



SO₂ emissions and sulphur balances of soda lime glass melting furnaces

Report of the International Commission on Glass (ICG) Technical Committee 13 "Environment"

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Different analytical techniques for the determination of sulphur balances of glass furnaces have been compared by the Technical Commission 13 (TC 13 "Environment") of the International Commission on Glass (ICG). The calculation of sulphur balances are demonstrated for float glass and container glass furnaces. The results show the importance of accurate chemical analysis and mass flow measurements for cullet, glass, raw materials and filter dust to predict the sulphur oxide emissions. For float glass furnaces with and without air pollution control and filter dust recycling, the measured sulphur balances show that the difference in calculated sulphur input and sulphur output of the glass furnace plus air pollution control system can be limited to 5 %. For container glass furnaces the fluctuations in cullet fraction and cullet quality and instabilities in the melting process (foaming) may cause larger differences in measured sulphur balances: deviations in the range of 5 to 15 % have been determined. In case of a requirement for very low SO₂ emissions, the filter dust recycling for a fuel oil fired furnace is limited according to the sulphur balance and consequently the filter residue has to be partly disposed.

SO₂-Emission und Schwefelbilanz von Schmelzöfen für Kalk-Natrongläser

Verschiedene analytische Methoden für die Bestimmung der Schwefelbilanzen von Glasschmelzöfen sind durch das Technical Committee 13 (TC 13 „Umwelt“) der International Commission on Glass (ICG) verglichen worden. Die Berechnung der Schwefelbilanzen wurden für Floatglaswannen und Behälterglasschmelzöfen durchgeführt. Die Ergebnisse zeigen, daß die chemischen Analysen und die genaue Bestimmung der Massenströme der Scherben, des Glasproduktes, der Rohstoffe und der Filterstäube sehr wichtige Voraussetzungen sind, um die Schwefeloxidemissionen genau ableiten zu können. Für Floatglasöfen mit und ohne Abgasreinigungssystem und Filterstaubrückführung zeigen die gemessenen Schwefelbilanzen eine sehr gute Übereinstimmung zwischen den berechneten Mengen des ein- und ausgetragenen Schwefels. Die Abweichungen bleiben innerhalb 5 % des gesamten Schwefeleintrags. Die Schwefelbilanzen der Hohlglasschmelzöfen mit Einsatz von größeren Mengen Scherben zeigen Abweichungen von 10 bis 15 %, hervorgerufen durch Schwankungen im Scherbengehalt, in der Scherbenqualität und durch die oft relativ instabilen Schmelzverhältnisse (Schaumbildung) in der Wanne. Im Falle von sehr niedrigen Grenzwerten für die Schwefeloxidemissionen zeigt die Schwefelbilanz bei schwerölbefeuerten Wannen, daß ein Teil der Filterstäube nicht mehr eingeschmolzen werden kann und daß dieser Teil entsorgt werden muß.

1. Introduction

The Technical Committee 13 (TC 13 "Environment") of the International Commission on Glass (ICG) mainly focuses on methods to reduce emissions from glass industries and compares the legislations on emissions for

the glass industry in the different countries. However, the main activities also include the evaluation of measuring techniques for characterizing the flue gases of glass furnaces. Measuring methods have been compared and results have been published by this TC 13, for determining particulate concentrations in flue gases [1] and for the analysis of chlorides and fluorides in the waste gas streams of glass furnaces [2].

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Other important components in flue gases of glass melting furnaces are sulphur compounds. In the period between 1994 to 1997, TC 13 has organized a task force for the quantitative analysis of sulphur species in glass, filter dusts and in flue gases in order to be able to determine sulphur balances for float glass and container glass furnaces.

The majority of glass products are produced from raw material batches containing sulphates. In almost all cases, sodium sulphates and recently sulphate containing filter dusts are used as fining agents for the melting of float glass, container glass, tableware glass and E-glass. Also for some lighting glass products, sulphates are applied for aiding the removal of dissolved gases and gas bubbles from the melt. Sulphates in the batch perform three major functions:

- releasing fining gases by sulphate decomposition at high temperatures. The fining gases SO_2 and sometimes O_2 , in case of oxidized glass melts, will enhance bubble growth and bubble ascension in the glass melt, the bubbles will release their SO_2 contents in the furnace atmosphere.
- oxidizing the batch by supplying oxygen during decomposition.
- decreasing the surface tension of the primary melt in the batch blanket, improving the wetting of silica grains by the aggressive melt phases, in this way sodium sulphate acts as a melting flux.

In most glass furnaces 50 to 80 % of the added sulphates will dissociate during batch melting and fining. This will cause formation of SO_2 gas. When melting amber glass sulphur gas (S_2) may be released from the batch or melt, but the S_2 gas in the flue gases will be oxidized, forming SO_2 whenever some free oxygen is available. Sulphur impurities in batch ingredients as limestone, dolomite, clays and sulphur in cullet also contribute to the input of sulphur in the glass furnace, the introduced sulphur partly will evolve from the batch or melt.

The sulphur containing fuel will also be responsible for a large part of the SO_2 present in the exhaust gases of fuel oil fired glass melting furnaces. A level of 1 wt% sulphur in the fuel oil will lead to a contribution of 1180 to 1250 mg SO_2 per m^3 flue gas (= 1 m^3 flue gas standardized on 101.3 kPa, 273.15 K, dry conditions and 8 vol.% O_2 ; in this document m^3 always refers to standardized flue gas conditions in the case of air firing). For pure oxygen instead of air firing, the SO_2 concentrations in the flue gases will be much higher mainly due to the much smaller flue gas volume flows.

During the cooling process of the exhaust gases in the flue system, part of the sulphur oxides will react with sodium or potassium vapors or even lead vapors forming sulphate deposits (Na_2SO_4 , K_2SO_4 and PbSO_4) or condensation products in the temperature range from 700 to 1100 °C. This process will lead to fouling of regenerators or recuperators and particulate formation. At lower temperatures [3] sulphur trioxide and sulphuric acid can be formed, sodium sulphate particulates absorb

sulphur oxides creating sodium pyrosulphate or sodium bisulphates below about 275 °C. In scrubbing systems, using hydrated lime ($\text{Ca}(\text{OH})_2$) injection or absorption by soda, part of the sulphur oxides are captured by the scrubbing agent. Using lime as a scrubbing medium, calcium sulphite or calcium sulphate will be formed. Sodium sulphate is the major reaction product, when using soda or a soda solution as the scrubbing medium.

The chemistry of sulphur species in the batch blanket and flue gases appears to be complex. The mechanism of the reactions of sulphur species in the batch blanket depends on the redox state of the batch, which for instance depends on the presence of organic contaminants or cokes [4 and 5]. The maximum fining temperature and composition of the furnace atmosphere [5] appears to have an important impact on the sulphur distribution among the flue gases and glass products.

Figure 1 shows the sulphur retention in soda-lime-silica glasses, depending on the redox state of the batch or glass at three different temperature levels and depending on the furnace atmosphere humidity. For the oxidized compositions (low $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio), the decreased sulphate retention at higher water vapor pressures is shown, comparing curve 3 and curve 4. Sulphur retention decreases at higher melting/fining temperatures or at increasing water vapor pressure in the furnace atmosphere. Humidity and temperature seem to be less important for the sulphur solubility or retention in reduced glasses. In very reduced glasses, sulphur dissolves mainly as sulphide.

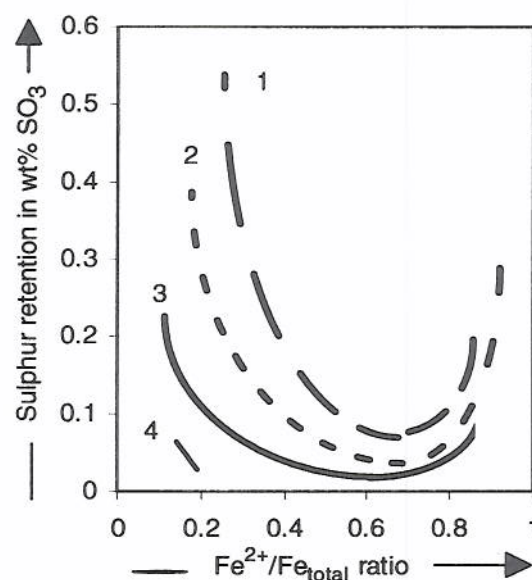


Figure 1. The sulphur retention in soda-lime-silica glass after melting and fining depending on redox state, furnace atmosphere and temperature [4 and 5]. Reference glass composition (in wt%): 70.8 SiO_2 , 14 Na_2O , 10 CaO , 2 MgO , 2 Al_2O_3 , 1 K_2O , 0.2 Fe_2O_3 and 0.02–0.3 SO_3 . Curve 1: maximum temperature = 1250 °C, dry atmosphere; curve 2: maximum temperature = 1350 °C, 0.17 bar water vapor; curve 3: maximum temperature = 1500 °C, dry atmosphere; curve 4: maximum temperature = 1500 °C, 0.55 bar water vapor.

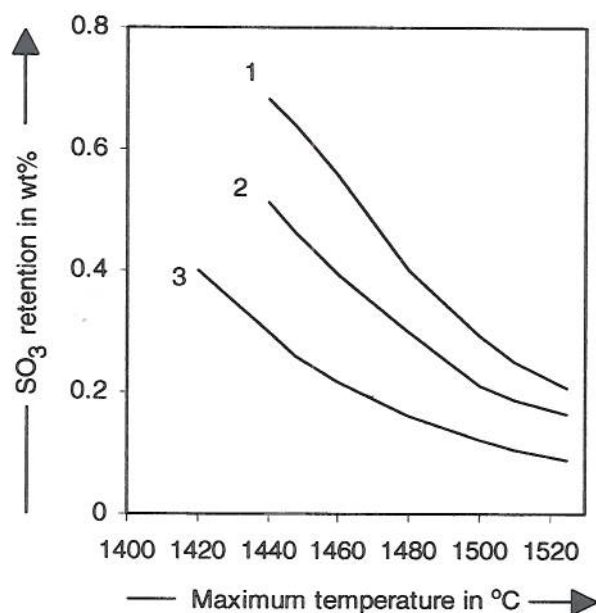


Figure 2. Impact of water vapor pressure and temperature on sulphate retention in oxidized flint glass melt. Glass composition (in wt%): SiO₂:Na₂O:CaO = 75.1:15.5:9.4 plus 1 wt% Na₂SO₄ addition per 100 kg glass [4 and 5]; curve 1: p_{H₂O} = 0.01 to 0.02 bar; curve 2: p_{H₂O} = 0.18 to 0.21 bar; curve 3: p_{H₂O} = 0.5 to 0.6 bar.

An increase in melting temperature or a shift to more reducing batches (for instance by introduction of increased levels of organic contaminants) will increase the release of SO₂ from the glass melt. This behaviour shows that the specific SO₂ emissions depend very much on temperature of the melt, the humidity of the furnace atmosphere and the redox of the batch which might vary, due to organic contaminants in the cullet [5]. Figure 2 shows the impact of the water vapor pressure in the furnace atmosphere on sulphate retention and figure 3 the impact of the furnace atmosphere humidity on the specific SO₂ release from the oxidized soda lime glass melt using 1 kg sodium sulphate for 100 kg glass.

The figures 1 to 3 show that the sulphur retention or emissions of sulphur species depends on the redox state of the batch, the maximum melting/fining temperature and the water vapor pressure above the melt. Water infiltrating the melt, may lower sulphate retention and can influence the redox state (Fe²⁺/Fe³⁺ ratio) in the glass. Also reducing conditions in the furnace atmosphere may cause enhanced sulphate decomposition, especially at the surface of the batch blanket or glassmelt.

2. Objectives of the determination of sulphur balances

Nitrogen oxides, dust particulates, fluorides, chlorides and SO₂ are important components in flue gases of glass furnaces. The determination of sulphur balances for glass furnaces gives important information on the major sources of SO₂ emissions but also will identify possible

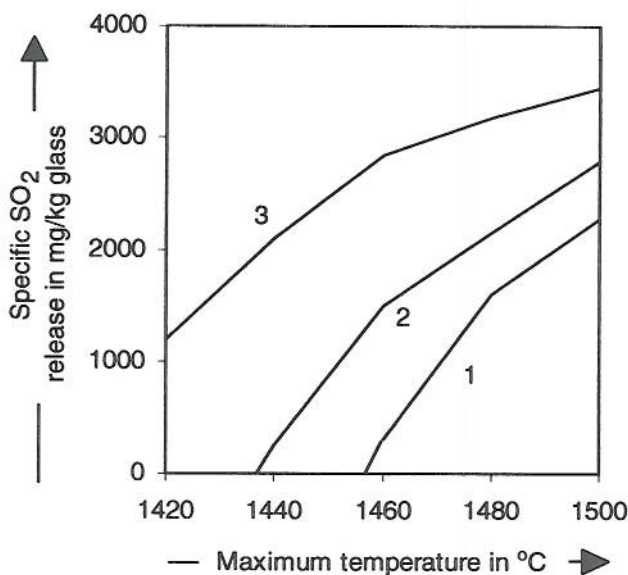


Figure 3. Specific SO₂ release from oxidized flint glass melt depending on water vapor level and temperature in furnace atmosphere. Glass composition (in wt%): SiO₂:Na₂O:CaO = 75.1:15.5:9.4 plus 1 wt% Na₂SO₄ addition per 100 kg glass [4 and 5]; curve 1: p_{H₂O} = 0.01 to 0.02 bar; curve 2: p_{H₂O} = 0.18 to 0.21 bar; curve 3: p_{H₂O} = 0.5 to 0.6 bar.

ways to reduce the emissions of sulphur oxides. From these sulphur balances, one may derive the impact of batch or process changes on sulphur oxide emissions. Sulphur balances can also be used to estimate, within 10 to 20 % accuracy (maximum error), the SO₂ emissions without using expensive flue gas analytical systems, but by a precise analysis of batch components and the glass.

This paper summarizes sulphur balances determined for float glass and container glass furnaces by TC 13 members and will show the accuracy of a sulphur balance and possibilities to predict SO₂ emissions from furnaces by measuring sulphur input by the batch components and fuel and sulphur concentration in the produced glass (and when applying fabric filters or electrostatic precipitators: measuring sulphur in the collected filter dusts).

3. Sulphur species in flue gases

After the regenerator or recuperator, flue gases contain gaseous and particulate components. In most soda lime glass furnaces the dust exists for more than 80 % of sodium sulphates as sub micron sized particulates. However, most of the sulphur is still in the gaseous form, above 500 °C mainly as SO₂. At lower temperatures sulphuric acid (<200 °C) and SO₃ may also be present. Generally the SO₃ content will be only a few percent of the total sulphur oxide concentrations in glass furnaces flue gases. Only in the case of slow cooling rates of oxygen and water rich flue gases, as might be the case for oxygen fired glass furnaces, sulphur trioxide formation might become more important.

Since 1980, glass furnaces in Western Europe are increasingly being equipped with scrubbing systems in order to separate gaseous fluorides, chlorides, sulphur oxides and selenium oxides from the flue gases. A powder, solution or suspension of lime, hydrated lime, dolomite, magnesium oxide or soda are injected in the flue gases and particulate fluoride, chloride, sulphate/sulphite, selenate/selenite components will be formed which can efficiently be separated by fabric textile or polymeric bag-house filters or electrostatic precipitators. The collected filter dusts often can be used as fining agents in the melting process.

For the determination of the total sulphur emissions of glass furnaces, the sulphur in all relevant flue gas species such as SO_2 , SO_3 , H_2SO_4 (g or l), NaHSO_4 (s), Na_2SO_4 (s), CaSO_4 (s), CaSO_3 (s), MgSO_4 (s) has to be taken into account (g, l and s stand for gaseous, liquid and solid).

4. Sulphur balances of glass furnaces

Only at stable conditions, which includes constant temperatures in the furnace, no fluctuations in batch composition, no variations in the impurity levels in the batch, constant fuel consumption and fuel composition and hardly changing furnace atmospheres, the input of sulphur species in the furnace by batch and fuel at each moment will be the same as the output by the glass melt and flue gases together, assuming no accumulation of sulphur species in the glass furnace system. However, deposition of sulphates in the regenerators, recuperators or flue gas channels will decrease the output of sulphur species by the flue gases. Especially in the initial stages of a furnace campaign, deposition at the clean surfaces of the checker bricks or elements in the regenerator chambers will lower the sulphate concentrations in the gas flows.

Analysis of sulphur concentrations in the flue gases before the regenerators and in the flue gases behind the checkers and the amounts of sulphates collected from regenerators after cleaning of the checkers, lead to the conclusion that only 1 to 5 % of the sulphur in the flue gases will be retained in the flue gas system [6]. An example: for three container glass furnaces the total amount of removed deposits during a period of five years has been weighed. The total amount of salts from the regenerators of these three furnaces during five years was 233 t after a total production of $1.34 \cdot 10^6$ t of glass. The average sulphur content in this salt is 20.6 %. The total sulphur deposition per t glass is 33 g. The total input of sulphur is about 3000 to 4000 g per t glass. Thus, the measured average sulphur deposition in the regenerators is about 1 % of the sulphur input.

In the industrial practice, fluctuations in the sulphur emissions and sulphate or sulphide retention levels in the glass occur, because:

- batch compositions may change due to errors in weighing of the single batch ingredients;
- sulphur (sulphide/sulphate) concentration levels in some batch components will be variable, this is especially the case for sulphate and sulphide concentrations in external recycled cullet [7];
- the sulphur content in the fuel oil may change due to changes in supplier or oil quality;
- the temperature in the melting furnace is not stable, the maximum temperature during fining will influence the sulphate retention in the melt: for example an increase of 10°C in the fining area may decrease the residual sulphate content in the oxidized flint glass by 0.02 to 0.04 wt%;
- the redox state of the batch, i.e. presence of reducing agents in float glass, in flint glass, in green glass or in E-glass batches will lead to increased sulphate decomposition rates during heating of the batch blanket. However, very reduced conditions, as might be met at very strongly polluted cullet will increase the sulphur retention in the glass by the formation of sulphides, responsible for the amber coloring in presence of ferric iron (Fe^{3+}) in the glass.

The accurate determination of a sulphur balance for a glass melting furnace requires very stable raw material compositions, constant batch formulation and a steady combustion process. For regenerative furnaces, average compositions of the flue gases should be measured over a longer period including an even number of combustion cycle periods. In these furnaces, the SO_2 levels measured in the flue gas might depend on the firing side. Even at stable conditions, a reliable sulphur balance analysis requires:

- precise sampling methods for the single raw material ingredients or the well mixed complete batch and
- an accurate flue gas diagnosis, taking all sulphur containing species into account.

An extra complication will be encountered when determining the sulphur balance of a glass furnace, using a scrubbing and filtering system with recycling of the filter dusts into the batch. Representative sampling of the dusts from filters seems to be problematic since the dust composition might be dependent on the section of the filter system and variations in composition may be caused by unstable conditions in the scrubbing systems. Temperature and humidity have an important effect [8] on the measured filter dust composition or redox state of the dust [7]. The absorption efficiency by scrubbers depends on temperature and applied absorption medium, as shown by Kircher [9] for chlorides, fluorides and selenium oxides. The highest sulphur oxide absorption efficiencies are reported for low scrubber temperatures ($<200^\circ\text{C}$) using soda or sodium bicarbonate as scrubbing agents [7]. The SO_2 absorption by $\text{Ca}(\text{OH})_2$ powder, applying slightly over-stoichiometric additions, reaches levels of 40 to 60 % in the temperature range of 300 to 425°C , injection of a soda solution below about 200°C at stoichiometric conditions shows SO_2 absorption ratios of 80 to 90 % [10].

5. Sampling and analytical methods

The sampling procedure of mass streams containing sulphur species, necessary to determine sulphur balances, includes:

- collection of well mixed batch or individual batch components;
- sampling of the cullet;
- sampling of the glass products;
- sampling of the filter dusts;
- extraction of flue gas before and/or behind the air pollution control equipment;
- sampling of the fuel oil.

In all cases, at least three samples should be taken from each individual sulphur containing flow of materials or gases, to investigate reproducibility of the sampling procedures and of the analysis methods.

The average residence time of the melt in the furnace should be taken into account for determining the suitable time to take the glass product samples after the moment of sampling of the raw materials and flue gases. Not only the sulphur concentrations in the flue gases, raw materials and glass product have to be measured, but also the mass or volume flows of batch components, cullet, filter dusts, flue gases and glass melt should be precisely known. It is recommended to determine the sulphur balance during a period of apparently stable production conditions during a period of at least five days.

As sampling method of the dusts from the flue gases, often the in-stack method [11 and 12] is used. The particulates are collected by isokinetic sampling techniques. The collected dust in the filter is completely dissolved in an acid solution (HNO₃/HCl) or occasionally by HF and then analyzed by ICP-ES or AAS methods [13]. The dust concentration is calculated from the weight gain of the filter and from the extracted gas volume flow through this filter. The gas is dried before measuring the volume flow rate. The oxygen contents in this gas and the temperature should be measured as well in order to express the dust concentration in mg per m³ dry flue gas, standardized to 8 vol.% O₂ at 1.013 bar and 273 K. Sometimes also out-of-stack filters conditioned at 200 or 300 °C are used, however this might give different dust concentrations as measured by in-stack filters [1], due to extra condensation of gaseous components such as sulphuric acid in combination with sodium bisulphate (NaHSO₄).

The total mass flow of sulphur incorporated in flue gas dust can be derived from the dust composition, dust content in the flue gases and volume flow rate of the flue gases.

Sampling and analysis of gaseous sulphur oxides in flue gases: the flue gases are extracted from the flue gas channel by a heated probe with a temperature of at least 200 °C but preferably above 250 °C (depending on the fuel, firing oil with 1 % sulphur may require temperatures > 300 °C) to avoid condensation of sulphuric acid

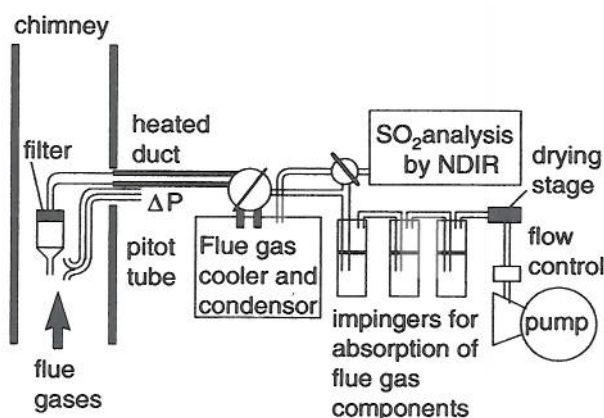


Figure 4. Extraction and filtration of flue gases and collection or continuous analysis of sulphur components.

components in the sampling system. The flue gas dust is separated using an in-stack filter or out-stack filter in the sampling system. Then, the gaseous sulphur oxides are collected in an H₂O₂ solution which absorbs SO₂, SO₃ and H₂SO₄. To measure the SO₃ content, the application of the method in [14] (to assure complete absorption of the SO₃ components in the solvent and to avoid slip of sulphuric acid aerosols) is preferred. In this method, the extracted gas (kept above 220 °C up to the scrubber in this analytical system) is scrubbed by a peroxide-free solution from 80 % 2-Propanol and 20 % water which will absorb the SO₃ at the surface and in the pores of a filter plate. Droplets of the solution and the gas are brought together in the filter which allows efficient absorption of the SO₃ gas. Finally, the installation will be rinsed by the 2-propanol solution and then the final solution will be purged by air to remove the physically absorbed SO₂. The amount of chemically absorbed SO₃, in the form of sulphate can be measured by a barium perchlorate titration. Another method for the determination of sulphuric acid mist and sulphur dioxide concentrations in flue gases is given in [15].

For SO₂ sampling and the analysis of SO₂ in flue gases, other methods can be used based on extraction of gases and dissolution of SO₂ in H₂O₂ solvents plus titration of the sulphate formed [16]. Other methods are based on continuous analysis of SO₂ in extracted and predried flue gases using infrared non-dispersive Infrared Spectroscopy (NDIR) methods or non-dispersive Ultraviolet Differential Absorption (NDUV) methods [17]. Figure 4 presents the extraction and filtration of flue gases from a flue gas channel. SO₂ gases can be continuously analyzed by NDIR (or NDUV) or gaseous sulphur species can be collected in impingers filled with an absorption medium.

Sampling of single raw materials appears to be rather simple, but filter dusts and recycled cullet may show very strong composition fluctuations. Awareness of the fluctuating compositions of these raw materials and some minerals is important. Sometimes a large number of samples have to be collected to obtain a representative

Table 1. Round robin test on the analysis of filter dust from a float glass furnace; the dust was collected from electrostatic precipitator with Ca(OH)_2 pretreatment

	concentrations in dust given in wt%							average value	standard deviation
	Lab 1, XRF method	Lab 2, XRF method	Lab 3, XRF method	Lab 4, wet chemical method	Lab 5, wet chemical method	Lab 6, XRF method	Lab 7, XRF method		
SiO_2	0.01			0.3	0.37				
Na_2O	5.5	4.92	5.72	5.3	5.4	5.01	5.75	5.371	0.322
K_2O	0.13	0.22	0.18	0.16	0.16	0.17	0.16	0.169	0.026
CaO	50.8	50.93	68.9	53.4	54.7	53.89	55.5	55.446	6.193
MgO	0.6	0.68	0.46	0.58	0.6	0.7	0.72	0.620	0.089
Al_2O_3	0.13					0.1	0.1		0.017
SO_3	15.3	15.75	17.5	14.96	15.53	15.41	15.41	15.695	0.831
Fe_2O_3	0.16	0.19	0.16	0.16	0.2	0.21	0.21	0.184	0.024
PbO	0.04	0.01			0.017		0.015	0.021	0.013
NiO	0.01	n.a.							
ZnO	0.01	0.02			0.024			0.018	0.007
V_2O_5									
As_2O_3	0.03								
SeO_2		1.95	0.91	1.88	1.76			1.625	0.483
Cl^-		2.80	3.15	2.95	3.02	2.98	2.88	2.963	0.120
F^-		0.425 ¹⁾							

¹⁾ Measured by ion chromatography.

analysis of the cullet or the filter dust material. Filter dusts from electrostatic precipitators or baghouse filters have to be collected from different positions in the filter system and the filter dusts have to be extremely well mixed to obtain a representative "average" filter dust sample. Differences in sulphur concentrations in the filter dusts can be caused by differences in temperatures in the filter, differences in the age of the dusts and local differences in the load of the scrubbing medium in the flue gases due to non-uniform conditions in the scrubber.

The analysis of the batch ingredients, filter dusts and cullet is often carried out by X-ray fluorescence methods. For low sulphur contents high-temperature sulphur/ SO_2 extraction methods are used coupled to IR analysis of the released sulphur oxides. Sometimes after complete dissolution of the material, ICP-ES, ion chromatography or other wet chemical methods will be applied.

In the framework of one of the ICG Technical Committee 13 task forces, a round robin test on the analysis of a well mixed dust from a regenerative furnace has been carried out. The well mixed dust originated from an electrostatic precipitator behind a dry scrubber using hydrated lime. This natural gas fired furnace produced float glass. The average measured sulphur concentration in this well mixed filter dust is 15.7 wt% with a standard deviation of 0.8 wt% which is about 5 % of the average value. However, excluding the lowest and highest value in the round robin tests, the average value is 15.5 wt% and the standard deviation drops down to 0.17 wt%. All values have been determined by X-ray fluorescence, each laboratory using its own calibration samples. Table 1 summarizes the results of the round robin test including

also the results of the analysis of other relevant elements in this sample. This table shows the fairly good agreement also for the components: Na_2O , K_2O , CaO (after exclusion of the highest value), MgO , Fe_2O_3 and Cl^- . In total 16 different laboratories (results of 7 laboratories are given here) analyzed the same dust and the wet chemical analysis showed an average value of 15.1 wt% sulphur and the XRF analysis 15.5 wt% sulphur in this dust. The relative error in the analysis is estimated on less than 5 %. A second round robin test on the analysis of salts from regenerators of container glass furnaces showed the same accuracy level. The regenerator chambers deposits contained 55.6 wt% SO_3 (± 1.6 wt%). The other major components in these deposits are sodium ((21.45 ± 0.1) wt% Na_2O), magnesium ((10.6 ± 0.6) wt% MgO), calcium ((4.5 ± 0.12) wt% CaO) and some potassium, lead and silicon probably in oxide, carbonate or sulphate form. From the results of these round robin tests, the conclusion can be drawn that sufficient accurate compositions for filter dusts or deposits, using these analytical techniques, can be obtained.

Another round robin test has been organized by TC 13 for the determination of sulphate or sulphide in two different glass samples. The first sample is a clear float glass sample analyzed by XRF, a high-temperature SO_2 extraction method plus IR analysis or ICP-ES after dissolution. The average SO_3 concentration measured by 8 different laboratories (9 analyses) is (0.23 ± 0.024) wt%. No systematic differences between the XRF and ICP-ES methods have been observed. Amber glass analyses performed by 8 different laboratories using the same techniques as for the float glass sample gave an average value for SO_3 of (0.041 ± 0.01) wt%.

Table 2. Redox number (Simpson) values [7, 19 and 20] and typical sulphur concentrations expressed as SO₃ (in wt%) in glass products

glass	sulphate or sulphide given as SO ₃ in wt%	Redox number (Simpson scale)
clear float	0.18 to 0.28	10 to 20
flint	0.15 to 0.22	10 to 15
reduced flint	0.10 to 0.15	0 to 5
oxidized green container	0.1 to 0.2	5 to 15
reduced green container	0.03 to 0.06	-10
feuille morte	0.02 to 0.04	-10 to -20
amber	0.03	-20 to -30
dark amber	0.05 to 0.1	-35

Accurate analysis of sulphur in all raw materials and the produced glass is a necessity when preparing useful sulphur balances. The largest fluctuations in sulphur input have been observed for glass furnaces using large quantities of recycled cullet, especially in the container glass industry. A recommended sampling procedure for cullet is given by Faber et al. [18]. For green glass production sometimes the total batch contains more than 50 % mixed cullet. Table 2 gives typical concentrations of sulphur (calculated as SO₃) in different types of glass [19 and 20]. Cullet mixtures with variable fractions of different colors will have fluctuating sulphur contents and variable redox states [7]. A flint glass rich cullet mixture contains more sulphate and is generally more oxidized than a cullet sample containing large quantities of reduced green glass. The sulphur concentration in the waste glass depends very much on the color mixture in the cullet. Another complication when using recycled waste glass is due to the presence of organic components in the cullet, these organic components will finally impose a reducing power on the glass melt. This leads to an increase in the ferrous/ferric ratio and a decrease in the sulphate retention in the glass products. At very reducing conditions, sulphide can be formed and sulphur retention increases again as reduction by organic components further goes up.

6. Sulphur balances for industrial glass furnaces

The sulphur balance of a glass melting furnace at steady state conditions is given by:

$$\sum_i S_{\text{batch}i} + S_{\text{fuel}} + \sum_j S_{\text{cullet}j} = S_{\text{glass}} + S_{\text{SO}_2} + S_{\text{SO}_3} + S_{\text{dust}} + S_{\text{deposition}}$$

where

$S_{\text{batch}i}$ = sulphur input by batch ingredient i (in kg/h),

S_{fuel} = sulphur input by fuel (in kg/h),

$S_{\text{cullet}j}$ = sulphur input by cullet type j (in kg/h),

S_{glass} = sulphur in glass pull (in kg/h),

S_{SO_2} = sulphur in the form of flue gas SO₂ (in kg/h),

Table 3. Data of float glass furnace

glass production in t/d	720
added own cullet in % (based on glass production)	12
added foreign cullet in %	0
type of glass	clear float (soda lime glass)
fuel	low sulphur fuel oil (< 1 wt% sulphur)
SO ₃ content (in wt%) in final glass product	0.292
filter system	electrostatic precipitator + scrubbing
filter dust recycling	completely

S_{SO_3} = sulphur in SO₃ or sulphuric acid form in flue gases (in kg/h),

S_{dust} = sulphur in the form of particulate species in the flue gas (in kg/h),

$S_{\text{deposition}}$ = sulphur deposition in flue gas system (in kg/h).

The mass flows S_{SO_2} , S_{SO_3} , S_{dust} should all be measured at the same extraction point in the flue gas system. The measurements should include the determination of the gas flows at standardized conditions, dust concentrations at this location in the flue gases and sulphur analysis in the dusts. The sulphur deposition in the regenerators, recuperators or flue gas channels down to this measuring location is given by $S_{\text{deposition}}$.

A sulphur balance can also be determined for a scrubber plus filter system:

$$S_{\text{SO}_2,1} + S_{\text{SO}_3,1} + S_{\text{dust},1} = S_{\text{SO}_2,2} + S_{\text{SO}_3,2} + S_{\text{dust},2} + S_{\text{filterdust}}$$

The number 1 refers to the flue gas before the air pollution control equipment and the number 2 refers to the cleaned flue gas behind the filter system. $S_{\text{filterdust}}$ is the amount of sulphur removed from the flue gas by the separation of the sulphur containing particulates from the flue gas. In most cases $S_{\text{deposition}}$ will be neglected, this might give an error of 1 to 5 % in the sulphur balance. In the case of complete filter dust recycling, one of the sulphur containing batch ingredients is the filter dust which contributes to the sulphur input in the furnace.

Even small errors in sampling, inaccuracies in the chemical analysis and fluctuations, due to small changes in batch or process conditions might lead to large errors in the sulphur balances. Most sensitive for errors are the sulphur balances of container glass furnaces using external cullet.

In the framework of the TC 13 task force "Sulphur balances of glass furnaces", the sulphur input and sulphur output for three industrial glass furnaces have been determined: two float glass furnaces and one container glass furnace. Compositions and mass or volume flows of the raw materials, cullet, flue gases and glass products have been determined.

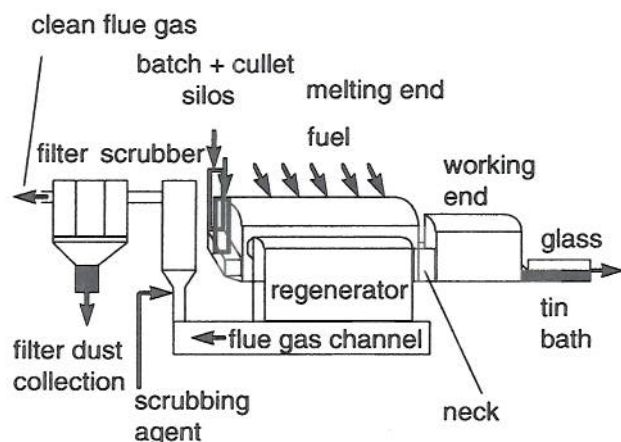


Figure 5. Float glass furnace and air pollution control equipment.

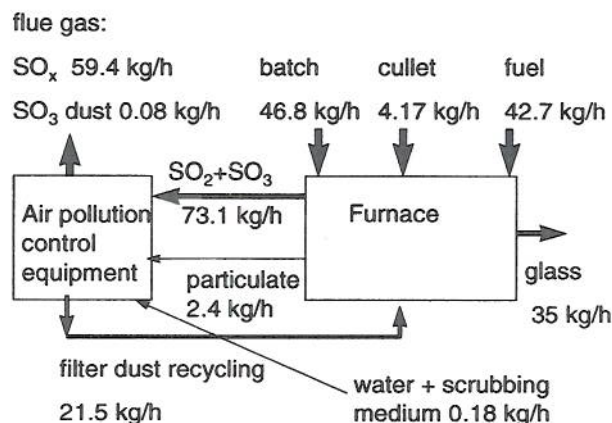


Figure 6. Sulphur mass flows (in kg sulphur/h) in float glass furnace equipped with scrubber and electrostatic precipitator.

The first example is derived for a float glass furnace. Table 3 shows the relevant process data of this furnace. Only internal cullet recycling is applied. Some scrubbing solution has been injected in the flue gases upstream of the electrostatic precipitator (ESP) to remove part of the chlorides, SO_2 and SO_3 from the waste gas. The original flue gas particulates and the scrubbing reaction product are precipitated in the ESP. The major contributors to the sulphur input are salt cake, filter dust, fuel oil, iron blast furnace slag and the own cullet. Sulphur dioxide gas, sulphur containing dust in the flue gases and sulphur in the glass products represent more than 95 % of the sulphur output. Table 4 shows the results of the sulphur balance measurements. The table shows also the estimated maximum errors in the measured mass flows of sulphur. The difference between the sulphur input and output is about 4 %, which is within the expected accuracy range. A small part of this 4 % difference is probably also caused by sulphate depositions in the regenerators and flue gas channels. Prediction of the SO_2 emissions from sulphur balances would lead to maximum er-

rors (worse case) of 15 % for this case. Some sulphur not included in the sulphur balance might originate from the sorbent, suspended or dissolved in the water which is used as scrubbing medium, but generally the contribution of this sulphur source is very small. Figure 5 shows schematically the glass furnace and air pollution control equipment. The sulphur balance is presented by the scheme in figure 6.

The SO_2 concentration in the flue gas of this furnace can theoretically be reduced down from 1840 till about 800 mg/m^3 and still complete recycling of the filter dust applied, instead of any salt cake addition to the batch. Reducing the SO_2 to lower levels in the flue gas of this oil fired furnace will generate a surplus of residues to be disposed. In oil fired furnaces, reduction of sulphur oxide emissions by application of scrubbers is limited if complete filter dust recycling is requested in order to avoid solid waste. Especially for glasses with low sulphate solubility melted in oil fired furnaces, a high SO_2 scrubbing efficiency will lead to generation of filter dust to be treated and disposed.

Table 5 presents the sulphur balance for another float glass furnace, in this case a natural gas fired furnace, producing 600 t glass per day for clear flat glass production. The cullet to normal batch ratio based on glass weight is 40:60, only clear float glass cullet is used. In this case flue gas treatment by scrubbers or filters is not operated. The examples show that 99 % of the total sulphur input could be found back in the identified output mass flows for the case of this float glass furnace operating at constant conditions with constant glass and cullet quality. In three other float glass furnaces, all fired with natural gas, sulphur balances could be obtained with hardly any difference between input and output.

Stable conditions, as can be met in float glass operation using own cullet and constant raw material compositions and precise analysis, allows accurate predictions of sulphur oxide emissions derived from the sulphur balances.

The next example is the situation for a container glass melting furnace, 72.5 % of the glass is produced from externally recycled cullet. Due to the relatively large uncertainties in the sulphur levels of the recycled cullet, the sulphur balance of the container glass furnace shows a larger mismatch between input and output. Fluctuations in redox state of the cullet will cause variations in sulphur dioxide release during melting and fining. The measured SO_2 concentrations in the flue gases are not stable and also the produced glass shows fluctuations in sulphate contents. Figure 7 shows the fluctuations in the continuously measured SO_2 flue gas concentrations for a container glass furnace, using recycled cullet from external sources, the process performs at apparently constant process conditions and without intended batch changes. The sulphur balance for the container glass furnace is schematically presented in figure 8, table 6 gives some process data for this container glass furnace.

Table 4. Sulphur balance of float glass furnace (case 1)

	sulphur concentration analyzed in different materials		sulphur mass flow in kg/h	maximum error of sulphur mass flow in kg/h
	in kg/t material	in mg/m ³ flue gas		
<u>input in the furnace</u>				
sand, dolomite, limestone etc.			15.13	0.55
sodium sulphate	170.4		31.64	1.11
own cullet	1.168		4.17	0.25
filter dust	212.72		21.55	1.51
fuel oil	9.25		42.67	1.92
total sulphur input			115.16	5.34
<u>output from the furnace</u>				
glass	1.168		35.04	2.10
flue gas before scrubber		920.5	73.05	7.31
as particulates before scrubber		30.31	2.41	0.48
total sulphur output			110.50	9.89
ratio sulphur input/output 1.042 = 115.16/110.50				
<u>input in the scrubber + ESP</u>				
flue gas before scrubber		920.5	73.05	7.31
as particulates before scrubber		30.31	2.41	0.48
sorbent plus water	0.04		0.18	<0.01
cooling water	0.031		0.13	0.01
total sulphur input			75.77	7.81
<u>output from the scrubber + ESP</u>				
flue gas after scrubber		749	59.44	5.94
filter dust	212.12		21.49	1.29
as particulates after scrubber		1.072	0.09	0.02
total sulphur output			81.02	7.25
ratio sulphur input/output 0.935 = 75.77/81.02				

Table 5. Sulphur balance of float glass furnace fired with natural gas/air, without air pollution control (case 2)

	sulphur concentration analyzed in different materials		material mass flow		sulphur mass flow in kg/h	maximum error of sulphur mass flow in kg/h
	in kg/t material	in mg/m ³ flue gas	in t/h	in m ³ /h		
<u>input in the furnace</u>						
normal batch	1.783		15 ²⁾		26.75	1.61
own cullet	0.96		10		9.6	0.58
natural gas	0				0	0.000
total sulphur input					36.35	2.19
<u>output from the furnace</u>						
glass	0.96		25		24	1.44
flue gas – sulphur as SO _x		148		74078	10.96	1.10
– sulphur in particulates		20			1.48	0.18
(SO ₃ in dust 53.3% and dust in flue gas 93.7 mg/m ³)						
total sulphur output					36.44	2.71
ratio sulphur input/output 0.997 = 36.35/36.44						

²⁾ Based on mass glass production.

The average SO₂ concentration in the flue gas measured directly by flue gas analysis after the air pollution control equipment is, at standardized conditions, 955 mg/m³. The prediction of the average SO₂ gas concentration derived from raw material sulphur input,

sulphate level in the glass and dust composition is 1053 mg/m³ and 10 % different from the measured value. A critical analysis of the maximum errors expected for the prediction of the sulphur oxide emission of this furnace derived from sulphur mass balances would give a

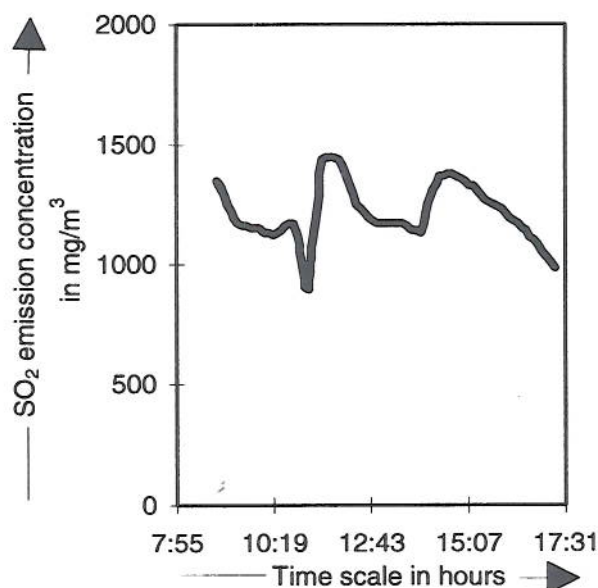


Figure 7. Measured SO_2 concentrations by on-line IR analysis of extracted flue gas for a container glass furnace using 40 % mixed external cullet, the plot has been drawn from 1/2 h average values.

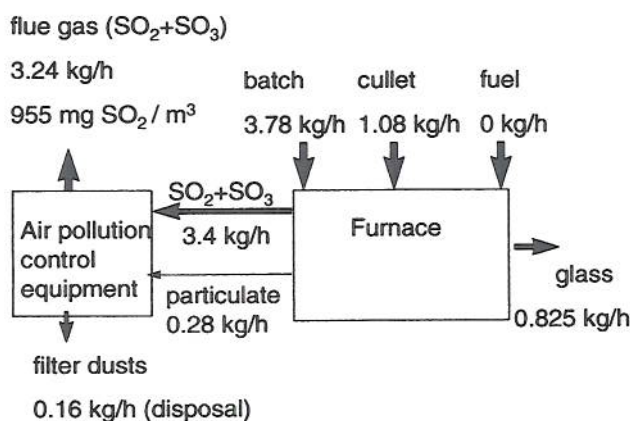


Figure 8. Sulphur mass flows (in sulphur/h) measured for a container glass furnace.

range of 850 to 1250 $\text{mg SO}_2/\text{m}^3$. The measurement of the sulphur level in the batch and cullet and the total flue gas volume flow will lead to the largest inaccuracies.

Batches prepared for container glass furnaces using cullet with large quantities of organic contaminants often contain extra sodium sulphate, necessary to oxidize the reducing components in the batch in order to obtain the required redox state and color of the glass. This extra sulphate will be completely decomposed and leads to foaming and extra SO_2 emissions. Batch compositions frequently have to be corrected based on the (measured or expected) level of organic contaminants using sulphate as an oxidant and this may cause strong fluctuations in the day-to-day measured SO_2 concentrations in the flue gases of these furnaces.

Table 6. Data of container glass furnace

glass production in t/d	99
added own cullet in % (based on glass production)	72.5
added foreign cullet in %	about 60
type of glass	medium dark green glass
fuel	natural gas/air
SO_3 content (in wt%) in final glass product	0.05 ± 0.01
scrubber agent	dry hydrated lime ($\text{Ca}(\text{OH})_2$)
filter system	baghouse fabric filter plus water quenching
filter dust recycling	yes
SO_3 content (in wt%) in cullet	0.09 ± 0.015

7. Accuracy of sulphur balances

The mass flows of sulphur are calculated from the concentrations of sulphur in the raw materials, in cullet, in glass, in filter dusts or in the flue gases multiplied by the mass or volume flows of these streams into or from the furnace. Of course the analysis of raw materials, flue gases, filter dusts and fuel has to be carried out very accurately in order to obtain reliable sulphur balances.

In case of accurate determinations, the relative error in measuring glass melt loads of furnaces is estimated on 1 %, for the single batch components the error is about 1 to 2 %. The flue gas flow at standardized conditions can be determined by pitot tubes correcting the volume flow to standardized conditions (dry flue gas, 8 vol.% oxygen) after determining the humidity and oxygen concentration of the flue gas. The error might reach levels of 5 %. Flue gas volume flows can also be estimated from the fuel consumption, the fuel composition, from the volume of the batch gases (CO_2 , O_2 , SO_2) and the measured oxygen or CO_2 concentration in the predried flue gas. After carefully performed analysis and calculations, the maximum error in the determined flue gas volume flows will be about 3 to 5 %.

The analysis of sulphur in the glass by ICP-ES, XRF or extraction methods leads to errors of about 5 %. In raw materials this error is 2.5 to 5 % depending on the solubility of the raw material in acid solutions. The dissolution of slags or cullet is much more difficult than the dissolution of raw materials like limestone, dolomite, sodium sulphate and soda. The dissolution of slags and glasses asks for rather complicated techniques using acid solvents and for instance dissolution procedures in closed teflon vessels to be heated in microwave furnaces. Therefore precise sulphur analysis for slags and glass is more complicated compared to other materials and therefore a larger error has to be taken into account, especially at low sulphur concentrations.

The largest error is expected for the sulphur contents in the filter dusts, this error is mainly caused by fluctuations in sulphur levels, the determination of the amount

of filter dust production and the inhomogeneity of filter dusts collected from baghouses or electrostatic precipitators. An error of 5 % has been assumed for the average sulphur content measured in filter dusts.

Inaccuracies in the analysis of the average SO₂ concentrations in the flue gases are caused by small calibration errors (error: 1 %), inaccuracy of chemical analysis (1 to 2 %), interference with other components (1 %), fluctuations of SO₂ levels in time (3 to 5 %), losses during extraction of flue gas sample (1 %). The total maximum error for the measured SO₂ concentration in the flue gases is about 8 to 10 %.

The determination of the dust concentration in the flue gases might also be rather inaccurate, errors up to 5 % can be expected if the measurement is properly applied, in some cases this error can be much higher.

Table 4 shows the absolute errors which can be made for the individual sulphur mass flows for the previously discussed float glass furnace (table 3).

8. Conclusions

The within 5 % closed sulphur mass balance for the float glass furnace equipped with scrubber and electrostatic precipitator, given in table 4, leads to the conclusion that it is possible to predict emissions of sulphur from glass furnaces, derived from accurately measured sulphur concentrations in raw materials, in the fuel and the analyzed sulphur concentration in the final glass product. The largest errors are made in determining the average SO₂ concentration in the flue gases and the average sulphur contents in the filter dusts since these values may fluctuate strongly within a timescale of a few hours. Sulphur mass balances generally become less accurate for furnaces using large quantities of foreign often mixed colored cullet. This is often the case for green and amber glass furnaces in Western Europe, sometimes using up to 60 to 70 % mixed cullet in the batch. The determination of sulphur balances requires very accurate analytical methods for determining the flue gas volume flows, the concentration of sulphur dioxides in the flue gas, the filter dust production rate and filter dust composition and the glass/cullet composition. The sulphur balances identify the most important sources of SO₂ emissions and gives valuable information on the conditions like cullet quality, redox state of batch and glass, which will determine the sulphur release during the melting of the batch blanket and fining of the glass. Sulphur dioxide emission levels can be predicted by sulphur balances using information of sulphur input by batch materials, fuel, cullet and filter dusts and output by the sulphur carried away by the flue gas particulates and the glass products. Then, errors of 5 to 15 % have to be taken into account, only for cases with very constant and well defined cullet, flue gas volume flows and batch composition, the error might be kept within a few percent. This is often the case for float glass furnaces or container glass furnaces using constant cullet qualities.

In cases with very low SO₂ concentrations in the flue gas compared to the total sulphur input, accurate predictions of sulphur dioxide emissions are not to be expected. Sulphur balances of oil fired glass furnaces equipped with scrubber and filter show that only part of the SO₂ can be eliminated from the flue gases in order to be able to recycle the collected filter dusts completely in the same furnace. Larger errors (± 10 %) in the determined sulphur balances have to be taken into account for container glass furnaces using external cullet, especially when using waste glass with fluctuations in organic contaminants.

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