clearly the decrease of the NO_x emission as the air number is decreased (decreasing O₂ content on X-axis). But below about 0.8 % oxygen in the exhaust gas (5 % excess air), the CO concentration, SO₂ content increases rapidly by further decrease of the air number.

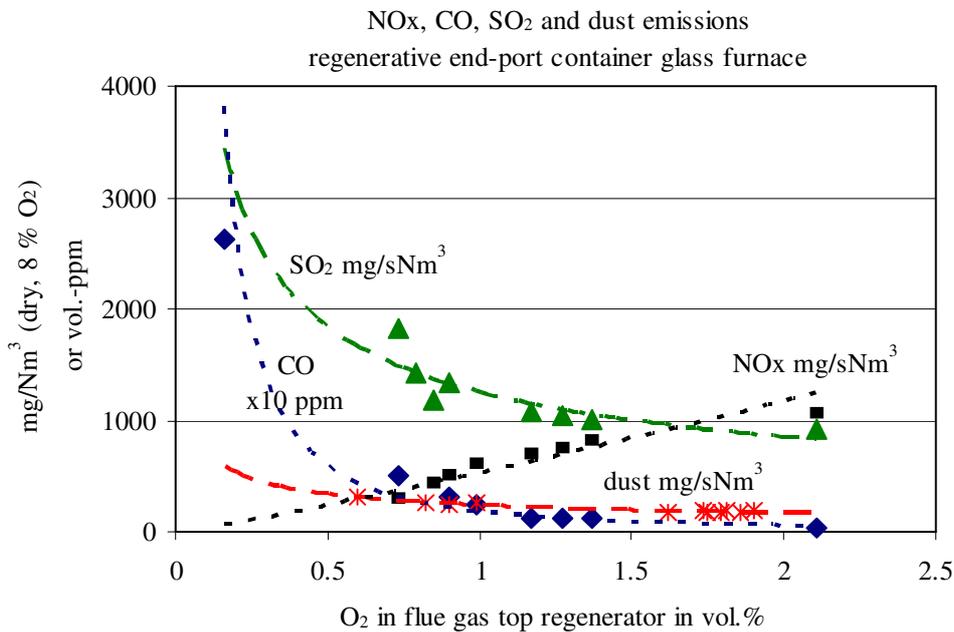


Figure AI.1 Measured concentrations of exhaust gas components in the top of the regenerator of an end-port fired container glass furnace depending on the oxygen content in the exhaust gas (trials with reduction of air number).

The particulate emissions appear to be also dependent on the oxidation state of the furnace atmosphere. Reduced combustion conditions above the glass melt promote the evaporation [see lit. ref. 12] from the melt.

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Summary part II

SO₂ emissions Netherlands glass industry

The Netherlands glass industry emits about 1380 tons SO₂ per year from their glass melting furnaces anno 2005. Almost all furnaces are natural gas fired (92 % of the Netherlands glass melt production is fired with natural gas). About 600 tons/year of SO₂ is already removed by application of scrubbers combined with filters (without scrubbers the total SO₂ emissions in the glass industry in the Netherlands would be about 2000 tons SO₂ per year).

Filter dust waste

An amount of about 4000 tons of secondary waste is generated, that cannot be recycled in the glass melting process. This waste is filter dust or sewage sludge from wet scrubbers. This waste cannot be recycled internally (in glass furnaces), because of several reasons: a). carry-over in the furnace, b). damage to the furnace refractories by carry-over or c).accumulation of components (like alkali vapours) in the flue gases, making flue gases reactive and corrosive, d). handling problems or e). accumulation of certain chemical elements in the furnace system, when recycling filter dust in the glass furnace.

Air Pollution Control Equipment installed

In 2007, about 70 % of the Netherlands glass production is equipped with air pollution control. In the case that all larger (container glass, float glass) furnaces (production levels above 250 tons molten glass per day) in the Netherlands apply scrubbers in 2010, the total emission of SO₂ in 2010 is estimated on 1150 tons per year, taking into account an expected increase of the total glass production of 4-5 % compared to 2005. In that case, more than 90 % of the Dutch glass production is equipped with scrubbers and filters. Most filters are bagfilters and the applied scrubber systems are mostly based on dry scrubbing, but also wet and semi-wet scrubbers and electrostatic precipitators are used in the Netherlands glass industry.

Further SO₂ emission reduction potential

A further reduction down to ±950-1000 tons SO₂ emission per year may be possible by improving the efficiency of the (dry) scrubbers, for instance by using sodium bicarbonate or trona soda instead of hydrated lime or changing to more reactive hydrated lime qualities, probably without increasing the waste disposal.

A further reduction of the SO₂ emissions by increasing the ratio of absorption agent versus the amount of pollutant gas in the flue gases will consequently lead to an increasing amount of filter dust residue to be discharged and this will increase the amount of secondary waste that has to be disposed. The improvement of scrubber efficiency for SO₂ removal (by changing the absorption agent or process conditions) needs further investigations and the effect on HF emissions needs to be studied when changing from lime based absorption agents to other absorbents. The specific SO₂ emissions are on average about 0.55-0.7 kg SO₂/ton molten glass by 2010.

Typical costs for emission reduction

The costs for combined dust and SO₂ removal is about 3 – 4.5 Euro per ton molten glass for dry scrubbers, but these costs can increase considerably to more than 10 Euro per ton for semi-wet or wet scrubbers. Typical costs per kg SO₂ removal is 0.8-1.25 Euro/kg SO₂, but these costs are derived from the costs of combined particulate and SO_x emission reduction: Subtracting from the total costs, the costs for particulate removal with a weighting factor for SO_x of 0.5 compared to a factor 10 for dust removal (1 kg of dust removal is assumed to be 20x relevant than 1 kg SO_x (calculated as SO₂)). For other ratios of weighing factors, calculated SO_x removal costs may change significantly.

Other emission aspects

In the Netherlands, most furnaces are equipped with bag filters operating below 160-190 °C. The application of SCR for these de-dusted flue gases is questionable or needs reheating of the flue gases, because of the relatively low temperature level downstream the bag filters (160-200 °C). SCR (DeNO_x) systems for glass furnaces generally need to operate with flue gas temperatures above 330 °C because of residual SO₂ in the flue gases.

Figures and tables part II:

Figure II.1 Prediction of the development of the total SO_x emissions (given in SO₂) by the Netherlands glass industry in the period 2005-2010, based on estimated production development and use of air pollution control systems

Figure II.2 SO₂ removal from glass furnace flue gas by injection of sodium bicarbonate, caustic soda solution (via quench reactor) and hydrated lime.

Figure II.3 Removal of SO₂ in semi-wet scrubber (180-200 °C) by soda-solution, depending on molar ratio of injected soda and SO₂ in the flue gas of a float glass furnace

Table II. 1 Achievable specific SO₂ emissions of glass furnaces by application of indicated scrubbing method, per type of glass

Table II.2 Efficiency (%) of acid gas removal glass furnaces by Ca(OH)₂

Table II.3 Comparison of DeSO_x methods

Table II.4 Estimated costs for SO₂ and dust removal by different air pollution control methods based on Netherlands figures anno 2005

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ANNEX II.2: Schematic drawings of scrubber plus filter systems applied for air pollution control of glass furnaces, from literature reference 3 (Kircher).

ANNEX II.3: Example calculation of air pollution control costs for dust and SO₂ abatement in flue gases of glass furnaces. Example: glass furnace with 300 tons glass per day

ANNEX II.4: Visiting report REXAM glass factory Lünen Nordrhein Westfalen, Germany

Preface of part II

On the request of InfoMil-SenterNovem and VROM: Ministry of Housing, Spatial Planning and the Environment in the Netherlands, a study on SO_x emissions of glass furnaces in the Netherlands has been performed by TNO in co-operation with the Vereniging van Nederlandse Glasfabrikanten (VNG). The study formally started on 1. December 2006 after a start-meeting with participation of:

- a). representatives of permitting authorities for Dutch glass manufacturers (Provinces of Groningen, Zuid-Holland, Noord-Brabant and Gelderland were represented, in a second meeting, 6. February 2007, also the Province of Limburg was represented)
- b). representatives of a few glass companies (OI-Europe, REXAM Glass and Glaverbel),
- c). representative(s) of VROM,
- d). representatives from InfoMil and
- e). representative from TNO.

The requested study includes two parts:

Part 1: Inventory of current SO₂ emissions by Dutch glass furnaces in 2005 plus historical development (1990-2005) of the specific emissions, and applied SO₂-emission reduction techniques, plus an inventory of the observed bottlenecks in emission reduction until 2005;

Part 2: Potential for further SO₂ emission reduction by the year 2010 in the Dutch glass industry by primary and secondary measures and the associated costs (costs of SO₂ emission reduction per kg SO₂ emission reduced and per ton molten glass) for these air pollution control (APC) measures in the Netherlands.

The results of part 2 are presented in this report. Report 1 [II.1] has been submitted in January 2006 and contains information on the SO_x (expressed as SO₂) emissions in the Netherlands glass industry in 2005, the applied air pollution control systems in this sector and emissions of NO_x, SO_x, dust from 1992 – 2005.

The study is focused on glass melting processes with more than 20 tons molten glass per day (IPPC threshold) and includes the glass furnaces of the following companies:

- OI-Europe: installations for production of container glass in Schiedam, Leerdam and Maastricht;
- Libbey Glass: installations for tableware production in Leerdam;
- REXAM Glass: installations for container glass production in Dongen and Moerdijk;
- Saint Gobain Isover and Vetrotex Benelux: installations for glass wool (insulation) and fleece production in Etten Leur;
- Glaverbel Nederland: installation for float (flat) glass production in Tiel;
- PPG Industries Fibre Glass: installations for fiberglass production in Hoogezand;
- Philips Lighting: installations for lighting glass production in Roosendaal and Winschoten.

This document reports on part II of the study and includes the expected development of the SO_x emissions of the Netherlands glass industry in the period between 2006 and 2010. This expected SO_x emission of the Dutch glass industry, is based on the estimated production levels in this period and installed - or to be installed - air pollution control systems, e.g. scrubbers - and predicted changes in applied fuels.

Chapter II.2 will describe the expected developments. Chapter II.3 gives an overview of existing SO₂ abatement techniques in general. In this chapter, methods already applied in the glass industry and future developments, probably suitable for application at glass furnaces will be described.

Chapter II.4 shows a few technologies or systems used or developed for SO_x-emission reduction in other sectors. In the future these methods may be applicable in the glass industry, probably after some adaptations to these systems, that are developed for the other industrial processes.

Chapter II.5 describes the limitations and problems encountered by the application of scrubbers, the main focus is on the excess of filter dust or scrubbing residue that has to be disposed.

Chapter II.6 gives an overview of the average costs (capital, interest, operational costs) associated with the application of scrubbers and filters to eliminate or reduce SO₂ (often combined with a reduction of HF, HCl, and other acid gas emissions) and dust emissions.

The conclusions and recommendations are presented in chapter II.7. In this last chapter, scenarios are presented for SO_x emission reduction possibilities for the total Netherlands glass industry (emphasis on container and float glass production)..

II.1. Introduction

The objective of this report-part II is:

- a). to show the expected developments in the production volume and SO_x* emissions in the Netherlands glass industry in the period 2005-2010.
- b). to compare different methods of SO_x emission reduction for flue gases of glass furnaces;
- c). to show the problems encountered with SO_x emission reduction and to present, if possible, quantitative information on the problems (e.g. amount of secondary waste, cross media effects).

This second part of the study aims to obtain an estimate of the future course of the SO₂ emissions by the Dutch glass industry, based on current plans of applying SO₂ emission reducing methods between 2005 and 2010 and the potential for further reduction of SO_x emissions, plus the associated costs, expressed in costs per ton molten glass or costs per unit mass of reduced SO₂ emissions.

** Sulfur compounds in the flue gases of glass furnaces are: SO₂ gas, SO₃ gas, sulfuric acid and sulfate dust components. The gaseous part is called SO_x, the total SO_x emission is given as SO₂ and expressed in mg/Nm³ or kg per ton molten glass. In the glass industry the reported emission concentrations are generally based on flue gas volumes at 273 K, 1013 mbar at dry conditions with 8 vol. % O₂.*

II.2. Future SO_x emission trends in the Netherlands glass industry

II.2.1 SO_x emissions in Netherlands glass industry 2005/2006

Since 1992, SO_x emissions in the glass industry in the Netherlands have been reduced from about 2700 tons per year down to 1380 tons per year in 2005, despite the 39 % production increase (see report phase I).

The application of scrubbers*, for about 69 % of the current (2006/2007) glass production in the Netherlands, results in about 600 tons SO₂ emission reduction per year. The largest reduction of SO_x emissions is due to the change from fuel-oil firing to natural gas firing applied for 5 glass furnaces since 1992.

Today (2006/2007), only 1 furnace still applies some fuel-oil, in combination with natural gas firing. After several attempts it appeared that a full conversion to 100 % natural gas firing was impossible in this special case**.

**Several scrubbers apply dry scrubbing methods, based on hydrated lime injection in the flue gases. Hydrated lime, Ca(OH)₂, is often used to absorb HF and SO₃ (to avoid acid corrosion of filter parts) from the flue gases and this scrubbing method is most often applied in the glass industry, especially in Germany.*

***A full conversion to natural gas for this glass melting furnace results in an energy consumption increase of about 5 %. Normally the switch to natural gas leads to a substantial increase in NO_x-emissions (estimated on about 30%) when the furnace design remains unchanged. In the current situation, 100 % gas firing would harm the glass quality and the furnace lifetime, due to increased temperatures (in case of natural gas firing) in the combustion space and reduced heat transfer to the melt. At this moment the furnace is equipped with a semi-dry scrubber with an efficient reduction of the SO₂-emissions.*

There are float glass furnaces completely fired with fuel oil or using only natural gas (but applying other furnace designs), but several float glass furnaces also apply mixed fuel firing.

II.2.2 Factors determining SOx emissions of glass furnaces

See part I, table I.2 of this report and annex II.1 for a detailed overview of factors that determine SOx emissions of glass furnaces. The factors include: sulfur content of fuel, extra sulfate in the batch, required to oxidize the glass (dependent on glass color and fining quality), amounts of recycled glass in batch, types of recycled glass, sulfur contamination/impurities in raw materials and sulfate solubility of the glass.

II.2.3 Prediction of future SOx emission by Netherlands glass industry

In the period 2006-2010, the total glass industry SOx emissions (as well as other emissions) will change, because of the following aspects and developments:

- 1). Increase of expected glass production;
- 2). A few, mainly larger glass furnaces without scrubbers before 2005, will be equipped with scrubbers plus filter systems in this period 2006-2010;
- 3). Optimization of sulfate use in the raw material batch.

In 2005, the number of operating glass furnaces of the VNG (Vereniging van Nederlandse Glasfabrikanten) is 25. It is expected that in 2010 the same number of furnaces will still be in operation. The total melting capacity or the pull of these furnaces, however, is expected to increase slightly. The total melting capacity will increase from 157700 tons in 2005 up to 164000 tons in 2010 (4 % production increase).

In 2005 most, but not all large glass furnaces, with a melting capacity above ± 70000 tons (> 200 tons glass melting per day) molten glass per year are already equipped with a scrubbing device and filter system.

SO₂ emissions glass industry Netherlands 1992 - prognoses 2010

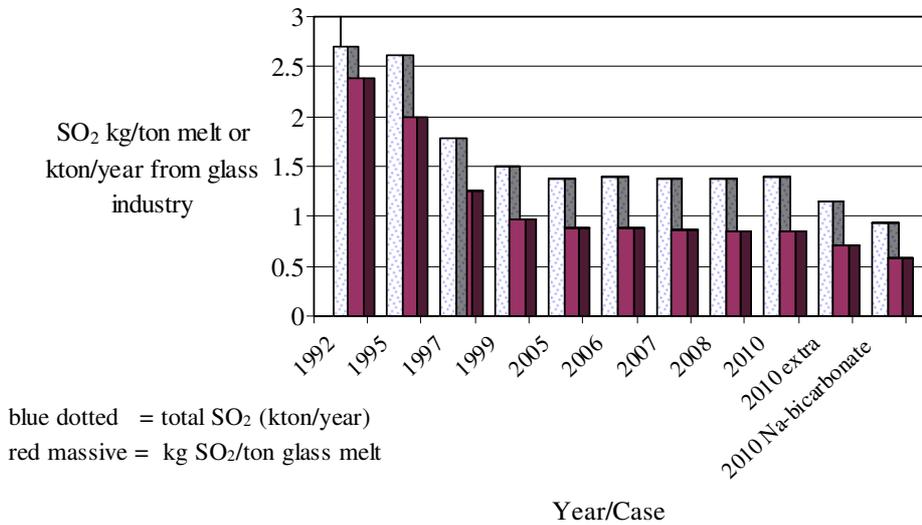


Figure II.1 Prediction of the development of the total SO_x emissions (given in SO₂) by the Netherlands glass industry in the period 2005-2010 based on estimated production development and use of air pollution control systems. 2005-2010 values are given for autonomic development. The case “2010 extra” is given for the case that all large glass furnaces (> 70000 ton/year) being equipped with scrubbers plus filters. “2010 Na-bicarbonate” is the case for most scrubbers based on sodium bicarbonate injection.

In 2006, an additional scrubber and bag filter has been installed for the treatment of the flue gases of one of the large container glass furnaces. This means that 69 % of the Netherlands glass production is equipped with scrubbing and filtering systems by the end of 2006. Figure II.1 shows the expected total-SO_x and dust emissions in the period 2005-2010 according to the predictions, based on production development and the today planned (scheduled) application of air pollution control systems.

Without additional scrubbing, the SO_x emissions will hardly change and still being about 1400 tons (as SO₂) per year or 0.85 kg SO₂ per ton molten glass in 2010. (In 2005: 0.875 kg SO₂/ton molten glass).

In figure II.1, the SO_x emissions and dust emissions are also presented for a case (data for “2010-extra”), that all large glass furnaces (> 70 kton glass production per year) operate a scrubber plus filter, this would represent 92 % of the Netherlands glass production in 2010 and would include all container and float glass production. In that case the total annual SO₂ emissions of the Netherlands glass industry would reach a level of about 1150 tons (0.71 kg SO₂/ton glass melt). But in this case, the amount of filter dusts or sewage sludge to be disposed may increase up to more than 6000 tons/year. A further improvement may be achieved by replacing in the dry scrubbers, the Ca(OH)₂ by sodium bicarbonate or by more reactive hydrated lime qualities (if possible): this may result in a maximum of 950 -1000 tons SO₂ per year (0.58 kg SO₂/ton glass melt).

The SO_x emissions would only drop to about 1150 tons/year (0.71 kg/ton molten glass) in the case that all large glass furnaces are equipped with scrubbers. Most scrubbers are dry-scrubbers using hydrated lime powder (Ca(OH)₂), but one semi-wet scrubber (soda solution), two wet scrubbers (lime-suspension) and a dry scrubber based on sodium bicarbonate injection are installed as well.

A further reduction, without major changes of the existing hardware, is only possible by using larger amounts of absorption agent (soda, sodium bicarbonate, Ca(OH)₂, lime) or changing the type of absorption agent to increase the absorption levels of SO_x by more effective types of (hydrated) lime or soda, raw trona or sodium bicarbonates. Some modifications or additional equipment might be necessary when changing the absorption agent, such as a mill to grind coarse sodium bicarbonate agglomerates before injecting this agent into the flue gases. When converting to another absorption agent, the changed properties such as rheology of the powder have to be taken into account (some absorption agents are very hygroscopic).

An increase of the addition of the absorption agents to the flue gas, however would increase the residue from the filter to be disposed. In 2005, about 4100 tons of filter dust had to be disposed. For the case of 2010 it would be about 4250 tons and for “2010-extra”: 6000 tons.

A significant extra reduction of SO_x emissions by the injection of additional absorption reactants will increase the amount of secondary waste material to be disposed to much more than 6000 tons per year.

An example: In case of a reduction, from 1380 down to a total of 1150 tons SO₂ per year in the Netherlands glass industry (< 0.7 kg/ton molten glass), by an increase of the amount of dry Ca(OH)₂ injection, leads to an increase from 4200 tons to about 6000 tons filter dust residue per year. Thus, about 1800 tons more calcium sulfate/sodium sulfate containing filter dust would be produced in order to lower the SO_x emissions by about 230 tons/year.

The application of sodium bicarbonate (or a more efficient hydrated lime quality) probably will result in lower SO_x emissions (< 1000 tons/year) and then, the estimated amounts of filter dust residues are between 3200 and 4400 tons per year, depending on the possibility of internal filter dust recycling (depends on filter dust characteristics and sulfur balance).

II.2.4 Conclusions: predicted SO_x emission reduction potential Netherlands glass industry

Dry and semi-dry scrubbers are BAT and have been successfully applied in the Netherlands glass industry, but create secondary waste. This waste material can only partly be recycled in the glass forming batch, due to accumulation problems in green glass furnaces and carry-over problems associated with fine filter dusts.

According to the estimated glass production figures for the period 2005-2010 and scheduled scrubbers to be installed, the total SO_x emissions will hardly change in the Netherlands glass industry. A decrease to levels below 1200 tons SO₂/year by increasing use of hydrated lime would lead to a fast increasing amount of secondary waste (filter dust residue) that cannot be recycled and has to be disposed. However, some improvements may be achieved by changing the absorption agents from a less reactive

(lime based) material to much more reactive media, such as a more reactive $\text{Ca}(\text{OH})_2$ quality or sodium bicarbonate or raw trona. The extra costs for disposal and to purchase the absorption media (soda, lime, sodium bicarbonate) would be about 1.5 to 2 million EURO/year (for the extra reduction of about 400 tons SO_x /year), assuming that disposal costs in 2010 remain unchanged compared to 2005. Thus, this extra effort to reduce SO_x emission reductions further would cost about 4-5 Euro/kg SO_x removed.

About 350 tons of SO_x emission per year of the Dutch glass industry is caused by the fuel-oil combustion in one glass furnace. A full conversion to natural gas firing would lead to production problems in this furnace and furthermore to approximately 240 tons/year additional NO_x emissions.

The following table shows the achievable maximum SO_x emissions for container and float glass furnaces and the methods that can be applied.

Table II.1

*Achievable specific SO_2 emissions of glass furnaces by application of indicated scrubbing method, per type of glass**

Table 1 Achievable SO_x emissions in kg/ton molten glass									
Glass type	without APC	Fuel	APC	downstream APC	estimated				
	kg/ton			kg/ton	potential lowest emission/year ton/year (2010 production)				
Tableware, soda-lime-silica	0.85	nat. gas	no scrubber	0.85	35				
Flint container glass	1	nat. gas	dry scrubber - reactive $\text{Ca}(\text{OH})_2^*$ / NaHCO_3	0.5	250				not all filter dust can be recycled
Ultra white flint	1.5	nat. gas	dry scrubber - reactive $\text{Ca}(\text{OH})_2^*$ / NaHCO_3	0.65	80				not all filter dust can be recycled
Green container glass	1	nat. gas	dry scrubber - reactive $\text{Ca}(\text{OH})_2^*$ / NaHCO_3	0.5-0.8***	180				not all filter dust can be recycled
Amber container glass	1	nat. gas	dry scrubber - reactive $\text{Ca}(\text{OH})_2^*$ / NaHCO_3	0.5-0.6	105				
Float glass	4	nat. gas & fuel oil	semi-dry scrubber	1.5-2.5**	300 - 450				not all filter dust can be recycled
Glass wool	<0.1	nat. gas	no scrubber	<0.1	5				
Glass fiber	0.6	nat. gas	wet scrubber	<0.2	15				filter residue cannot be recycled
Special soda-lime-silica glass	0.6	nat. gas	dry scrubber - reactive $\text{Ca}(\text{OH})_2^*$ / NaHCO_3	0.3	5				
Total					950-1100				
*reactive $\text{Ca}(\text{OH})_2$ with BET > 40 m ² BET/m ²									
** depends on amount of filter residue that can be disposed									
*** depends on net input of SO_3 via cullet (mixed cullet)									
BREF-BAT (2001)									
kg SO_2 /ton glass	oil-filter dust minimalisation	oil- SO_2 minimalisation	gas-filter dust minimalisation	gas- SO_2 minimalisation					
Flat glass	3.75	1.25-3	2	0.5-1.25					
Container glass	2.25	0.75-1.8	1.2	0.3-0.75					
Tableware		1.25-3		0.5-1.25					

**The estimated potential lowest SO_2 emissions indicated in this table have to be verified with tests*

II.3. End-of-pipe SO_x emission reduction methods applicable in the glass industry

This chapter describes the different methods currently applied in the glass industry, in and outside the Netherlands, to eliminate or reduce the SO_x concentrations in the flue gases exhausted from glass furnaces. For each method the costs associated with the SO_x emission reduction are estimated and the reduction potential of each method will be presented. In most cases, the reduction of SO_x emissions by secondary measures (end-of-pipe) will generate filter dust or scrubbing waste water or sludge. Only a part of this collected secondary waste can be recycled as a raw material in the glass melting process. For each method the problems of secondary waste generation are discussed. The possibility of filter dust recycling depends on the type of fuel (sulfur content in fuel) and sulfur solubility of the glass and of course the characteristics / chemical composition of the filter dust. Dusting of filter dust (carry-over) in the furnace or accumulation of sulfur oxides or chlorides (in the form of NaCl vapour) in the flue gas system may respectively reduce the furnace lifetime or refractory lifetime and can limit the reduction of residual SO_x emissions, when re-cycling this dust in the batch.

II.3.1 Scrubbing technologies in general

Almost all methods for SO_x emission abatement are based on so called acid gas scrubbing technologies [II.2]. These technologies often involve multi-phase reactions (gas-liquid, gas-solid or gas-liquid-solid). Phase transitions (liquid to solid) may occur during scrubbing, for instance in the quasi-dry (semi-dry) scrubbers where a solution or suspension is injected in the flue gas flow, the droplets are dried in the hot gases and simultaneously absorb the acid gases (SO₃, SO₂, HCl, HF, HBO₂, H₃BO₃) from the flue gases. The reaction kinetics itself between absorbing agent and the acid compounds of the flue gases is fast (reaction is fast when absorbing agent and acid gas make direct contact), but the overall conversion rates are mass transfer limited. This means that the rate of absorption of the acid gases depends on the mixing of the absorbing agent into the gas stream or the diffusion of the acid into the grains or grain pores of the absorbing medium. At the surface of the reacting grains (in dry and quasi-dry scrubbers) a layer of reaction product can be formed. This layer will limit or block the reaction of the non-reacted core of the grain (limestone, Ca(OH)₂ or soda for instance) with the acid gas species. The

effective reaction rate depends on the mass transfer to and into the grains or droplets and reactive surface areas (BET values) of the powder particles. In most scrubbers, the available reaction time is in the order of a few seconds. The most important parameters that determine the absorption efficiency or SO_x removal efficiency are:

- Type of scrubber: wet, quasi-dry or dry scrubber, the type of scrubber has a large effect on the mass transfer. The packing of the scrubber that may improve the contact between gas phase and absorbing agent is also important;
- Composition of flue gas, competitive reactions may occur with HCl, HF or boric acids;
- Available reaction time (volume of scrubber and volume flow of flue gas);
- Temperature: the temperature should be as close as possible (just above) to the dew point of the flue gas in a dry scrubber system to improve the absorption rate or on the other hand side this temperature should be much higher. The intermediate temperature range of 180-350 °C seems to be less suitable for dry SO₂-absorption by hydrated lime;
- Molar amount of absorption agents compared to molar amount of acid gas to be absorbed, often an over-stoichiometric dosing of absorption agents is applied, but will create a large amount of secondary waste (filter dust);
- Humidity of flue gas;
- The filtration system: a bag filter forms a filter cake at the cloths, this layer contains the deposited absorption agent. Acid gas absorption continues in the filter cake layer on the filter bags. The filter cake layer will cause a pressure drop in the flue gas. This pressure drop has to be compensated by a flue gas fan to obtain sufficient draught and to avoid problems with too high furnace pressure.

The different methods applied in the glass industry can roughly be distinguished by the state of the absorbing medium to be injected and the chemical nature of the absorption agents. The most applied agents are: limestone, hydrated lime powder (Ca(OH)₂) with high BET (reactive surface area), soda, sodium bicarbonate (NaHCO₃) or trona (sesquicarbonate): Na₂CO₃·NaHCO₃·2H₂O.

A very important aspect in the selection of the absorption agent (soda, sodium bicarbonate, limestone or Ca(OH)₂) is the composition of the reaction product. This

reaction product of the scrubber is collected by a filter, or sedimentation process in case of wet scrubbing. The filter dust not only contains the non-reacted absorption agent plus the absorbed sulfites or sulfates, but also the primary dust and absorbed fluorides and chlorides. Especially, in case of soda or sodium bicarbonate based absorption agents, chlorides are formed, because sodium reacts with HCl to form NaCl dust. In case of filter dust recycling in the glass forming batch, part of the recycled NaCl (NaCl is rather volatile in the glass furnace) will evaporate again. Chlorides are present in raw materials such as dolomite, limestone, cullet, but especially in the filter dust and (synthetic) soda. Recycling of chloride rich filter dusts will increase the NaCl evaporation and NaCl-vapor concentrations in the furnace atmosphere and exhaust gases. Since, this chloride is partly captured by the scrubber and filter and re-introduced in the batch, an accumulation of NaCl in the glass furnace system takes place, because of new chlorides entering the furnace by the other raw materials, and consequently the sodium vapor pressures (Na+NaOH+NaCl) in the furnace atmosphere will increase due to this filter dust recycling. High vapor pressures of sodium species in the furnace atmosphere leads to chemical attack of silicate refractories in the furnace [23] or regenerator. In the case of soda-based scrubbers with high chloride absorption efficiency, this accumulation of sodium chloride and increase of sodium vapor pressures (NaCl vapor) will present a risk of severe attack of the regenerators. The choice of soda (or sodium bicarbonate) based absorption agents, mainly to improve SO_x absorption and removal, compared to lime based absorption media, may consequently jeopardize the possibility of filter dust recycling.

For the different air pollution control processes, the total costs are calculated and include writing-off of the capital costs (scrubber, filter, ducts, electricity supply, monitors for flue gas analysis, foundation), interest costs, operational costs such as: maintenance, renewals, repair, energy, absorption agents, disposal costs. These total costs have to be made to remove (primary) dust and SO_x from the flue gases. The NER (Nederlandse Emissie Richtlijnen) gives a method to relate these costs to the costs per kg removed pollutant (particulates or SO₂), using a weighing factor for dust of 10 and SO₂ of 0.5. See chapter 6.

The three most applied systems (sections: 3.1-3.3) are, see also the annex 2 of this report:

II.3.2 Dry scrubbers [references: II.2-II.8]:

The absorption medium is injected as a powder into the flue gases upstream of a filter unit. The filter: a bag filter system or Electro-Static Precipitator (ESP) will separate most of the dust particles (particulates) from the flue gases. These particulates are the primary dust particles* already present in the flue gas before entering the scrubber, plus the un-reacted absorption agent and the reaction product of the scrubber.

II.3.2.1. Description of method of scrubbing

Acid gas removal by dry scrubbing requires multi-phase mass transfer, it occurs between the gas phase and the solid phase, rather than between the gas phase and the liquid plus solid phases, as with wet and semi-dry scrubbing. The acid gas must first contact the solid surface of the dry alkaline material rather than being *absorbed* (dissolved) in a scrubbing liquid or slurry. Once the acid gas contacts the alkaline surface it is neutralized to form a solid salt that can remain as part of the solid alkaline material particles or will be “popped off” as fine dust (reaction products) as a result of gas evolution from the absorption agent (water or CO₂ evolves from carbonates or hydroxides). This fine dust or the solid particle alkaline material has to be separated from the flue gases by efficient filtering systems. Chemically, the conditions in dry scrubbers present less ideal neutralization reaction conditions than in wet or semi-dry scrubbers, since one reactant is in the gas phase and the other is in the solid phase. Mass transfer is rather poor and needs extra residence time or over-stoichiometric injection of absorption agent to obtain high SO₂-absorption rates.

**primary dust: dust particles caused by carry-over (dust formation in furnace by fine raw materials exposed to gas flows in the furnace or due to decipitation of carbonates) and evaporation from the melt or batch. These vapor products in the furnace will form solid condensation products (fine dust) during the flue gas cooling process.*

Secondary dust: reaction products from scrubber or non-reacted scrubbing agents.

Decipitation: Bursting of grains by an increasing internal pressure, due to decomposition of carbonates (limestone and dolomite show decipitation).

As a result, dry scrubbers usually require the greatest stoichiometric excess (this produces large amounts of filter dust) of alkaline or earth alkali material to achieve high acid removal efficiencies.

II.3.2.2. Scrubbing agents for dry scrubbers

Dry injection systems can employ either calcium or sodium alkaline materials for neutralizing acid gases. With a calcium based system, dry hydrated lime (Ca(OH)_2) is directly injected. The overall neutralization reactions are essentially the same as those for the semi-dry scrubber:

$\text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$ (further oxidation of CaSO_3 into CaSO_4 may take place to form gypsum).

Sulfites in the filter dust can have a reducing effect on the batch and glass when this filter dust is collected and recycled in the glass furnace. Lime based absorbing agents are mainly used for HF absorption or SO_3 removal, but soda based absorption agents are more effective to remove SO_2 and HCl.

For the soda-sorbent based systems, the neutralization reactions are via sodium carbonate:

$\text{Na}_2\text{CO}_3 + \text{SO}_2$ in air (contains oxygen) $\rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2$

The source of the sodium carbonate can also be synthetic sodium bicarbonate, naturally occurring sodium bicarbonate (nacholite), or naturally occurring sodium sesqui-carbonate (trona). When these materials are injected into a hot (oxidizing) gas stream they react according to the schedule:

$2\text{NaHCO}_3(\text{s}) + \text{O}_2 + \text{heat} \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + 2\text{CO}_2(\text{g})$

$2(\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O})(\text{s}) + \text{heat} \rightarrow 3\text{Na}_2\text{CO}_3(\text{s}) + 5\text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$

These reactions and especially the release of water vapor and CO₂ gas will cause the trona particles to pop-off (like popcorn) and thus these decomposition reactions increase the active surface area of the injected powder grains.

II 3.2.3 Reaction space of dry scrubbers

The reaction chamber can be simply be the gas duct upstream of a particulate capture device (filter) or a mixing chamber designed specifically to achieve a longer contact time and efficient mixing of the reactants. The key system performance factors are turbulent mixing of alkaline powder with hot gas while maximizing the time that the alkaline powder is suspended in the presence of the hot acid gases. There are systems in operation where dry scrubbing has been employed in conjunction with both a hot side and/or cold side ESP for particulate capture. Most studies have been done utilizing a fabric filter, but commercially most large scale soda-based injection systems are combined with ESP's. With an ESP the available acid-base contact time is limited to the time the alkaline powder and gas are in contact between the point of injection and the fields of the ESP. In a system with a dry sorbent or semi-dry injection in combination with a bag filter (fabric filter), unconverted alkaline material in the suspended particulate matter becomes part of the filter cake on the bag filters and provides additional acid-base contact time as the cake accumulates on the bags between cleaning cycles. In some cases, the absorbing agent can even decrease the resistance (less pressure drop) of the filter cake compared to the pressure drop caused by a filter cake of primary dust, improving the APC operation.

II.3.2.4 Application of dry scrubbers in the glass industry

In the glass industry, the majority of glass furnaces that are equipped with Air Pollution Control (APC) systems apply the dry-scrubbing methods in combination with an ESP (this is the most applied combination in the German glass industry [II.3, II.4]) or in combination with a bag filter. In the Netherlands, several furnaces, especially in the container glass sector, apply dry scrubbers. Most of them are based on the injection of a fine (high reactive surface area) Ca(OH)₂ powder into the flue gas stream. The injection

takes place in a reaction tower or in a special system, developed by Lühr [II.5] to contact the powder particles with the flue gas flow and to recycle part of the separated powder (separation by bag filters) after milling/grinding back into the un-cleaned flue gas flow to improve the absorption efficiency (because the powder still contains non-reacted lime hydrate) and to limit the amount of absorption agent to be used. However, the absorption efficiencies for SO₂ are rather low (15-30 %) when using Ca(OH)₂ powder at the prevalent temperature levels in most cases in the Netherlands glass industry. Often, Ca(OH)₂ has been chosen for HF- and SO₃ (H₂SO₄)- removal and to protect the filter against corrosive condensates, instead of selecting the optimum agents for SO₂ or HCl absorption. Increased SO₂-absorption efficiencies have been observed for sodium bicarbonate injection [II.8] or trona-soda injection [II.2].

II.3.2.5 Improving efficiency of dry scrubbers

Especially for expensive absorption agents or high disposal costs it is important to select an agent with a high conversion efficiency. Mazurk [II.2] showed the use of refined (mechanically ground trona) Na₂CO₃·NaHCO₃·2H₂O in dry form to absorb SO₂, for flue gas treatment, according:

1. $2(\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + 2\text{H}_2\text{O}) + 3\text{SO}_2 \rightarrow 3\text{Na}_2\text{SO}_3 + 4\text{CO}_2 + 5\text{H}_2\text{O}$
2. $3\text{Na}_2\text{SO}_3 + 1.5\text{O}_2 \rightarrow 3\text{Na}_2\text{SO}_4$

At 400 °C flue gas temperature and an over-stoichiometric injection (50 % more than stoichiometrically required) of the trona soda, the SO₂ absorption was about 80-85 %. At stoichiometric addition of trona soda, a removal efficiency of about 75-80 % is reported [II.2].

Injection of trona soda upstream of an ESP can also improve the ESP filtration efficiency. The trona particles injected in the flue gas, above at least 135 °C, rapidly start to decompose into soda. The decomposition leads to a kind of popcorn effect and creates a large and reactive surface area of the fine soda particles. The trona is simply injected in dry state into the flue gases and forms such reactive soda particles. First it reacts with SO₂ into sodium sulfite (Na₂SO₃) and subsequently Na₂SO₄. The reaction product slows down (due to pore blockage) the reaction. Therefore it is important to achieve the

popcorn effect (to create large reactive surface areas) by evolution of CO₂ and H₂O from the trona (Na₂CO₃·NaHCO₃·2H₂O) particles.

The particle size is also important, especially when using sub 30-micron-sized trona particles, the SO₂ removal efficiency can be very high (> 80 % depending on temperature and other gas species in the flue gas) even at stoichiometric dosing.

In general it can be concluded that for the removal of SO₂, especially in flue gases with other acid gas species as well, lime (reacts mainly with HF and SO₃) based dry agents are much less effective compared to reactive soda powder such as trona, milled sodium bicarbonate or nacholite. Refined trona (about 100 dollars per ton, excluding transport costs) is relatively cheap compared to sodium bicarbonate, but difficult to purchase in Europe since it is only exploited in the USA.

Kircher [II.3] mentioned the very high absorption efficiencies of dry Ca(OH)₂ injection upstream of an ESP for HF-gas and SO₃, but the absorption of SO₂ by dry Ca(OH)₂ powder was rather poor at these temperatures (< 350 °C). By additional injection of water into the flue gases, the SO₂ absorption can be improved considerably.

In the Netherlands glass industry (container glass), dry hydrated lime injection is applied in combination with bag filters (T = ±200 °C) or in combination with an ESP operating at temperatures between 350-400 °C. In both cases it seems that only about 15-30 % of the SO_x in the flue gases is captured.

II.3.2.6 Filter dust

High SO₂ absorption rates require over-stoichiometric dosing of hydrated lime and consequently leads to a large amount of filter dusts. In several glass furnaces in the Netherlands, this filter dust has been mixed into the raw material batch in the past. But, in some of these cases it appeared that the filter dust is very fine and contains species (such as NaCl) that are volatile and start to accumulate in the exhaust gases. The fine dust is very sensitive for carry-over (dust formation in the glass furnace) when this dust is recycled in the glass furnace.

The primary dust (dust directly from the furnace) in flue gases of container glass furnaces contains mainly sodium sulfate (> 75 %) and small amounts of other compounds (NaCl, K₂SO₄, SiO₂, CaO, MgO, PbO). Secondary dust is the dust formed by the scrubbing system: reaction products and non-reacted absorption agent. In most cases, both dust fractions have to be separated from the flue gas by efficient filtering systems, before the flue gas is released to the environment.

In the German glass industry most of the filter dust seems to be recycled in the glass melting process when SO₂ emissions are only moderately reduced [II.9], in the Netherlands a few glass furnaces also re-melt the filter-dust by recycling it in the batch. But, in the Netherlands few glass furnaces experienced severe problems during filter dust recycling when using chloride rich filter dust or very fine dust or when applying batch preheating (the fine dust is very dry after batch preheating and prone to dusting in the furnace). The reason for the larger problems in the Netherlands, in case of filter dust recycling (internally), compared to the German situation is still not completely clear. In most German cases the reduction of SO_x and chlorides is rather moderate by dry scrubbers and therefore filter dust recycling hardly leads to chloride and sulfur accumulation in the flue gases system as observed in some specific Dutch cases.

The dust (primary and secondary) separated by the filter, when using hydrated lime typically contains 30 to 40 wt % CaO, 25-45 wt.% SO₃ (part of it from the primary dust), 10-25 wt.% Na₂SO₄ (mainly from primary dust), 1-3 wt. % chloride, about 0.5-1 % fluorides and less than 8 % other compounds.

II.3.2.7 Removal efficiencies dry scrubbers

It can be concluded that lime based absorption agents are much more efficient for HF removal from flue gases compared to SO₂ emission reduction. Kircher tested absorption efficiencies for different flue gas species by the addition of hydrated lime into the glass furnace flue gases.

	Efficiency (%) of acid gas removal glass furnaces			
	Dosing of Ca(OH) ₂ (dry) in kg / hr			T in °C
	50 kg/hr	100 kg/hr	150 kg/hr	
SO ₂	15.9	39.4	39.9	350
	24	43.6	54.4	400
SO ₃	80.5	82.5	87.6	350
	73.5	80.1	76.4	400
HF	91.2	95	96.6	350
	89.9	93.3	95.1	400
HCl	26.6	45.2	53.7	350
	58.9	78.7	91.8	400
Se	47.3	79.6	71.4	350
	86.5	93.9	91.5	400

Table II.2 Absorption efficiencies for dry scrubbers using Ca(OH)₂ powder measured by Kircher [II.3]

Table II.2 derived from Kircher [II.3] shows the measured results. The table II.2 shows the excellent removal efficiencies for HF. The SO_x removal efficiency depends on the Ca(OH)₂ dosing, but an increase from 100 to 150 kg/hr hardly changed the SO₂ removal. Such dosing quantities however are probably strongly over-stoichiometric. The removal efficiency for SO₂, Se and HCl improves by an increase in temperature from 350 up to 400 °C. There seems to be a temperature with minimum absorption efficiency. At very low flue gas temperatures and high humidity the absorption efficiency can increase by lowering this temperature close to the flue gas water dew point 60-90 °C [II.6]. This however, is not always recommended, because of the required higher temperatures levels in the chimney (required stack operation temperatures), and a compromise is 140-160 °C. At these temperature levels, SO₂ absorption efficiency is rather low.

II.3.2.8 Experiences with dry scrubbers described in literature and elsewhere

Riepe [II.10] shows that the application of a dry scrubbing system based on lime hydroxide (Ca(OH)₂) in combination with bag filters (equipped with a jet-pulse cleaning system for automatically, from time to time, cleaning of the filter bags) for a glass furnace producing 200 tons container glass per day will cost about 2.82 EURO/ton

molten glass. These costs are based on the assumption that all collected filter dust can be recycled. Without the possibility of filter dust recycling, the costs would be about 3.5 EURO/ton (year 2000 figures), these extra costs are due to disposal and increased costs of raw materials. For the Dutch glass industry we found for the costs of dry scrubbing in combination with a bag filter: 2.5 to 4 EURO/ton molten glass. For abatement cost information, see chapter II.6.

Very important for the efficiency of SO₂ removal from glass furnace flue gases by the dry method using hydrated lime (Ca(OH)₂) at temperatures **below 300 °C** is the humidity (water vapor content) and temperature of the flue gas. Cariboni and Mereu [II.6] showed that the absorption of SO₂ by Ca(OH)₂ powder injected in the flue gases increased strongly by reducing the temperature of the flue gas, especially when approaching the flue gas dew point. (Just above the dew point, by capillary forces, the external surface and pores of the Ca(OH)₂ particles act as condensation sites for water vapor and the SO₂, moreover the lime solubility in this absorbing water also increases with decreasing temperature and this makes the absorbing condensed water more effective for SO₂ absorption). It was demonstrated that SO₂ removal efficiencies, indeed can be very poor in case of temperatures between 180 and 260 °C and under-stoichiometric dosing of Ca(OH)₂ powder into the flue gases of two Italian glass furnaces [II.6].

Tests with different hydrated lime qualities showed that the BET (total specific surface of the grains including pore surfaces) values, purity (% Ca(OH)₂) and particle sizes of the injected Ca(OH)₂ powder are crucial for SO₂ removal efficiency. The SO_x removal for dry scrubbers using hydrated lime is almost proportional to the BET value [II.7].

Although in the 'low' temperature regime SO₂ absorption by hydrated lime generally increases with decreasing temperature, in the high temperature regime above 350 °C, the absorption mechanisms is different and removal efficiency of SO₂, as observed by Kircher [II.3], often increases by increasing flue temperatures at this temperature level.

Thus, for dry Ca(OH)₂-scrubbing systems, using bag filters operating at temperatures below 180 °C, the removal efficiency can be improved by reducing temperature and increasing water content (e.g. by extra injection of water in the flue gas stream). For ESP filtration systems (flue gas temperatures, generally above 300 °C), an increase of the flue

gas temperature may be effective in improving the absorption efficiency of the hydrated lime towards SO₂.

From experiences in the German glass industry, it is obvious that indeed the type of hydrated lime plays an important role in the absorption efficiency with respect to SO₂. In Annex 4 a short report of a visit to a German container glass factory is presented. The plant operates since the 1980-ties a dry scrubber upstream of an Electrostatic Precipitator. Experiences with two types hydrated lime as absorbing agent, soda and sodium bicarbonate are reported for the same installation. The scrubber temperature is between 290 and 320 °C. The two different types of Ca(OH)₂ powder resulted in significant different absorption efficiencies. A special Ca(OH)₂ powder with a special pore structure for selective absorption of SO₂ is now in use (Lhoist-Rheinkalk SP) and SO₂ emissions can be reduced from 1600 mg/Nm³ down to 400-500 mg/Nm³. The filter dust contains up to 46-53 % SO₃, showing the high SO_x- removal efficiency of this type of lime hydrate. This type of lime hydrate is much more effective than a quality used before. Sodium bicarbonate as absorption agent has been applied in the same installation from 1996 until summer 2006. Due to temperature fluctuations and the formation of different sulfates (sodium pyrosulfate, sodium bisulfate) that are probably caused by to rather low temperatures in the EP itself and downstream the EP (< 300 °C), the filter system, electrode plates, flue gas ducts and the heat exchanger downstream the filter required regularly cleaning. Sometimes the deposits at the filter and in the flue gas system started to melt. Every 4 years the electrode plates had to be replaced due to severe corrosion.

The use of sodium bicarbonate instead of hydrated lime is shown by Kahale [II.8], he pointed out and demonstrated that the molar excess of NaHCO₃ addition to the flue gas, relative to the total concentration of the acid gas species: SO₂ plus HF plus HCl (molar ratio of NaHCO₃ versus moles of HCl, HF, 2 times SO₂ and 2 times SO₃), needs to be only small to achieve already very high removal efficiencies. For instance addition of sodium bicarbonate powder in flue gas (after a quench reactor) of a glass furnace at a temperature of 170-175 °C resulted in 65 % SO_x emission reduction for a stoichiometric ratio of 0.75 (relative to SO_x+HF+HCl molar concentration in the flue gas from a glass furnace). For the same flue gas, a ratio of 1.35 had to be applied when using Ca(OH)₂ and only 30 % of the original SO_x concentration level could be decreased. The injection

of a caustic soda solution (in the quench reactor) resulted in 35 % SO_x removal for a stoichiometric ratio of 0.41 (NaOH injection versus SO_x+HCl+HF in flue gas). Also at higher temperatures, between 300-400 °C, sodium bicarbonate: NaHCO₃ showed a rather high removal efficiency for SO_x removal in the flue gases of an oil-fired float glass furnace: 85 % at a molar ratio of 1.35. The filter dust collected by bag filters or ESP systems downstream dry NaHCO₃ scrubbers, when using under-stoichiometric injection of absorbents, is mainly sodium sulfate (typically > 90 % Na₂SO₄ plus smaller quantities of other compounds such as NaCl and NaF). The use of sodium bicarbonate powder as absorption agent, however may lead to problems in relatively cold (< 300 °C) and SO_x-rich flue gases due to formation of sticky and corrosive sodium bisulfates (see annex II.4).

In case of dry scrubbing by hydrated lime or using caustic soda solution, the filter dust shows varying compositions and some sulfites. Such variations and reducing properties of these filter dusts makes recycling into the glass forming batch more difficult.

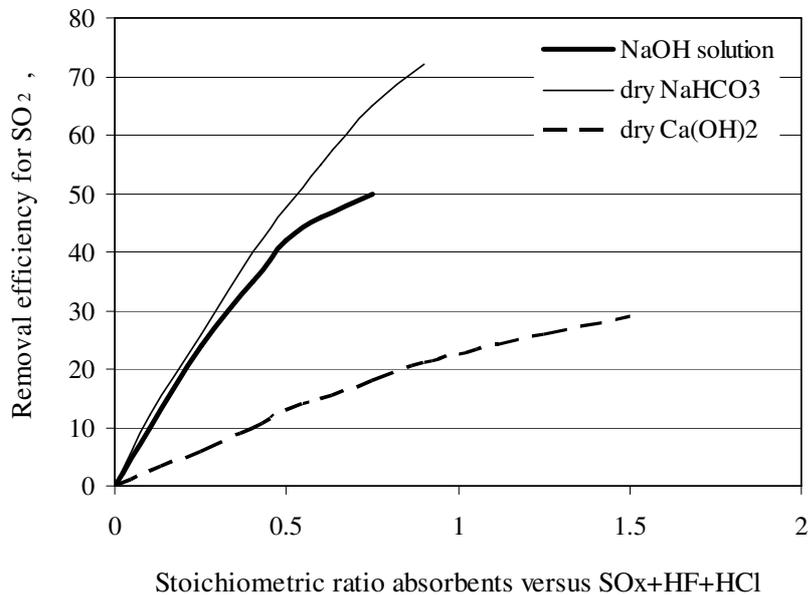


Figure II.2 SO₂ removal from glass furnace flue gas by injection of dry sodium bicarbonate, caustic soda solution (via quench reactor) and hydrated lime.

Efficient dry scrubbing of flue gases by hydrated lime requires high molar ratios of injected agent versus pollutant and will result in high levels of free lime in the filter dust and probably larger amounts of filter dust residue compared to the more efficient sodium bicarbonate process (Neutrec^(R) process [II.8]).

Figure II.2 shows the measured removal efficiency for SO₂ in a glass furnace flue gas of 170-175 °C equipped with a quencher, injection of dry absorption agent or caustic soda solution and a bag filter. The figure is derived from lit. Ref. [II.8]. This figure II.2 shows the large difference in absorption efficiency of sodium bicarbonate (NaHCO₃) compared to hydrated lime Ca(OH)₂, injected in the flue gas with a temperature of 170-175 °C, and no recycling of the filter dust within the scrubber. From this figure we can also observe that the removal is not proportional to the absorption agent addition above stoichiometric ratios of 0.5-0.6. Sodium carbonate solutions (semi-dry) or caustic soda solutions require also a rather high excess of soda to achieve high absorption levels. 85 % SO_x removal could be achieved by injecting a soda solution in a flue gas at 300-400 °C at a stoichiometric ratio of 1.38 (relative to molar concentrations of SO_x+HCl+HF). In the Dutch semi-dry scrubber (see section 3.2 for semi-wet scrubbers), about 47 % of the SO_x is removed by adding a soda-solution with a stoichiometric ratio of 0.7. The application of NaHCO₃ as an absorption agent for dry scrubbers, especially the composition of the resulting filter dust and the possibility to recycle this filter dust in the batch needs further investigations. Accumulation of chloride in the dust or the fine structure of the dust may limit the possibility of recycling the filter dust into the glass furnace. Also the experienced problems of deposition, fouling and corrosion of the filters and ducts downstream a NaHCO₃ scrubber by aggressive sulfates needs attention (see annex II.4).

Use of hydrated lime with an absorption efficiency of 30 % at stoichiometric addition to the flue gas will form 4.8 kg filter dust per kg SO₂ removed. In case of sodium bicarbonate, with 75 % removal at stoichiometric injection in the flue gas, the filter dust production will be about 3.7 kg/kg SO₂ removed. Thus for the same amount of SO₂ reduction, 25 % less filter dust will be formed.

One of the observed problems in few glass furnaces in the Netherlands when recycling the fine filter dust from the bag filter or ESP into the glass forming batch that is charged to the glass furnace is: Carry-over of this fine dust (entrainment of these fine particles

from the batch into the combustion gases in the glass furnace). This phenomenon has presented severe problems in some Dutch glass furnaces such as: corrosion of regenerators, attack of refractory materials, blocking of the passages in the checkers of the regenerators. Several, Dutch glass companies using dry or semi-dry scrubbers limit the amount of filter dust recycling in their batches to avoid this problem. Therefore, external disposal or recycling outside the glass industry is required especially in case of scrubbers with high SO_x removal efficiencies. Disposal costs range from 200 to 450 EURO per ton filter residue. The costs for the filter dust that cannot be internally recycled, depends on the composition (presence of polluting compounds or metals) of the filter dust and whether it can be used to recycle externally or has to be disposed.. Some of the filter dust material (lime based) can be used as a raw material in cement production.

On the other side, when it is still possible to recycle the filter dust from dry Ca(OH)₂ scrubbers, the non-reacted Ca(OH)₂ in the batch can improve the melting and fining process according to Cariboni and Mereu [II.6].

II.3.2.9 Experiences dry scrubbers in the Netherlands glass industry

In the Dutch situations where Ca(OH)₂ dry scrubbing is applied, the temperature of the flue gases between the injection point and filter are in most cases in the range 170-200 °C (bag filters downstream the absorption agent injector). In one case, the temperature is between 350 and 400 °C (case of dry Ca(OH)₂-scrubber with ESP).

SO₂-removal efficiencies for dry-scrubbers, based on hydrated lime, Ca(OH)₂ injection upstream a bag filter are typically 15-30 %. For semi-wet scrubbers 40-65 % and wet scrubbers more than 90 %. For sodium bicarbonate dry scrubbing upstream an ESP about 50-60 %. But these efficiencies, of course, depend on process conditions and amount of injected absorption agent.

II.3.3 Quasi-dry or semi-dry (sometimes also called semi-wet) systems

The acid gas species to be removed are absorbed by a liquid phase. This liquid phase is mostly injected into the flue gas stream in the form of fine droplets (atomized liquid). The liquid phase is a solution (e.g. a soda solution) or a suspension (e.g. lime suspension). The atomization (mechanically and/or pneumatically) of the liquid suspension or solution into the flue gas often takes place in a vertical vessel or reaction tower. The mass transfer is optimized by turbulent gas flows. These semi-wet systems are more expensive than dry scrubbers and maintenance is more complex due to fouling and plugging of the ducts or nozzles.

II.3.3.1 Method description semi-dry scrubbing

During the absorption process, the water evaporates and the suspension is dried or the solution turns into salt particles including the absorbed species. During the absorption and water evaporation process the temperature of the flue gases decrease (quenching), the concentrations of the acid gas species in the gas phase decrease and salts are formed such as NaCl, NaF, Na₂SO₃, Na₂SO₄ (in case of soda based solutions) or CaCl₂, CaF₂, CaSO₃, CaSO₄, Calcium borates (in case of lime based suspensions or slurries). The resulting salt particulates are removed by bag filters or an ESP unit. Prior to filtration, the flue gas temperature should be quenched to the acceptable temperatures levels, depending on the materials used for the filtering systems.

II.3.3.2. Application of semi-dry scrubbers

In the Netherlands glass industry, these semi-dry systems are applied in only one case, using a soda solution as scrubbing agent and a bag filter to remove the obtained reaction product salt particulates and primary glass furnace dust.

The absorption rate or removal efficiency depends strongly on the amount of soda solution injected into the flue gases. Absorption rates from 40 % up to 95 % [II.11] are possible, see figure 3. High absorption efficiencies for SO_x (most of the SO_x in the flue gases exists in the SO₂ form) however, requires an excess of soda injection and therefore increased amounts of sodium salt particulates have to be removed by the filter unit.

II.3.3.3 Costs for semi-dry scrubbing and filtering

The abatement costs, for this case of semi-dry scrubbing in combination with a bag filter, are about 10 EURO per ton molten glass or 1.2 EURO per kg SO_x removed and 25 EURO per kg dust emission reduction (based on the primary dust content of the flue gases) removed from the flue gas. The costs per kg SO_x removal are derived by calculation from the total abatement costs (to remove particulate and SO₂) and distribution of the costs to SO_x removal and dust removal using weighing factors (10 kg SO_x removal equivalent with 0.5 kg dust removal for these calculations).

II.3.3.4 Removal efficiency and reaction products

A typical dust composition is 55-70 wt % Na₂SO₄, 15-25 % Na₂SO₃, about 10-15 % non-reacted soda, 4 to 8 % NaCl and 0.5 % NaF, for an under-stoichiometric injection ($n = 0.7-0.75$) of soda solution into the flue gas (about 50 % SO₂ removal). An increasing amount of soda solution injection to increase the SO₂-removal efficiency will result in a higher percentage of non-reacted soda in the increased amount of separated filter dust.

Riepe [II.9] reported about the use of caustic soda solutions in semi-dry scrubbing systems to absorb SO_x from flue gases of a container glass furnace. A caustic soda solution is applied to quench the flue gases and to absorb about 90 % of the SO_x at 180 °C. The removal of HF and HCl appeared to be excellent as well. Downstream the semi-dry scrubber a bag filter separated the primary and freshly formed dust (mainly sodium sulfate) from the flue gases. However, due to the non-reacted sodium hydroxide in the filter dust and the reduced lifetime of the filters (because of the corrosive caustic soda) it was decided to change from a semi-dry to a dry system.

Figure II.3 shows that above a certain amount of addition of soda (Na₂CO₃)-solution to the semi-wet scrubber, relative to the molar amount of SO_x present in the flue gases, the SO₂ absorption by extra addition of soda will have reduced extra removal efficiency. Up to a molar ratio of about 1.3, 1 mol Na₂CO₃ absorbs about 0.85 mol SO₂.

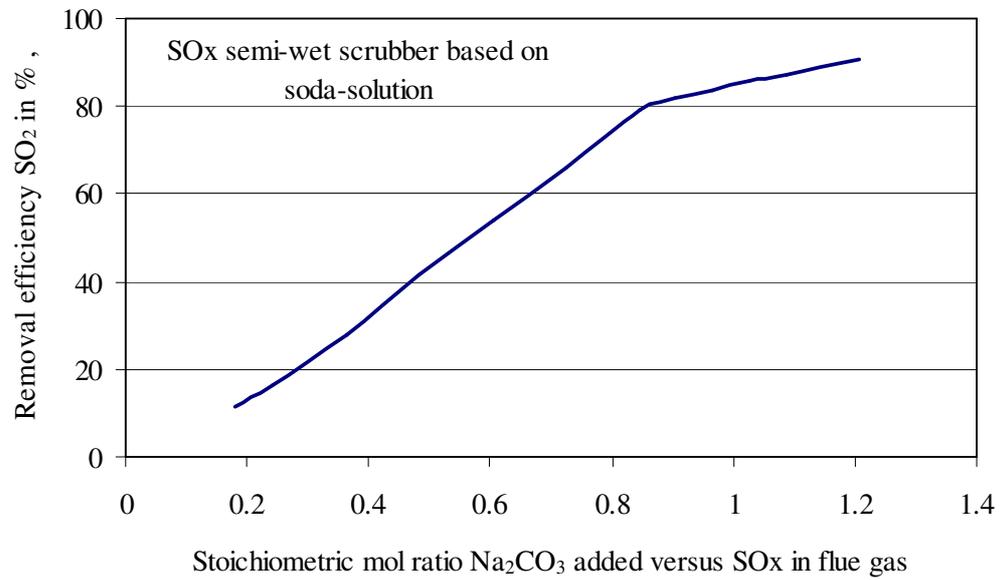


Figure II.3 Removal of SO₂ in semi-wet scrubber (180-200 °C) by soda-solution, depending on ratio of moles injected soda versus moles of SO₂ in the flue gas of a float glass furnace

II.3.4 Wet scrubbers

Wet scrubbers are hardly used in the glass industry, because of the higher costs (costs are relatively high for smaller flue gas volume flows) and the waste water treatment aspects. The waste water treatment often produces a sludge of material containing the non-reacted material (e.g. lime), the reaction products and water. This sludge cannot always be used as a raw material for glass production and most of the water in the sludge has to be removed before discharging this waste material and before transporting it to external disposal sites.

II.3.4.1 Method description wet scrubbers

In the wet scrubbing process, the gas species (such as HF, HCl, SO₃ and SO₂) are first dissolved in a liquid, because of the solubility of these gases in this liquid. The solubility increases for increasing basicity (solution of soda or suspension of lime) of the solution or suspension. The dissolution rates can be improved by using reactive solutions and special packed towers, enabling an intensive contact between flue gas and dosed liquid. Generally, the liquid is an aqueous solution of ionic species that increase the gas solubility. An example is a soda solution. The required excess of reactant in the solution to achieve high acid gas dissolution rates is very small. The rate is mainly determined by the absorption of gas by the liquid. The design of the reactor is important and often counter current gas/liquid flows are applied and a high level of turbulence is maintained in liquid and gas flows to improve the contact. Sodium hydroxide and soda are often used for wet scrubbing, although sometimes suspensions or slurries of limestone/lime are applied. Downstream the wet-scrubber, the flue gases are saturated with water and separation of the droplets (containing absorbed gases) is required before emitting the flue gases. The separated liquid may contain insoluble particles, the reaction products and non-reacted soda or lime. The liquid has to be treated by a waste water process and the non-soluble matter is collected by sedimentation or by filtration to extract the solid material or sludge in concentrated form. The concentrated sludge is often dried or part of the water is removed before disposal. In most cases it is very difficult to re-use the sludge as a glass raw material. Removal efficiencies of more than 90 % are achievable with wet-scrubbers.

II.3.4.2 Costs of wet scrubbers

Typical costs (for this specific Dutch situation) are: 15 to 20 EURO per ton molten glass or 1-1.25 EURO per kg SO_x removed in combination with dust removal (15-25 EURO per kg dust removal: the total costs in case of wet scrubbers are considerably higher, give a much better SO_x removal efficiency, but not a much better particulate emission reduction compared to dry or semi-dry scrubbers in combination with filters).

II.3.5 Summary of different scrubbing methods applied/applicable for flue gases of glass furnaces

Table II.3 summarizes the performance, advantages, disadvantages, boundary conditions and costs associated with the different DeSO_x methods applicable for flue gas desulfurization of glass furnaces. The costs per emission reduction method in this table, are presented in costs per ton molten glass for container or float glass furnaces. Information on abatement costs in case that all filter dust can be recycled internally (in glass furnace) and in the other case that filter dust residue has to be disposed/externally recycled are both given. The differences (indicative) are the typical costs for disposal of the filter dust.

**A part of the total costs of air pollution control by the scrubbers plus filters is assumed to be associated to dust removal and the other part of the costs is pre-described for SO_x emission reduction, using weighting factors 0.5 for SO_x and 10 for dust, see section II.6.2*

Table II.3 Comparison of DeSOx methods									
	Dry	Dry	Dry	Dry	Dry	Semi-dry	Semi-dry	Wet	SGA Hellmich
	Ca(OH) ₂ bag filter	NaHCO ₃ bag filter	non-calcined trona ESP	Ca(OH) ₂ ESP	NaHCO ₃ ESP	lime solution bag filter	soda solution bag filter	lime solution	Fixed bed of limestone plus Ca(OH) ₂
Application in glass industry	high	very low	low	very high	medium	low	low	low	very low
Typical temperature (range) °C	140-180	140-180	300-350	300-400	250-350	160-180	180-200	60	< 350
SO ₂ -removal efficiency in % at stoichiometric dosing n=1	10 to 25	75	75-90	30-40	>> 60	??	70-90	> 90 %	85 (n>> 1)
Filter dust composition*	CaSO ₃ , CaSO ₄ , CaF ₂ , CaCl ₂ , CaCO ₃ Ca(OH) ₂ Na ₂ SO ₄	Na ₂ SO ₄ NaCl	Na ₂ SO ₄ NaCl	CaSO ₄ CaSO ₃ CaF ₂ Ca(OH) ₂	Na ₂ SO ₄ NaCl	CaSO ₄ CaSO ₃ CaF ₂ Ca(OH) ₂	Na ₂ SO ₄ Na ₂ SO ₃ Na ₂ CO ₃ NaCl	CaSO ₄ CaSO ₃ CaF ₂	CaSO ₃ CaSO ₄ CaCO ₃ Ca(OH) ₂ CaF ₂
Advantages	simple process only cooling of flue gas bag filter provides filter and reaction	simple process only cooling of flue gas bag filter provides filter and reaction	simple process only cooling of flue gas bag filter provides filter and reaction	low consumption of absorption agent low costs of chemicals	simple process only cooling of flue gas bag filter provides filter and reaction	low consumption of absorption agent lower investment costs compared to wet scrubbers		low consumption of absorption agent low costs of chemicals	low investment and simple system configuration
Disadvantages	high consumption of reactant large amount of filter dust	reactant can be expensive	reactant is difficult to purchase in Europe	high consumption of reactant large amount of filter dust	expensive reactant	spray dryer is costly expensive materials for bag filter higher investment compared to dry scrubber	spray dryer is costly expensive materials for bag filter higher investment compared to dry scrubber	reheating of flue gas before stack production of waste water and gypsum complex and fouling of equipment high investments	high costs absorption agent dust filtration might be necessary
Important parameters	temperature (improvement close to dew point) and Ca(OH) ₂ dosing size and BET of Ca(OH) ₂	dosing and size of bicarbonate particles	dosing and size of trona particles size < 30 microns is preferred mixing into flue gas	higher temperatures > 350 °C preferred and size and BET of Ca(OH) ₂ powder	dosing and size of particles mixing into flue gas	dosing of lime	dosing of soda	contact between liquid and gas temperature basicity of suspension	temperature and amount of lime additions/refreshment
Costs per ton molten glass with filter dust recycling in EURO	2.5-3	3.5	3.5	3	4	not known	5 to 6	10 to 16	not known
Costs per ton molten glass without filter dust recycling in EURO	3 to 4	4.5	4.5	3.5	5	not known	7 to 10	12 to 20	not known
Combination with DeNOx	No SCR possible without gas re-heating	No SCR possible without gas re-heating	Temperature downstream ESP should be > 330 °C	Temperature downstream ESP should be > 330 °C	Temperature downstream ESP should be > 330 °C	No SCR possible without gas re-heating	No SCR possible without gas re-heating	No SCR possible without gas re-heating from 60-350 °C	No SCR possible without extra filtration and T> 330 °C
Literature	II.4, II.6		II.1	II.2, II.3			II.5	II.6	
* depends on glass type, in flint glass production CaSeO ₃ or Na ₂ SeO ₃ can be formed [3]									

Table II.3

II.3.6 Batch preheaters

Apart from the previously discussed scrubber systems, which are also used in other industrial sectors, the glass industry sometimes applies specially designed direct contact glass-forming-batch pre-heaters [II.12- II.14]. Direct contact means no division wall between the batch and the flue gas. The flue gases are in direct contact with the raw materials containing dolomite, limestone, soda etcetera. In the eighties, the German glass industry searched for technologies to reduce the energy consumption of glass furnaces. Because, a very large part of the supplied energy is lost by the heat contents of the flue gases of glass furnaces [II.15], for obvious reasons, the use of this energy for steam production, hot water, hot air or for the preheating of the raw materials has been extensively investigated in the glass industry. Especially batch preheating, bringing the part of the flue gas heat contents directly back into the glass melting process, appeared to be efficient in decreasing the energy consumption of the glass furnaces, typically by: 10-20 %. Different systems have been developed with a). separated channels for the batch (powder plus recycled cullet) and the flue gases in a heat exchanger or b). direct contact between batch (plus recycled waste glass) or cullet and the flue gases: the direct contact pre-heaters.

Nienburg and Interprojekt [II.12-II.13] developed a direct batch pre-heater. The soda, limestone and dolomite particles in the batch appeared to absorb acid gases from the flue gases and thus decreased the concentrations of HF, HCl en SO_x in the flue gases and returned these species together with the batch into the glass furnace. Downstream the pre-heaters, ESP units are applied to separate and remove the dust from the flue gases, before releasing the waste gases to the chimney. Enninga et al [II.12] reported a decrease of the concentrations of HF, HCl and SO₂ after the flue gases passed the batch pre-heater. The SO₂ concentration decreased from 586 (upstream pre-heater) down to 274 mg/Nm³ (dry flue gas conditions, 8 % oxygen) downstream the pre-heater. In the Netherlands, one batch/cullet preheater is applied in the container glass sector. This, however is an indirect system without direct contact between batch and flue gases: thus no absorption of SO₂ by the batch.

II.4. Other De-SO_x technologies from applications in other sectors and emerging methods

In other industrial sectors or in the electric energy generation sector (power plants) or in the field of waste incineration, other end-of-pipe methods are tested or applied, differing from the methods given in chapter II.3. Few, of these other De-SO_x methods, are already applied for one or few glass furnaces (often as demonstration or pilot units), but are not considered as common technology for abatement of emissions of glass melting furnaces. Also some emerging technologies for combined DeSO_x and DeNO_x at low temperatures are recently tested for glass furnace like situations.

Among these methods are:

II.4.1 Ionizing wet scrubbers

Ionizing wet scrubbers operating typically at temperatures at which the flue gases are saturated with water (40-70 °C). This method is applied to eliminate dust particles, SO_x and HCl or HF. Most known applications in the glass industry are for relatively small flue gas volume flows [II.16] or for the flue gases of mineral wool post-processing (curing ovens, application of binders).

The particles are electro-statically charged in a high voltage electrical field before entering the packed bed scrubber section for instance containing Tellerette® packings. On their way through the Tellerette® Tower packed bed the charged particles either approach the surface of a Tellerette® Tower packing or the surface of a droplet. They are attracted by an induced opposite charge, then separated and discharged by the scrubbing liquid. In addition, particle sizes of 10µm and bigger are separated by impact while passing through the tower packed bed. Simultaneously toxic and noxious gases are absorbed and removed in concert with a chemical reaction. In principle the SO₂ absorption mechanism is identical with wet-scrubbers. There are no long-term experiences with this techniques in the glass industry and the costs for container and float glass furnaces is not known, but probably much more expensive than the conventional dry or semi-dry scrubbers plus filters used today in the glass industry.

II.4.2 Fluid bed systems

Fluid bed absorption methods: lime based materials are fluidized by flue gases and absorb acid gas species. Temperature is a very important parameter and the flue gases need to be filtered (probably in few subsequent steps) after passing the fluid bed. This technique has been tested in the glass industry in the USA [II.17] in the eighties using raw material glass forming batch, but this method caused problems with high dust formation above the fluid bed. This technique leading to dust formation has not become a mature technology in the glass industry.

II.4.3 Cascade absorber or “Kalksplitreactor”

The fluorine cascade absorber (FKA fluorine cascade absorber) [II.18a] is the standard solution for flue gases with relative high fluorine and low chlorine and low SO_x concentrations. The absorbents, crushed limestone granules for example, are to be found in a silo on top of the absorber. The absorbent trickles vertically from the storage silo and passes the horizontal cascades in the reaction chamber. As a result, the contaminated gas flows through the absorbent and reacts with the crushed limestone granules. The saturated limestone granules are collected in the system funnel and discharged continuously or intermittently. In addition to this, a peeling drum increases the economic efficiency of the system: The lime grains can be covered by the reaction products, but the core contains non-reacted limestone. The peeling drum removes the skin of reaction products and the core is returned into the reactor. The reaction product separated from the limestone grains is collected. This very cheap method is mainly effective for the absorption of fluorides, but shows a low efficiency for SO₂. These reactors are mainly applied in the ceramics industry for HF-abatement. Experiences of this cascade absorber in the glass industry are rare and probably needs a downstream filter to eliminate lime dust emission.

II.4.4. Static Bed Counter flow lime absorber

Static Bed Counter flow absorber SGA [II.18b], where the flue gases are flowing through a fixed bed of limestone and/or hydrated lime. These systems are used since 1996 in the ceramics industry. The SO_x absorption efficiency is very much improved compared to

the previously described fluor cascade absorber. The operation of HELLMICH's SGA counter current absorber is similar to the fluorine cascade absorber. The SGA reduces SO_x concentrations of approx. 2,500 mg/Nm³ to less than 300 mg/Nm³. The reaction chambers (cascade blocks) are connected in series and the flue gas passes through the absorbent several times. This utilizes the absorbent material fully and maximizes the reduction in contaminants. No moving parts come into contact with the dirty flue gas, which minimizes maintenance. HELLMICH's SGA can be operated at high temperatures. Artificially produced calcium carbonate granules are used as an absorbent. It is possible to use conventional limestone granules in cases where only small concentrations of sulfur dioxide are present in the flue gases. There are probably no experiences with this technique in the glass industry, but this method might be interesting for SO_x emission reduction of glass furnaces.

II.4.5. SNRB process

SNRB process: SO_x-NO_x-ROX-Box using a ceramic filter and injection of Ca(OH)₂ powder or sodium bicarbonate (dry) [II.19]. This system has been demonstrated in a research project in the USA, but experiences within the glass industry are not known. The so-called SNRBTM system combines removal of SO_x, NO_x and dust in one unit. SO₂ removal is based on injection of lime or sodium based sorbents in the flue gases. NO_x removal is based on selective catalytic reduction with ammonia as a reagent. The dust (particulate) is filtered by a high temperature bag filter. Here the SCR catalysts (in the SNRBTM system a zeolyte for high temperatures is used or below 370 °C TiO₂ and V₂O₅ modules can be applied) are located upstream (dirty side) of the bag-filter. The system has been demonstrated at a coal fired power plant in Ohio-USA. The dust characteristics for power plant flue gases (size, sticking properties, composition) differ from dust particles in flue gases of glass furnaces. The temperature of the catalytic reduction is above 700 F. Baghouse (bagfilter) temperatures of 830 F (440 °C) have been applied. The filter materials are woven ceramic or glass fiber fabrics. Because of the high filtration temperatures, heat recovery (by waste heat boiler) from the cleaned flue gases downstream the SNRBTM process is possible. The filter is a pulse-jet fabric filter (the filter is a long bag with dust collection on the outside of the bag). Compressed air is used

from the inside of the bags, expanding the bags and releasing the filter dust from the bags. The filter dust is collected. At high temperature (of about 440 °C, SO₂ removal efficiency, using over-stoichiometric (1.8-2) hydrated lime dosing, can be as high as 80 % for high flue gas SO₂ concentrations. For sodium-based sorbents a higher efficiency (up to 90 %) can be achieved and also at low temperatures SO_x removal efficiency is still high. So far there is no application known in the glass industry. The long term behavior of the ceramic filter and catalyst for flue gases of glass furnaces has not been investigated yet.

II.4.6 Electron Beam Flue gas treatment [II.20]

This system is used for simultaneous removal of NO_x and SO_x from flue gases. The flue gases are irradiated by electron beams in a dry process. The humidity of the flue gas however should be rather high to achieve a high efficiency. Ammonia water or ammonia gas is injected into the flue gas before the flue gases enter the reaction unit where the irradiation with electron beams (typically 700 keV) and the main reactions take place. The energy of the electrons causes formation of highly reactive species, and NO and SO₂ react with these reactive species and with ammonia gas to form ammonium sulfate and ammonium nitrate. Also ammonium chloride (in presence of HCl) can be formed. The ammonium salts are collected by a downstream located ESP. The ammonium sulfates/ammonium nitrates collected by the ESP can be processed into agriculture fertilizers. Simultaneous reduction (depends on initial concentrations) of SO₂ and NO_x concentrations in humid flue gases is possible with an energy consumption of the reactor of about 3-4 Wh per Nm³ flue gas. SO₂ removal efficiencies of about 80 % and NO_x removal levels of about 50 % are reported. Some ammonia slippage might occur! Rather large reactor volumes seem to be necessary (residence time for the gas flow in the corona discharge reactor is about 8 seconds). This method is probably not suitable for glass furnaces, because of the generation of secondary waste (ammonium salts) that certainly cannot be recycled in the glass forming batch. So far the system is only commercially applied for very large flue gas volume flows. Experiences within the glass industry are not known. It is expected that the costs and complexity of this type of process makes this method less suitable for small flue gas volumes.

II.4.7 Pulsed sub-microsecond dielectric barrier discharge (DBD) processes [21]

Removal of NO_x and SO₂ from flue gases at atmospheric conditions using sub-microsecond pulsed dielectric barrier discharge. A plasma containing energetic electrons is generated by electrical discharge. The electrons ionize or dissociate the gas species in the flue gas and form gas phase radicals such as OH, HO₂, O. These very reactive radicals can oxidize simultaneously NO to NO₂ and SO₂ into SO₃. The flue gas should be humid, the water reacts with NO₂ and SO₃ to form HNO₃ and H₂SO₄ respectively or in case of SO₂, first OH radicals react with SO₂ to form HSO₃ and then H₂SO₄ in a second step. These acids, however have to be neutralized and captured by subsequent steps for instance by injection of ammonia to form ammonium salts. The process has been tested [II.21] for a simulated flue gas from a glass furnace. The main parameters that determine the SO₂ and NO emission reduction are: discharge pulse energy into the plasma or the energy consumption by generation of the electric pulses (80 ns pulses of 30 kV), the flue gas humidity and temperature (best results around 100 °C). At this time, the DBD process is still in an experimental stadium and the neutralization of the acids formed needs more investigations. The NO_x removal efficiencies are rather low: < 30 % but the SO_x emission reduction measured is in the range of 40 to 100 %. A similar process based on pulsed corona discharge (in short time-intervals releasing of electrons from a wire to electrode plates and forming pulses of electrons in the flue gas or vapor flow) in which electrons activate gas molecules forming ions, radicals etcetera is the PPCP process [22]. These radicals or other reactive species, such as OH, O, HO₂, H₂O₂ react with NO and SO₂ and form HNO₃ and H₂SO₄. These molecules can be neutralized by the addition of ammonia to the flue gases, this addition is preferably be performed upstream the pulse corona discharge reactor. Addition of water vapor improves the conversion efficiency. The PPCP or DBD processes require ammonia or ammonia solutions, low temperatures (< 100 °C). But ammonium salts are generated. These salts have to be separated from the flue gases by filtering systems downstream the corona discharge reactor. The process development of DBD and PPCP is still in an experimental stage, although large scale experiments have been performed. The complex chemistry (addition of ammonia and generation of ammonium salts) and complex physics (pulsed corona discharge) make this process less suitable for application in the glass industry at this moment.

II.4.8 Activated carbon processes

Activated carbon is often applied to remove heavy metals, dioxins, furans and other volatile organic matter from the flue gases. But, also SO_x emissions are also reduced by injecting activated coke or by contacting activated coke with SO₂-containing flue gases. Typical operational temperatures are 90-150 °C. The waste products in the activated coke can be elemental sulfur or sulfuric acid. This method is not used in the glass industry, but has been applied in many municipal waste incinerators, especially to remove mercury and dioxins/furans from the flue gases. The SO_x removal efficiency can be as high as 98 %, but the costs for activated carbon and waste disposal have to be examined in more detail. A special product, called Sorbalit® [II.6] has been brought on the market for simultaneous absorption/removal of SO₂ and other components such as VOC (furans, dioxin) or mercury (these components are not relevant for the glass industry in most cases). This Sorbalit® is a mixture of lime and small amount of activated carbon. The application of this material, however, may limit the possibilities of recycling of the collected filter dust as glass furnace raw material (activated cokes leads to reduction of the glass melt). There are some (very few) experiences with the application of Sorbalit for air pollution control of glass furnaces. Not known are the costs and the possibility to recycle the collected filter dust.

II.4.9. Ceramic filters combined with catalytic DeNO_x

High temperature filtration techniques combined with DeNO_x. An example is the high temperature filter system existing of filtration modules to which a DeNO_x catalysts has been added: such as the low density cerafil-topkat system. Ammonia or urea is used as reduction agent. The filter material exists of ceramic fibers for high temperature particulate filtration. With this system simultaneously NO_x and particulate matter can be removed from flue gases at temperatures above 220 °C. The application of this method in combination with SO_x removal is tested in the glass industry, but because of confidentiality reasons, detailed information is not available [II.24]. Tests have been performed for an extracted flow of flue gases from a float glass furnace at a flue gas temperature of 400-470 °C. The flue gases are treated in a combined filter and catalyst system, consisting of Cerafil Topkat catalytic elements. The pilot test facility has run for

3 months, the filter is regularly cleaned by a pulse cleaning system. Sodium bicarbonate is injected in the flue gas before the filter plant and ammonia is supplied to the flue gas for NO_x removal. The sodium bicarbonate absorbs SO_x. The ceramic filter traps the dust, including the absorption agent. Results of the test are not available, but this method might be an emerging technology for glass furnace emission control.

II.4.10 Conclusions

The methods presented in this chapter may show several important disadvantages, such as high level of complexity, the production of secondary waste that cannot be recycled as a raw material in the glass industry and high operational or investment costs. Some technologies, need further optimization and solution for problems such as ammonia slippage or solutions for the use of the waste- or by-products such as ammonium sulfate or ammonium nitrates. The application of a fixed bed lime reactor (SGA [II.18b]) for the treatment of SO_x-containing flue gases of glass furnaces might be worthwhile for future investigations or demonstrations in the glass industry, because of its simplicity and low costs.

The so-called SO_x-NO_x-ROX-Box method or the high temperature ceramic filters in combination with catalytic NO_x reduction (Cerafil Topkat) system may be interesting emerging technologies for flue gas treatment of glass furnaces at the time of 2007. However, at this time (2007) these methods can not be considered as BAT for the glass industry, because there are no direct experiences of the application of these methods for glass furnace flue gases during sufficient long time. The chemistry and behavior of the flue gases of glass furnaces, with a complex combination of different components such as HCl, HF, SO₃, SO₂ and some times selenium and boron components and the typical sodium sulfate or sodium bisulfate dust contents (in soda-lime-silica glass furnaces) is different from flue gases of other processes. Therefore, the most suitable flue gas treatment for glass furnaces may be very different from APC, suitable for flue gas treatment of power plants or ceramic kilns. Within the glass industry, different types of glasses are molten and the flue gas chemistry depends on glass type and applied fuel type. This means that there is not only one optimum APC system for the entire glass industry sector.

In almost all cases, secondary waste will be generated. Important, in that respect and in case that filter dust recycling is limited or even prohibited, is the application of a method and absorption agent with a very high efficiency to avoid large masses of filter dusts or sludge to be disposed.

II.5. Limiting conditions for the application of SO_x-emission reduction methods

In the Netherlands glass industry, several trials to use the secondary waste generated by the application of scrubbers in combination with filter systems, have been undertaken. During longer time periods, the collected filter dusts have been used as a raw material in the multi-component batch charged to the glass furnaces. However, several problems have been encountered in some cases:

a). In case of fuel-oil firing, the input of sulfur by the fuel might be much larger than the output of sulfur by the produced glass. Some glasses, such as green container glass or E-glass (continuous filaments) contain very small sulfur concentrations and the sulfur entering the glass furnace as an element of the fuel (or impurities in the batch raw materials) has to be mainly discharged from the system: a). as filter dust, to be disposed or b). as SO_x emissions. Low SO_x emission limits consequently lead to large volumes of filter dusts or waste water sludge (in case of wet scrubbers), to be disposed as a consequence of the sulfur-balances.

b). Filter dusts collected by bag filter or ESP units, are very fine and are very sensitive for carry-over in the furnace (the filter dust particles are easily entrained in the combustion gas flows in the glass furnace). This carry-over can settle in the recuperators, regenerators or flue channels and leads to fouling or even blockage of the flue channels. The dust, (alkali or earth alkali sulfate or chlorides and fluorides) in case of filter dust recycling in the batch is often aggressive or contains volatile components that accumulate in the flue gas system between the furnace and the filter unit. A few Dutch glass furnaces, stopped the recycling of the filter dusts, because of severe damages in the flue gas channels and regenerator systems of these furnaces. These problems have been caused by this filter dust carry-over and NaCl evaporation (by NaCl rich filter dusts). Sodium vapors (high NaCl vapor pressures in the furnace atmosphere when recycling sodium chloride containing filter dust) may react with the glass furnace or regenerator refractory materials.

c). The waste material from the treatment (sedimentation) of the waste water collected from a wet scrubber is collected as a sludge and it is very costly to remove all the water.

The variation of the composition, the high water content and the sticky behavior limits or even prevents the use of this sludge as a raw material in glass production. Also in this case, accumulation of some chemical elements (like chloride or sulfur) in the flue gas system may take place (sulfur and chloride is recycled all the time and all the time extra chlorine and sulfur is still added to the process by fresh raw materials and fuel). Glasses, which have a very low sulfur solubility, cannot accommodate this sulfur, that is re-introduced by recycled waste. Therefore the recycling of waste water sludge is hardly or only partly possible in this case and when using wet scrubbers.

d). The applied absorption agents in combination with the selected scrubbing methods are not always efficient, a strong overdose is required to achieve a high level of SO_x emission reduction. Many glass furnaces are equipped with dry scrubbers based on Ca(OH)₂ injection in the dry flue gases. Ca(OH)₂ has been chosen to protect the filter against sulfuric acid attack (SO₃ absorption) and to reduce HF emissions effectively. However, the absorption efficiency for SO₂ at stoichiometric dosing can be very low: 10-25 %, especially at temperatures between 130-250 °C. Other absorption agents or Ca(OH)₂ qualities with higher BET values (reactive surface area) and smaller grain sizes might be more efficient: creating less filter dust and using less absorption agent material to achieve the same SO_x reduction or to improve SO_x removal. Considering the costs of filter dust disposal (landfill residue), which often exceeds the raw material and absorption agent costs, it is recommended to investigate the use of more efficient scrubbing agents for SO_x emission reduction. Candidate materials are: trona soda or sodium bicarbonate or other hydrated lime qualities with BET values > 40 m²/g. These materials should preferably be injected as very fine particles.

e). The application of the today existing SCR technology for catalytic reduction of NO_x by reducing additives such as ammonia (gas or aqueous ammonia solutions) requires certain conditions of the flue gases:

- The concentration of fine dust in the flue gases should be as low as possible to avoid fouling of the catalyst surfaces or to prevent infiltration of sub-micron dust in the catalyst pores. Fouling would lead to a fast drop of the catalyst activity. For

glass furnace flue gases, it is strongly recommended and probably necessary to apply SCR systems downstream of an efficient filter system.

- In flue gases containing (even with small SO_x concentrations) SO_x, the injection of ammonia leads immediately to the formation of fine and sticky ammonium bisulfate dust at temperatures below 320-330 °C. Therefore the SCR system should only treat flue gases above this temperature.

These conditions can only be met for an air pollution control system based on a high temperature scrubber and filtration processes, such as a high temperature ESP or ceramic filters operating above 350 °C. In case of low temperature scrubbers in combination with bag filters (< 200 °C), reheating of the flue gases above 330 °C would be necessary for SCR operation and this requires an additional heat exchanger or the input of large amounts of extra energy. Especially in case of dry hydrated lime scrubbing, low temperatures are preferred with respect to SO₂ removal efficiency (< 110 °C) and reheating of the de-dusted flue gases downstream the filter prior to SCR-DeNO_x would cost a lot of extra energy (10-15 % of the energy consumption of the glass furnace).

II.6. Overview of estimated costs for SO₂ removal

Based on the method given in the NER [II.25] section 2.11, the total costs for reduction of SO₂ and particulate emissions are calculated taking into account:

II.6.1 Capital and operational costs of air pollution control

Capital costs of:

- Scrubber (dry scrubber, semi-wet (soda-solution), or wet scrubber (lime suspension) including silo for absorbing reagents and injector and if necessary a mill to grind the absorption agent prior to injection into the flue gases;
- Filter (Bag filter or Electrostatic Precipitator);
- Fans and fan motor;
- Piping to APC and from APC to chimney and by-pass ducts;
- CEMS (Continuous Emission Monitoring System) to control and check the abated emissions;
- Electricity supply;
- Engineering of installation.

In the cost calculations, interest rates of 10 % per year and writing-off in 10 years are applied and the real costs made by the companies are used in the calculations. (This leads to: Interest rates & writing-off costs per year of 16.3 % of the capital (investment) costs). Thus, the contribution of writing off and interest costs per year are 16.3 % of the investment costs.

For the foundation, buildings and civil engineering, the writing-off period is 25 years. Interest & writing off per year: 11 % of capital costs of foundation & building.

Operational costs due to:

- Maintenance & repairs;
- Electricity (fans, injectors, cleaning devices, pressurized air);
- Absorbing medium (soda, quick lime, Ca(OH)₂, NaHCO₃);
- Disposal or removal of filter dust or sewage sludge;

- Water;
- Diverse.
- Reclaim of costs of raw materials that can be saved by filter dust recycling.

Annex II.3 shows an example of the calculation of the total costs of air pollution control for a glass furnace and the decrease of SO₂ and particulate emissions per year. The total annual costs: operating costs, interests and writing-off of the investments are determined. The costs per ton molten glass and per kg reduced emissions (SO₂ and dust) are calculated. **The costs are distributed over SO₂ reduction and dust emission reduction costs, taking a factor of 10 for dust and weighing factor 0.5 for SO₂. The calculated costs for SO₂ removal depend strongly on these factors!**

Most important costs are writing-off and interests of the investments, energy consumption costs and disposal costs. The relative costs for purchasing the scrubbing agent and the raw material savings (in case of filter dust recycling in the glass melting processes) are generally very small.

The costs of Air Pollution Control per ton molten glass for the wet scrubber systems applied to two Netherlands glass furnaces are up to more than 20 EURO per ton molten glass for these specific cases. The costs of the application of dry scrubbers based on Ca(OH)₂ injection in the flue gases plus filters is 3 to 5 EURO /ton molten glass, similar to figures given by Riepe [II.10]. Disposal costs of residual filter dust can contribute up to 20 % of the total costs (capital plus operational costs), on average about 15 % of all costs are caused by disposal of filter residue.

The semi-wet system applied for the NL glass furnace costs about 10 EURO/ton molten glass for this particular case.

II.6.2 Costs of emission per unit mass of emission reduction

Most air pollution control systems applied in the glass industry combine the absorption of acid gases (SO₂, SO₃, HCl, HF, SeO₂, boron gases, etc) with filtration of the original (primary dust) and added particulate (secondary dust: non-reacted scrubbing agent and reaction product). Therefore the applied APC systems reduce at least SO_x and particulate

emissions and the costs per mass emission reduced has to be divided between costs to reduce SO_x emissions and to remove particulate emissions.

In this report, the method described in the NER [II.25] has been used, taking a weight factor for dust W_d of 10 and for SO_x: W_s=0.5.

When Q is the total annual cost (capital and operational) for APC and R_d the kg of particulate emissions reduced per year and R_s the SO_x emission reduction in kg per year, the specific SO_x abatement costs are given as:

$(Q \cdot W_s \cdot R_s / (W_s \cdot R_s + W_d \cdot R_d)) / R_s$ in Euro per kg SO_x emission reduction

II.6.3 Average results of cost estimations

(Sharing the air pollution control costs among dust and SO_x emission reduction, according the NER calculation method [II.25]).

Removal of particulate:

For the small furnaces, dust emission reduction appeared to be very expensive, about 30-50 EURO per kg particulate and 10 to 15 EURO per ton molten glass.

For larger furnaces (> 250 tons glass per day), the costs for particulate emission reduction are about 15-25 EURO /kg dust.

Removal of SO₂:

All SO_x removal methods give cost figures in a rather narrow range, typically between 0.6 and 1.25 EURO/kg SO₂ emission reduction, using the weighing factor of 0.5 for SO₂ compared to a factor of 10 for dust.

Table II.4 shows the estimated costs for removal of SO₂ and dust from flue gases of medium and large glass furnaces (> 200 tons glass/day) applying different APC methods. These figures are based on information from the Dutch glass industry anno 2005. The costs depend on furnace size, total SO₂ emission reduction level, applied APC method and local disposal costs for the filter dust waste to be removed. Therefore the given cost levels should be considered as indicative and are only applicable for relative large furnaces (> 200-250 tons glass per day). In the container and float glass industry, all

furnaces in the Netherlands (12 container glass furnaces and 1 float glass furnace) produce more than 200 tons molten glass per day.

Table II.4

Table 4. Estimated costs** for SO₂ and dust removal by different air pollution control methods based on Netherlands figures anno 2005			
For float and container glass furnaces (> 250 tons glass/day) and medium sized furnaces (> 100 tons/day)	Euro/kg SO ₂ removed	Euro/kg dust removed	Euro per ton molten glass
Dry scrubber plus bag filters and hydrated lime injection	0.65 - 1	13-20	2.7-4
Dry scrubber plus EP and hydrated lime injection	0.8 - 1.0	15-20	3-3.5
Dry scrubber plus bag filters and sodium bicarbonate injection	0.7 - 1	16-20	3-3.5
Dry scrubber plus EP and sodium bicarbonate	0.8 - 1	16-20	4 to 5
Semi-dry scrubber using soda solution (large furnace)	1 - 1.5	20-25	10
Wet scrubbers (medium sized furnace)	1-1.25	15-25	15
Dry scrubber plus bag filters and hydrated lime injection for oxy-fired container glass furnace			2 - 2.5
<i>* for oxygen fired furnace, flue gas volume flows and costs for APC are smaller</i>			
<i>** based on weighing factor 0.5 for SO₂ and 10 for dust.</i>			

The costs per kg SO₂ or per kg dust emission reduction are calculated for a weighing factor of 10 for dust and 0.5 for SO₂ (assuming a 20 times lower emission limit for dust expressed in mg/Nm³ than the emission limit for SO₂).

The values however depend very much on the weighing factors. For instance for a weighing factor of 2 instead of 0.5 for SO₂ emissions and 10 for dust, the calculated specific costs for SO₂ emission reduction (in Euro/kg SO₂ emission reduced) would be about 3 times larger (2-4 Euro/kg SO₂) and the calculated specific costs for dust emission reduction about 20 % lower.

II.7. Conclusions and recommendations

The SO_x emissions in the Netherlands glass industry have been reduced from about 2700 tons in 1992 down to 1380 tons in 2005. The specific SO_x emissions decreased from 2.38 kg per ton molten glass to 0.875 kg/ton. In 2005, 63 % of the glass production takes place in glass furnaces equipped with scrubbing systems. According to planned future developments about 70 % of the glass production will apply DeSO_x systems after 2007. This development, however will probably not lead to strong total SO_x emission reductions of the total Dutch glass industry compared to the 2005 situation, because of the increased production volume expected for the period 2006-2010.

A potential for further SO₂ emission reduction by the glass furnaces in the Netherlands might be offered by using more reactive absorption agents such as hydrated lime with high BET value or using sodium bicarbonate. For the future, new technologies that combine DeSO_x and DeNO_x could present cost-effective solutions, but need investigations before the technical and economical feasibility for application in the glass industry can be confirmed, see section II.7.6.4.

II.7.1 Different scenarios for SO_x emission reduction in the Netherlands glass industry

Additional SO_x emission reduction can be achieved by:

II.7.1.1 Fuel choice changes

Conversion from mixed fuel-oil – natural/gas firing to all natural gas firing (100 %) for the glass furnace still operating with fuel-oil burners. However, this option appears to be not feasible from a technical point of view, at least not before the next major rebuild* (scheduled after the year 2011). Thus, this possibility is not taken into account for the potential SO_x emission reduction until 2010. But, in case that a conversion to 100 % natural gas firing appears to be possible at the next major cold repair, a reduction of 250-350 tons SO₂ emission per year, seems possible for the Netherlands glass industry. Another option for the future might be the use of de-sulfurized oil (or fuel oil with very low sulfur content), this would offer another potential SO₂ emission reduction option without the operational problems encountered in this case with natural gas.

II.7.1.2 Extension of the application of scrubbers in the glass industry

Increase of the application of scrubbing systems to all large glass furnaces, producing more than 70 ktons of glass per year. This would give a reduction from 1380 down to about 1150 tons SO_x emissions per year, maintaining the same scrubbing technologies as being used in 2005.

**Before the major repair of this furnace (after 2010), a study on the most feasible options for air pollution control, fuel choice and energy efficiency improvement for this new furnace will be made by an integral approach and taking into account the Best Available Techniques at that time. The optimum economic and technical feasible solution for energy efficiency, abatement of SO_x, NO_x, dust, CO₂ emissions and with minimum secondary waste generation will be searched for.*

II.7.1.3 Improvement of efficiency of scrubber installations by increasing amounts of absorption agents

Optimize the efficiency of the current scrubbers applied in the glass industry, by increasing the added amount of absorption agent. This approach would increase disposal costs, since the amount of filter residue will increase by about 5x compared to the amount of SO₂ reduced: 300-400 tons SO_x emission reduction will cause an increased amount of about 2000 tons of waste to be disposed on landfill sites. Potential SO_x emission levels of the Dutch glass industry of ± 1000 tons/year could be achieved.

II.7.1.4 Improvement of efficiency of scrubber installations by improving the type of absorption agents or process conditions

Optimize the efficiency of the current scrubbers (especially the dry-scrubbers) by changing the type of absorbing agent or process conditions. 7 furnaces apply dry scrubbers based on the injection of hydrated lime powder. In most cases the temperature of the flue gases is far from the optimum temperature for efficient conversion of the hydrated lime into calcium sulfite / calcium sulfate. Optimization of the type of hydrated lime-Ca(OH)₂ (smaller grain size, higher purity, BET > 40 m²/g) is an option, without changing the scrubbing system. Replacement of hydrated lime by sodium bicarbonate is another option, but needs further investigations concerning the possibility of filter dust recycling in the batch and fouling problems of the filter and downstream ducts in case of low temperatures in the flue gases, causing sodium bisulfate formation. Although sodium bicarbonate may be more expensive for stoichiometric molar ratios relative to the SO_x+HF+HCl in the flue gases compared to Ca(OH)₂, the efficiency is higher and the amount of filter dust production will be (roughly estimated) 25-30 % less for the same SO_x removal. Today, hydrated lime qualities with special pore structures and high reactivity are used with a higher SO₂ removal efficiency as before. The application of sodium bicarbonate (instead of hydrated lime) and observed fouling and filter corrosion problems (especially for flue gases with low temperature and high SO_x-content) and the possibility of recycling the collected filter dust need more investigations in glass industry practice.

It is expected that (see table 5 compare scenario 3a and 3b with scenario 2) that the

replacement of hydrated lime by sodium bicarbonate will hardly lead to additional costs. However, when using sodium bicarbonate, the filter dust is mainly sodium sulfate and the composition will vary less compared to the filter dust from hydrated lime scrubbing. This material might be more suitable for recycling in the raw material batch, unless it contains high concentrations of chlorides or it is prone to carry-over in the furnace.

II.7.2 Filter dust recycling issues

In some cases, the sulfur balance restricts or limits the amount of filter dust recycling. These cases are:

- a). Fuel-oil (sulfur containing fuel) fired furnaces, since the sulfur input in the furnaces by the fuel is much higher in those cases than the glass can maximum dissolve. SO_x has to be discharged from the system: in the form of SO_x emissions and sulfate filter dust to be (at least partly) disposed.
- b). Furnaces using high quantities of recycled cullet, especially mixed colored cullet. The input of sulfur by this cullet might be much higher than the sulfur output by the glass melt. Also in this case, a net output of sulfur will take place either by SO_x emissions or filter dust to be discharged. For at least 6 natural gas fired Dutch glass furnaces, producing colored container glass, the input of sulfur via the cullet can be higher than the sulfur in the produced glass. Extra sulfur input via other raw materials may have to be taken into account as well. About 250 up to 400 mg SO₂/Nm³ concentrations in the non-cleaned flue gas are caused by the excess sulfur input from the cullet when using > 65 % cullet recycling in green or amber glass furnaces. Some extra SO_x is formed from S-input through other raw materials and from sodium sulfate or recycled filter dust. Without flue gas scrubbing, total SO_x emissions (input from cullet, sodium sulfate and S-in other compounds minus sulfur in glass produced) of such natural gas fired glass furnaces using large quantities (> 65 %) of cullet can be as high as 600-1000 mg SO₂/Nm³. When all filter dust can be recycled (to replace sodium sulfate) and sulfate addition is adjusted, the emissions (after scrubbing, with 50 % SO_x removal efficiency) for such natural gas fired glass furnaces producing amber or green glass can be reduced to about 300-500 mg SO₂/Nm³ (0.6-0.8 kg/ton molten glass).

Sodium sulfate is used as fining agent in most glass melting processes. Part of the

disposal costs could be compensated by recycling the sodium sulfate filter dust into the process. However, this aspect needs further investigations, since experiences in the Dutch glass industry showed that this sodium sulfate dust may cause carry-over problems in the furnace. The SO_x emissions in the Dutch glass industry will at least decrease by 200 tons/year after replacing hydrated lime by sodium bicarbonate in all the dry scrubbers (total SO₂ emissions of the Netherlands glass industry would be about 950-1000 tons/year). The increased annual costs (estimated) are about 500.000 EURO because of the increased cost of sodium bicarbonate and changed disposal costs. Thus, on average 2.50 EURO per kg additional SO_x reduction (assuming no internal re-use of the collected filter dust).

II.7.3 Conclusions related to application of existing technologies

Application of optimized scrubbing systems for all glass furnaces with a melting capacity above 70.000 tons glass per year (all container and float glass furnaces in the Netherlands), but still operating one glass furnace with a mixture of fuel-oil and natural gas will give a potential reduction of 440 tons SO_x per year. For that case, the total SO_x emissions would be about 1000 tons/year (on average 0.6 kg SO_x/ton molten glass) by the year 2010.

II.7.4 Future potential by application of new technologies

Use of technologies described in chapter 4: These technologies are still in development or are not suitable for the low volume flows of glass furnaces from an economical point of view. Several of these methods generate a secondary waste, such as ammonium salts that might be difficult to recycle or to dispose. However, some of these emerging technologies provide a method to abate simultaneously NO_x and SO₂ from flue gases of glass furnaces especially at low temperatures. It is not recommended to apply these technologies before 2010, but to investigate the potential and feasibility of these techniques for glass furnace flue gas treatment, especially for low flue gas temperatures where SCR DeNO_x techniques cannot or hardly be applied.

II.7.5 Comparison of different scenario's based on existing scrubbing technologies

Table II.5 shows the results (estimated and predicted) of SO_x emissions of the Netherlands glass industry, secondary waste (disposal) and associated costs for different scenarios.

Table II.5

Table 5 Comparison of SO _x reduction in glass industry according different scenarios							
Predictions for year 2010 Netherlands glass industry							
	SO _x ton/year	SO _x kg/ton	Filter dust disposal	average APC costs Euro/ton for large furnaces with APC	Total* costs APC large furnace/year	SO _x reduction costs range	dust reduction cost range (average for large furnaces)
		average	ton/year	Euro/ton	Million Euro	Euro/kg dust	Euro/kg dust
Scenario 0: 2005 situation	1380	0.874	4080	3.74	5.5	0.6-1.2	6 to 50 (17.95)
Scenario 1: According to existing air pollution control systems in NL glass industry 2010	1400	0.856	4240	3.82	5.9	0.6-1.2	6 to 55 (17.86)
Scenario 2: All large glass furnaces (> 70 kton/year) equipped with scrubbers & filters, most systems: dry Ca(OH) ₂ scrubbers	1154	0.705	6010	5.1	7.55	0.5-1.1	6 to 55 (17.98)
Scenario 3a: All large glass furnaces (> 70 kton/year) equipped with scrubbers & filters, all dry Ca(OH) ₂ systems converted to NaHCO ₃ / trona systems	943	0.576	4400	5	7.66	0.55-1.2	6 to 55 (17.9)
Scenario 3b: All large glass furnaces (> 70 kton/year) equipped with scrubbers & filters, all dry Ca(OH) ₂ systems converted to NaHCO ₃ / trona systems and filter dust recycling in 11 furnaces	943	0.576	3200	4.75	7.25	0.5-1.1	6 to 55 (17)
Capital costs: Filter, foundation, piping, monitor, engineering, electric supply							
Operational costs: energy, maintenance, repairs, filter dust disposal, additives							

Scenario 3b, assumes the application of sodium bicarbonate in most scrubbers and filter dust recycling in 10 glass furnaces. In this case the SO₂ emissions can drop just below 1000 tons/year and the filter dust disposal is estimated on 3200 tons per year.

For scenario 2 and 3, more than 90 % of the glass production in the Netherlands is equipped with scrubbing systems in 2010. In all scenarios, however, most of the flue gas temperatures downstream the filters are far below 200 °C. These low temperatures are not suitable for the application of SCR DeNO_x treatment, and therefore these scenario's exclude for most furnaces additional DeNO_x treatment by secondary measures. In 2005,

already 44 % of the Dutch glass production uses wet scrubbers or bag filters. Application of SCR systems for such furnaces is probably not feasible and would require major changes, des-investment (because of removing existing APC) or high extra energy consumption for reheating the flue gases. In 2005, 20 % of the Dutch glass production takes place in oxygen-fired furnaces and NO_x emissions are already reduced by this primary measure (oxygen-firing).

In the case that, for these air-fired glass furnaces, still not equipped (in the year 2005) with air pollution control systems, the decision will be made to install ESP filters instead of bag filters, there is an option for DeNO_x by SCR technology. However, the glass production of these remaining cases and the furnaces already equipped with high temperature ESP represents only 28 % of the Netherlands glass production. Thus, only 28 % of the Netherlands glass production could still be equipped with SCR, without having to reheat the flue gases. In that case, a 4th scenario has to be considered: all furnaces that are not equipped with scrubbers and filters could apply dry scrubbers plus high temperature ESP. Using highly efficient absorption agents (highly active hydrated lime or sodium bicarbonate), this option would lead to a total SO_x emission in 2010 of 900 to 1000 tons/year. The costs would be slightly higher (about 20 %) compared to bag filter systems. The effect on the amount of filter dust to be disposed is difficult to assess at this time.

II.7.6 Important issues for further investigations

II.7.6.1 More efficient absorption agents

SO_x flue gas emission reduction in the glass industry generates filter dust, a large part of this collected secondary waste cannot be recycled and has to be disposed to landfill. 1 ton SO_x emission reduction results in about 5 or 6 tons of solid waste. Investigations are recommended to search for a solution of recycling or re-use of this secondary waste instead of landfill. More efficient absorption agents may decrease the amount of filter dust generation or may enable filter dust recycling in the glass forming batch at certain conditions. But, this needs to be investigated by industrial tests, or new investigations on additional treatment of filter dusts to be suitable to be recycled in the glass furnace should

be undertaken.

II.7.6.2. Improved process conditions for scrubbers

In several scrubbing installations, the efficiency of SO₂ emission reduction by the application of hydrated lime is rather poor and can probably be improved by optimizing the process conditions of the scrubbing process (temperature, injection of water, choice of hydrated lime quality) or by a change to more reactive absorption agents such as trona soda or sodium bicarbonate.

II.7.6.3 Cross media effects

Important for the selection of the type of scrubbing plus connected filter device for abatement of dust, SO_x, HCl and HF is the choice of NO_x reduction methods. Primary measures such as oxy-gas firing or LowNO_x combustion technology may be sufficient to achieve low NO_x emissions, meeting IPPC-BAT and NER requirements. However, in case that primary measures are not sufficiently effective, SCR-DeNO_x systems have to be considered and this would almost exclude the choice for bag filter systems, semi-wet and wet scrubbing systems unless the flue gases can be heated up to > 350 °C in an energy-efficient (and cost effective) way.

7.6.4 Emerging technologies

For combined removal of NO_x, SO_x and dust, emerging technologies are the SO_x-NO_x-Rox-BoxTM method, and the high temperature ceramic filters combined with a catalyst, these methods need further investigations and long-time experience in the glass industry before these methods are considered as BAT in the different glass sectors. Examples are the Cerafil TOPKAT system of Madison or the in the USA (power plant) tested SO_x-NO_x-Rox-BoxTM method.

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ANNEX II.1: Factors determining SO_x emissions of glass furnaces

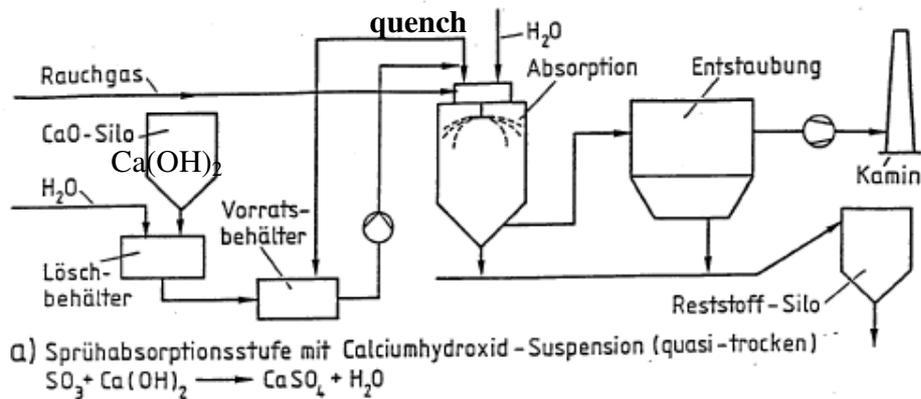
Apart from the type of applied fuel, the SO_x concentrations in the flue gases of glass furnaces, before these gases enter the scrubbing system, depend on many factors such as:

- Cullet fraction (mass fraction recycled glass) in the raw material batch and the type of cullet: some furnaces use only one color of recycled glass in rather small ratios (10-50% in the batch), other furnaces use mixed colored cullet and ratios of up to 90%. For instance, the production of green glass uses often 80% to more than 90% cullet and only 10-20% normal batch components. White glass (and recycled white glass cullet) contains much more sulfur than green or amber glass. Thus, especially container glass furnaces using large amounts of sulfate or white cullet may emit relatively high SO_x concentrations, especially when the glass product shows low sulfur solubility (as it is the case for the production of green container glass). Green glass production from large amounts of white cullet (high fraction of white glass in batch) is possible, but this will lead to extra SO₂ emissions due to the higher SO₃ content in white glass compared to green glass.
- The raw materials used: some raw materials contain sulfur contamination or impurities or organic components. The presence of organic components can lead to a deficit of oxygen (low oxidation state) in the molten glass and affects the glass color. Extra sulfate (as an oxidant) is required to supply extra oxygen to the batch to oxidize the organic contamination. In glass batches, containing large quantities of waste glass to be recycled extra sulfate addition to the batch might be necessary to compensate of the organic (chemically reducing) compounds in the waste glass (residues of food or beverages or oils or glues). This sulfate delivers oxygen, but also releases SO₂ gas upon decomposition during heating of the batch. This extra SO₂ will be emitted by the flue gases.
- The glass to be molten: Some glasses show very low sulfate solubility, such as E-glass for the production of glass fibers or green container glass for (esport) beer bottles. In these cases the sulfate added to the batch cannot be digested by the glass and has to be emitted. Filter dust cannot or only partly be recycled because of the low amount of sulfur absorbed by the glass. Especially in case of the requirement of low residual SO_x emissions, the filter dusts have to be (partly)

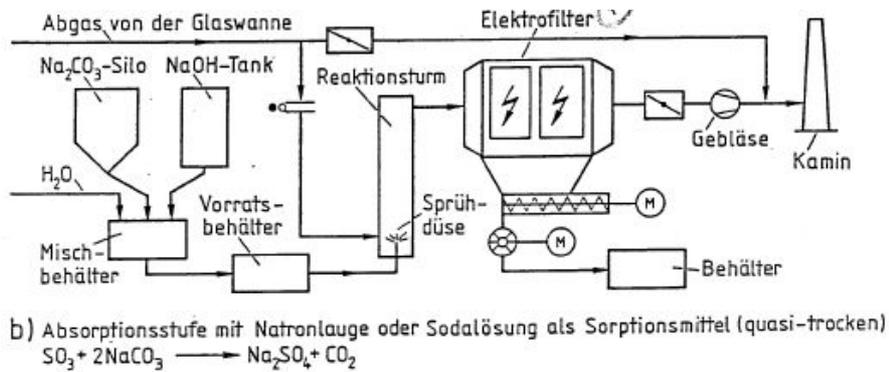
disposed. For these glass types (such as green container glass or E-glass) with low sulfur solubility and in case of fuel-oil firing, most of the filter dust cannot be recycled as a batch material, since SO_x would accumulate in the system (very small output of sulfur via the glass), .

Thus, a realistic pre-description of the achievable SO_x emission for a glass furnace is very complicated and has to consider the type of glass, purity (sulfur contents) of the available raw materials, use of recycled glass, mixture of recycled glass (large amounts of white glass cullet contains more sulfur than green cullet), type of fuel, color of the required glass product, and costs for filter dust transport plus disposal on landfill sites.

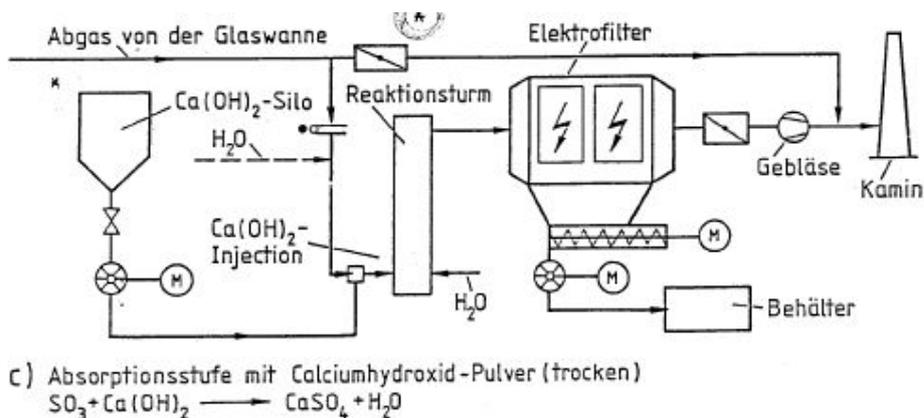
ANNEX II.2: Schematic drawings of scrubber plus filter systems applied for air pollution control of glass furnaces, from literature reference II.3 (Kircher).



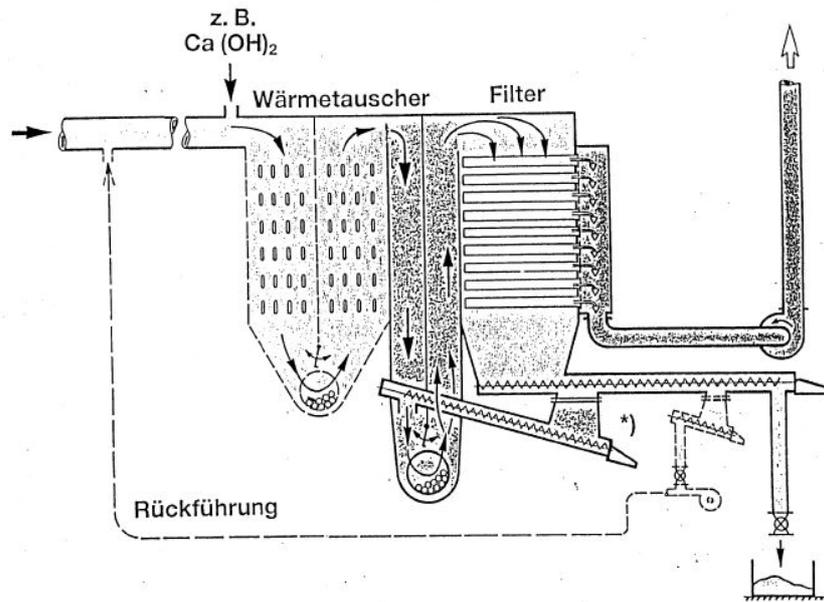
Semi-dry absorption of SOx by a suspension of calcium hydroxide in a spray-tower upstream of filter (Entstaubung) system [Kircher, II.3]



Semi-dry absorption of SOx by a solution of soda or caustic soda in a reaction tower upstream of ESP-filter system [Kircher, II.3]



Dry absorption of SOx by a powder of hydrated lime injected in a reaction tower upstream of ESP-filter system [Kircher, II.3]



Dry scrubber system from Lühr, with heat exchanger, bag filter and reactors for $\text{Ca}(\text{OH})_2$ - SO_x / HF / HCl reactions. Part of the removed filter dust from flue gas is recycled (Rückführung) within the scrubber system.

ANNEX II.3

Example calculation of air pollution control costs for dust and SO₂ abatement in flue gases of glass furnaces. Example: glass furnace with 300 tons glass per day

Example cost calculation emission reduction, removal of SO ₂ and particulate (NER method 2004)						
Glass furnace with dry scrubber plus bag filter						
		Units				
Capital costs equipment (10 years writing-off)		Euro	Euro/year	Tons/year	Euro/ton	Euro/kg removed
10 % interest rate						
Engineering costs		70000				
Scrubber system	dry-scrubber	200000				
Filter plus piping	bag filters plus piping & control & fan	1000000				
Monitor SO _x , NO _x , dust	in-situ analysis	50000				
Electric supply	supply fan, soot blowers etc.	35000				
Total capital cost equipment		1355000				
Building & Foundation costs (writing-off: 25 years)						
Building	building of filter & control room	20000				
Foundation		20000				
Total costs foundation		40000				
Writing off and interest	0.163 x capital cost equipment + 0.11 x cap. cost foundation		225265	1		
Operation/Variable Costs						
Maintenance	repairs & cleaning		40000	2		
Energy (0.08 EURO/kWh)	fan, injector of Ca(OH) ₂ , filter cleaning		90000	3		
Ca(OH) ₂ (175 EURO/ton)	230 tons/year		40000	4		
Disposal costs (200 Euro/ton)	175 tons/year		35000	5		
Saved raw materials			-6000	6		
Total annual costs scrubber (variable plus capital costs)			424265	(1+2+3+4+5+6)		
Glass melt production	300 tons/day			109500		
Costs per ton molten glass					3.87	
Removed dust per year	from 0.230 kg/ton to < 0.01 kg per ton			25		
SO ₂ emission removed per year	from 1.15 kg/ton to 0.84 kg/ton			35		
Cost SO ₂ removal in Euro/kg	weighting factor 0.5 for cost participation					0.793
Costs dust removal in Euro/kg	weighting factor 10 for cost participation					15.860
Assumption of cost prices						
Disposal				200	Euro/ton	
Ca(OH) ₂ powder				175	Euro/ton	
Soda				160	Euro/ton	
NaHCO ₃ crushed powder				207	Euro/ton	
Electricity				0.08	per kWh	
Natural gas				0.16	per Nm ³	

ANNEX II.4

Visiting Report REXAM Glass factory Lünen Nordrhein Westfalen, Germany

- Plant: Container glass, mainly flint glass
- Visit: 28. February 2007
- Furnaces: 2 end-port fired regenerative container glass furnaces, oil fired (one with gas atomization)
- Flue gas: High SO₂ contents because of heavy fuel oil firing, the SO_x content in the flue gas (upstream the air pollution control equipment) decreased also by changing from a fuel oil with >> 1 % sulfur to a fuel oil with about 1 % sulfur.

Flue gas treatment:

- Step 1.: Flue gases from regenerator at 450-500 °C of both furnaces are combined and flow to a raw gas (not treated flue gas) heat exchanger / waste heat boiler: for steam production (this steam is used by the city to generate electricity and heating for the neighborhood at the glass plant)
- Step 2.: Dry scrubber operating with flue gas temperatures of 290-320 °C.
- Starting in the 1980-ties with hydrated lime (Ca(OH)₂) as the absorption agent, result: rather poor SO₂ removal efficiency;
 - Beginning of the 1990-ties using soda powder: many problems with deposition of aggressive sodium sulfates (pyrosulfate, bisulfate) in filter and flue gas duct system. Probably the combination of sulfur oxide rich and rather cold flue gases with high amounts of sodium resulted to formation of corrosive sodium bisulfates or pyrosulfates. Deposition of such reaction products at electrode plates, in clean gas side boiler and chimney and fan took place. During maintenance of APC (air Pollution Control) equipment and by-passing this equipment, the higher temperatures in the ducts and chimney often lead to melting of these corrosive sulfates.
 - 1996-2006 Application of sodium bicarbonate (delivered material has to be grinded) as absorption agent in the scrubber. SO₂-removal efficiency was very high. Depending on the dosing of this absorption agent, the SO₂ emissions could

- be decreased from more than 2600 mg/Nm³ (heavy fuel oil with high S-content) to very low values << 400 mg/Nm³. Sodium bicarbonate is very reactive, but showed severe fouling on the electrodes and deposition plates of the electrostatic precipitator. At T < 300-320 °C deposition of sulfates took place and these deposited layers started to melt at increasing temperatures. The sticky and corrosive sodium sulfates and their melts required frequent cleaning and repairs (estimated on more than 100.000 EURO extra costs per year). The dust removal of the EP appeared to be effected by the use of sodium bicarbonate. The composition of the filter dust showed the high efficiency level for sulfur removal (53 % SO₃ in filter dust). Residual SO₂ emission levels of about 200 mg/Nm³ appeared to be possible. However, to avoid to high over-dosing and a surplus of filter dust collection, the dosing of sodium bicarbonate is adjusted to obtain sufficient SO_x removal, but still enabling full recycling of the collected filter dust
- Because of the maintenance problems of the air pollution control system (electrodes, plates) and the waste heat boiler (at clean gas side), the glass company decided to change from sodium bicarbonate to a reactive Ca(OH)₂ powder in summer 2006. A special type of lime hydrate (Lhoist Rheinkalk- SP) is used since 2006 and showed still high SO₂ removal levels: from 1600 mg SO₂/Nm³ down to 400-500 mg/Nm³. The efficiency is shown by the high contents of SO₃ in the filter dust: 46-53 %, this means that this type of lime hydrate is efficient for sulfur oxide removal even stiochiometric or under-stiochiometric additions. About 20-25 kg/hr hydrated lime is used. Temperature of the flue gases in the scrubber: 290-320 °C.

Step 3: The flue gases from the scrubber with primary and secondary dust enter an Electrostatic Precipitator to remove most of this dust. In case of the application of soda powder or sodium bicarbonate absorption agents, the EP corroded heavily by corrosive sodium sulfate* (sodium pyrosulfates, bisulfate, and water and sulfuric acid enriched sodium sulfates) and this behavior required frequent cleaning. Sometimes, the filter efficiency was poor, probably due to this fouling of the electrodes and electrode plates and slippage of dust or flakes of sodium sulfate/

bisulfates/pyrosulfates was observed and lead to fouling of the downstream heat exchanger and chimney.

Step 4: The treated flue gases pass a second heat exchanger to recover remaining flue gas heat for steam production. Although this waste heat boiler was downstream scrubber and EP, the fouling was considerable especially in case of soda or sodium bicarbonate as absorption agents in the scrubber.

The NO_x and SO₂ concentrations in the clean flue gases are monitored by a continuous analyzer. Since 2006, a new dosing system for powder injection into the reaction tower of the scrubber has been in operation. The addition/dosing of hydrated lime is now tightly controlled. The plant generates from the waste heat of the flue gases, steam (heat: 3 MW) and electricity (0.35 MW) for the city.

** Sodium sulfates in humid and SO₂/SO₃ rich flue gases may form below about 280-290 °C, sodium pyrosulfate (Na₂S₂O₇) and sodium bisulfate (NaHSO₄) Na₃H(SO₄)₂, these sulfates are reactive, sticky and may absorb sulfuric acid. The bisulfates react with steel. Deposition of these sulfates in the electrostatic precipitators, ducts or heat exchangers leads to fouling and corrosion.*

Literature: Mutsaers, P.L.M.; Beerkens, R.G.C.; de Waal, H.: Fouling of heat exchanger surfaces by dust particles from the flue gases of glass furnaces. Glastechn. Ber. 62 (1989) nr. 8, pp. 266-273

Signature

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