BEHAVIOUR OF BORATE RAW MATERIALS IN THE FUSION PROCESS

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ABSTRACT

Emissions are a widespread problem in the frit making industry. They lead to faster deterioration of the equipment, final product quality problems, loss of raw materials and are increasingly subject to environmental regulations.

The role of boron in the glass structure and its importance in ceramic frits is widely understood. What is not generally known is that the careful choice of borate source can significantly affect the amount of particulate and volatile emissions coming from the frit making process.

This paper will detail some of the experimental results we have found when looking at emissions from the frit making process, what the mechanisms are, what the emissions are composed of and how their levels can be reduced through a careful choice of raw materials.

INTRODUCTION

EMISSION CHARACTERISTICS

In the frit production process, gases containing solid particles are released into the atmosphere. The particulates involved, irrespective of their chemical composition, come from solid matter and/or the condensation of volatile compounds. However, except for the fusion step, emissions virtually occur at ambient temperature, for which gas cleaning is relatively simple and has found widespread implementation in industry.

In glass production processes, the most important source of emissions is undoubtedly the melting furnace, this is true from both the qualitative and the quantitative aspects. The high temperatures of the exhaust gases (400-800°C), which also contain condensed volatiles and partly fused material, will make the application of any cleaning system more complicated.

Released gas characteristics also depend on the type of frit produced, raw materials involved, operating mode (continuous or batch), fuel, furnace design, etc. Particulate emissions with current production systems are of the order of 1-10 g/kg produced frit, yielding particulate concentrations in furnace emissions ranging from 150 to 1000 mg/Nm^3 [1], [2].

ENVIRONMENTAL ISSUES

A key issue is the potential for environmental impact from emissions and the costs entailed in controlling and cleaning flue gases.

Abatement of emissions from frit production may involve primary or preventive measures to prevent losses from arising, and/or secondary or corrective measures to remove pollutants from flue gases by suitable treatment.

However, owing to the high particulate concentration in these gases, legal requirements on emission concentrations cannot at present be met just by applying primary measures. Meeting legal limits requires employing gas-cleaning systems.

The most widely used cleaning systems are bag filters. Their major advantages lie in a high particulate cleaning yield (around 95%), the possibility of using variously sized units, and their proven performance in ceramic frit production. Their major disadvantage lies in not allowing the flue gas' residual heat to be reused, as treatment temperatures of 150-200°C are needed.

Treatment costs and the investments involved in putting in place the necessary cleaning systems for such emissions depend on the facility (type of product, combustion system, cleaning system, etc.) and the targeted emission reduction. When high cleaning yields are called for, the costs involved in implementing and running currently available technologies tend to form quite an important part of product cost.

On a European level there is no specific legislation on air pollution for the ceramics and glass industry[3]. The European Commission issues Directives setting general criteria, which are subsequently to be applied by each Member State in its national legislation. Moreover, each individual EU Member State sets its own air emission limits.

This has led to the application of different emission limits among member States and sometimes even for different regions within a given State. Thus, for frit melting furnaces, the particle emission limit for a company located in Castellón is 150 mg/Nm^3, for a company located in Emilia Romagna in Italy it is 30 mg/Nm^3 , whereas a company in Great Britain is set a limit of 100 mg/Nm^3. Generally speaking, the particle emission limit in the European Union can be considered to be at around 50 mg/Nm^3.

Particle emission limits are typically expressed in terms of concentrations, although there is a tendency, already applied in certain member States, to also use emission factors

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[1]. BLASCO, A. et al. *Tratamiento de emisiones gaseosas, efluentes líquidos y residuos sólidos en la industria cerámica*. Castellón (España), AICE-ITC, 1992

[2]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G. *Piastrelle ceramiche & ambiente*. Edicer. Modena (Italia), 1995.

[3]. TACKELS, G. *Industrie du verre et environement: évolution, contraintes et opportunités*. Verre, vol 2, nº 2, 10-21, 1996.

(quantity released/unit product), or to express concentrations at a given flue gas oxygen content, to avoid the diluting effect that occurs on expressing the value in concentrations.

On the other hand, emission limits may also be changed, and the trend in the European Union is to implement ever stricter limits as new technologies surface, and progressively harmonise emission requirements among EU Member States. This principle has recently led to Directive 96/61/CE on integral pollution prevention and control (IPPC), in which the BAT concept (Best Available Techniques) is introduced. Future discussions aimed at defining the BAT for each industrial sector are bound to become of major importance.

PROCESS AND/OR PRODUCT-RELATED ISSUES

Besides environmental issues, other process and/or product-related aspects also need to be considered, such as:

- Deterioration of furnace refractory materials and flues as a result of abrasion and corrosion by gases and condensation.
- Inhomogeneity in the product caused by vaporisation or loss of certain constituents in different areas of the furnace.
- The need to use greater quantities of raw materials to compensate for fusion losses.
- Some processes are now looking into cleaning and reusing the flue gases in order to make use of their residual energy / heat. The greater the presence of pollutants in these emissions, the more difficult this operation will be.
- In certain cases, arising pollutants may act as a production-limiting factor in order to keep emissions within admissible limits.
- Health problems in the workplace as a consequence of pollutant emission inside the facilities.

ORIGINS OF EMISSIONS

WHAT ARE THEY

For the purpose of this paper, we have divided emissions in two categories: particulates and volatiles.

Particulate emissions are those which occur during the heating of the batch. As will be explained later, they are generally made up of unmolten crystals emitted from the batch raw materials or of glass microspheres.

While recognising that most of the volatile losses will eventually condense into solids, we have chosen to distinguish them from what we call particulate losses. Volatile losses will only seldom form solid / liquid deposits inside the furnace and will require different techniques than particulate losses to eliminate or reduce.

Previous SEM observation of emissions[4] have shown that a clear distinction can be made between the two emission types. This is best illustrated in Figure 1, showing an SEM picture of emissions collected from a frit batch for single fast fired tiles, where one

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[4]. VICKERY, W. AND NANCARROW, P., *"Borate raw materials for the ceramic frit industry"*, 5th European Ceramic Society conference, 1997.

can clearly see the presence of three distinct groups: spheres, coarse irregular material and a very fine deposit. Semi-quantitative analysis of these groups showed that the spheres were of glassy type, the coarse material was mainly made of quartz, calcite and dolomite and the submicron deposit was found to be rich in chlorine, sodium and potassium indicating its origins as condensed volatile losses.

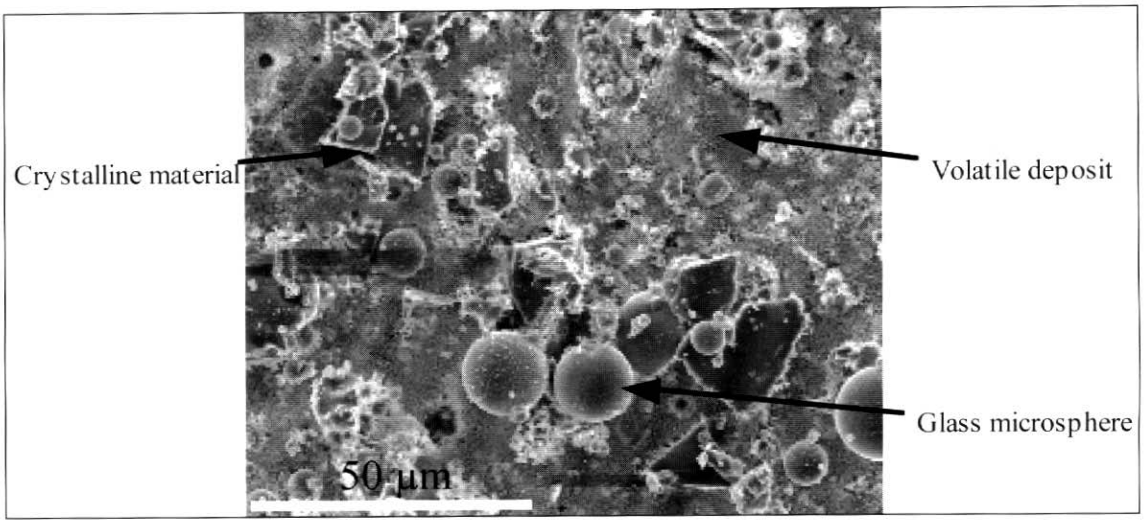

Figure 1. *Particulate emissions from a frit batch fusion.*

PARTICULATE EMISSIONS

The three major causes for particulate emissions are water vaporisation, decrepitation and puffing. The heating rate of a frit batch is in practice very high as the batch travels from a silo, or feeder, at room temperature to the inside of a furnace (up to 1500°C). For the borate raw materials, most of the water is lost in the first few hundred degrees of heating, typically up to 500°C (i.e. below the batch melting temperature). All the water is converted to steam which rises through the batch, carrying the finer particles in its flow. Once the particles have been swept clear of the surface of the batch, they are carried by the combustion gases out of the furnace. To set things in perspective, a batch containing 5% water will release about 300 times its volume of steam superheated at 1000°C (i.e. 1 tonne of such a batch would release about 30 m^3 of superheated steam).

When heated, some minerals will become more porous and develop micropores and fissures interspersed throughout their crystal lattice. Their thermal expansion will lead to internal stresses in the individual crystals causing them to fracture into small fragments, this is called decrepitation[5]. The movements caused by decrepitation will affect adjacent components, causing displacement of particles leading to dust emissions from the batch pile. The use of coarser products will enhance the effect of decrepitation.

Puffing is also known as the "pop-corn" effect. It is the sudden expansion that results from the dehydration of some products through heating. When heated, some materials swell to form hollow spheres which can be substantially larger than the original particles. This can happen at a set temperature, in which case the expansion will be very sudden and cause a lot of batch movement leading to dust emissions.

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[5]. SENER, S. AND OZBAYOGLU, G., *"Determination of calcination parameters of ulexite and possibility of separation from colemanite"*, Int. Symp. Miner. Process., 4th, 1992 (Antalya), p. 538-548, 1992.

Furnace gas flow can also have a significant effect on particulate losses, however this is more difficult to quantify as it will depend on the shape and size of the gas flame as well as on how it is directed towards the batch pile. The effect will chiefly be one of mechanical erosion / removal of product from the batch pile by strong turbulent gas flow.

Other causes for particulate emissions are:

- decomposition and evolution of gases such as water and CO_2;
- chemical reactions between components in the batch mix;
- dustiness of the batch.

VOLATILE EMISSIONS

Volatile losses are the result of mass transfer of glass components from the batch / glass melt to the furnace atmosphere. These occur in the following way[6]:

- diffusional transport in the glass phase towards the surface of the melt;
- vaporisation and / or reaction resulting in conversion of the constituents in volatile components;
- transport of the gaseous component into the furnace atmosphere.

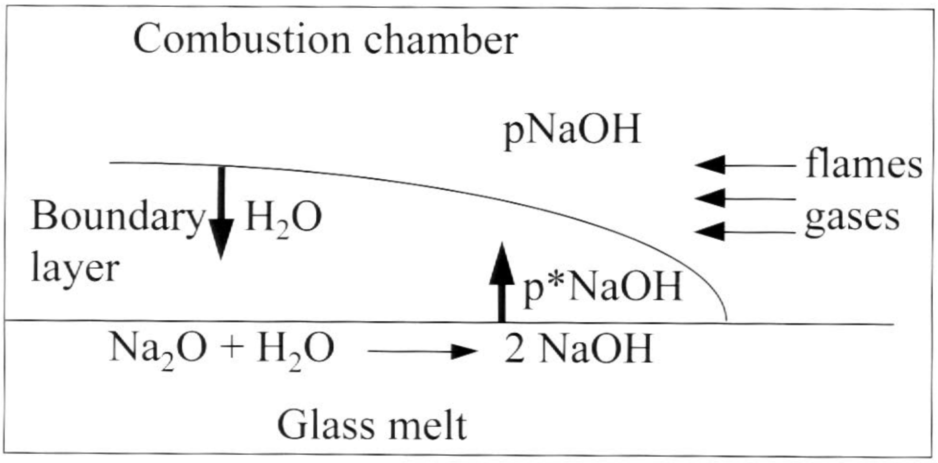

Figure 2. *Illustration of NaOH volatilisation process from a glass melt*[7]
p: average partial vapour pressure in the furnace
p: equilibrium partial vapour pressure at gas / melt interface*

The atmosphere of an industrial furnace is never saturated with components evaporated from the glass melt and the rate determining step for vaporisation can be the transport of the chemicals from the glass melt surface to the convective gas flow. Higher gas velocities will result in greater vaporisation rates, an increased fuel consumption will enhance vaporisation but will decrease the amount of volatilised matter per unit of exhaust gas volume.

The vaporisation mechanism depends on:

- the glass composition;
- the gas flow rate along the glass surface;
- the composition of the furnace atmosphere;

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[6]. BEERKENS, R.G.C. *"Deposits and condensation from flue gases in glass furnaces"*. Koninklijke Bibliotheek 22-23, 1986.

[7]. BEERKENS, R.G.C. AND KOBAYASHI, H., *"Volatilisation and particulate formation in glass furnaces"*, Proceedings of the 4th International Conference on Advances in Fusion and Processing of Glass, p. 118, 1995.

- the temperature;
- the reaction of the glass components with the components of the furnace atmosphere at the glass surface.

Water content in the furnace atmosphere will be an important factor for alkali and lead volatilisation, in a number of cases, the diffusion rate of the components through the melt will be a controlling factor.

OBJECTIVE AND SCOPE OF THE WORK

In order to examine the above issues, it was felt that a better understanding of the emission-forming mechanisms in frit production was required.

A literature survey was conducted[1, 2, 3, 8] which showed that few studies have been published on the individual behaviour of the different raw materials in the fusion process. It was therefore decided to:

- Develop an experimental set-up for a bench-scale study of the tendency of individual raw materials to release particles or vapours into the furnace atmosphere during fusion;
- Use this set-up to study the behaviour in the fusion step of the main borate minerals employed in ceramic frit making and determine how they affect the characteristics of emissions from ceramic frit production.

MATERIALS AND EXPERIMENTAL TECHNIQUES

MATERIALS

An opaque and a transparent frit were studied, of the kind typically used for manufacturing tiles by fast-firing schedules (30-50 min). The frit compositions were as follows:

Oxide	Opaque	Transparent
Al_2O_3	6.24	10.48
B_2O_3	6.48	6.56
CaO	9.01	8.12
K_2O	3.69	7.74
MgO	3.91	2.50
Na_2O	1.38	2.26
SiO_2	51.76	57.27
ZnO	8.42	5.07
ZrO_2	9.11	-

Table 1. *Frit compositions (in % w/w).*

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[1]. Blasco, A. et al. *Tratamiento de emisiones gaseosas, efluentes líquidos y residuos sólidos en la industria cerámica.* Castellón (España), AICE-ITC, 1992

[2]. Busani, G.; Palmonari, C.; Timellini, G. *Piastrelle ceramiche & ambiente.* Edicer. Modena (Italia), 1995.

[3]. Tackels, G. *Industrie du verre et environement: évolution, contraintes et opportunités.* Verre, vol 2, nº 2, 10-21, 1996.

[8]. Beerkens, R.G.C. *The role of gases in glass melting processes.* Glastech. Ber. Glass Sci. Technol. 68, nº 12, 369-380, 1995.

The raw materials used were sodium feldspar, potassium carbonate, dolomite, zinc oxide, zirconium silicate, alumina and quartz. Hydroboracite and colemanite were compared as borate sources, the quantities of the different raw materials were adjusted in order to obtain the required frit composition, this was due to the differences in chemical composition between the two borates.

EXPERIMENTAL TECHNIQUES

Particulate losses

The equipment consists of a 5 cm diameter horizontal electric tube furnace which is set at the desired temperature. The furnace temperature is set according to the type of material tested, normally between 1050°C and 1350°C. The filter is protected from melting by bleeding cold air onto it. The filter holder is connected to a vacuum pump. The rate of the pump is set so as to allow an air flow through the furnace which can carry the particulates without removing material from the combustion boat. Accordingly the air flow was set at 0.3-0.5 m s^{-1}. The combustion boat is used to contain 3g of frit batch and has dimensions 10 x 1 x 1 cm. With the vacuum operating, the combustion boat is placed in the furnace at temperature and only removed once particulate emissions from the batch have ceased, about two minutes. The filter is weighed to determine the mass of particulates. The results are expressed as the ratio of product collected on the filter over the amount of batch put in the combustion boat. This test is usually run in triplicate and the average of the three results is reported.

By removing the filter system from the end of the furnace it is possible to record the reaction / melt on video for visual comparison of the different batches.

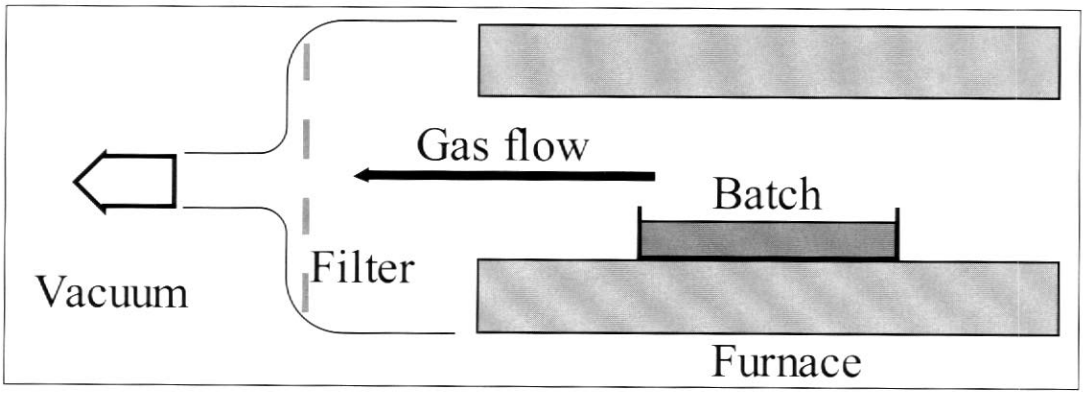

Figure 3. *Diagram of the apparatus used to quantify particulate emissions from melting batch.*

The advantages and key points of the equipment are:

- ease of set-up and use;
- good observation of behaviour;
- many experiments performed rapidly;
- the air speed over the boat can be accurately set;
- good reproducibility of the results;
- comparison of different products or mixes of components are well illustrated.

If the particulates are collected in sufficient quantities, analysis of the solids can provide further insight into the melt process. The techniques employed to observe the solids can include optical microscopy, scanning electron microscopy (SEM), laser particle sizing and X-ray analysis.

Volatile losses

The equipment consists of a 5 cm diameter horizontal electric tube furnace which is set at the desired temperature. The furnace temperature is set according to the type of material tested, normally between 1200°C and 1500°C. The trapping system is connected to a vacuum pump which is set at a rate of about 2000 cm^3/min. The combustion boat contains 20 grams of batch and the firing schedule used is the following:

- the batch is introduced in the cold furnace;
- the furnace is ramped up to peak temperature at a rate of 10°C/min in order to avoid particulate emissions;
- once at temperature, the batch is left in the furnace for an extra 30 minutes;
- the combustion boat is removed from the furnace and the system is left to run at temperature for another 30 minutes
- the system is rinsed and cleaned, the rinse water is kept for analysis;
- the system is reassembled and run at temperature for another 30 minutes, this is done without a sample in order to get a blank;
- the system is rinsed and cleaned a second time, the rinse water is kept for analysis;
- after chemical analysis, the results of the second rinse are added to those from the first.

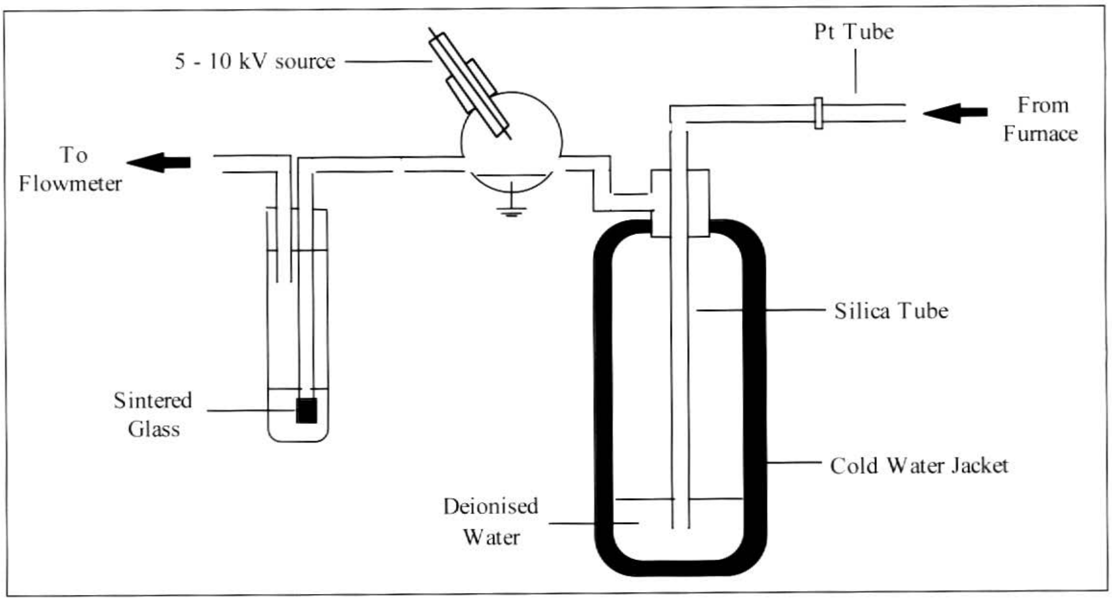

Figure 4. *Diagram of the apparatus used to quantify volatile emissions from melting batch*

RESULTS AND DISCUSSION

Volatile losses

The volatile losses were measured at 1400°C. The results found were as follows:

		As_2O_3	F	S (as SO_3)	B_2O_3	Na_2O	K_2O	SiO_2	CaO	ZnO	Cl
Transparent	Colemanite	0.15	0.18	0.69	7.28	0.73	5.93	0.01	0.01	0.00	0.04
	Hydroboracite	0.03	0.03	0.04	4.66	0.51	4.05	0.00	0.00	0.00	0.27
Opaque	Colemanite	0.21	0.29	1.26	5.93	0.67	4.09	0.01	0.02	0.00	0.04
	Hydroboracite	0.07	0.04	0.08	5.66	0.62	3.51	0.00	0.00	0.01	0.11

Table 2. *Volatile losses (in mg per g of frit).*

Zircon and magnesium were also analysed for and found to be below the detection limit of our apparatus.

From Table 2, one can see that using colemanite leads to the highest arsenic, fluorine and sulphur losses. This is a reflection of the high levels of these components in that borate mineral.

When compared with the frit compositions, one can easily see that the volatility of potassium is greater than that of sodium. It also seems that using colemanite will cause slightly higher boron, sodium and potassium losses than using hydroboracite. The reasons for this are unclear. It is already well known that borates will combine with alkalis when volatilising, forming $NaBO_2$ or KBO_2 instead of HBO_2. Some calculations from the results in Table 2 show that about half (in moles) of the borate volatilises as KBO_2 and the other half as HBO_2.

The higher chlorine losses obtained when using hydroboracite are due to its slightly higher chlorine content. As can be seen here, no significant amount of silica, calcium or zinc is lost through volatilisation and the same can be said for zircon and magnesium.

Particulate losses

The particulate losses were determined with a furnace setting at 1300°C. The results found for the particulate losses were as follows:

		Result
Transparent	Colemanite	0.07
	Hydroboracite	0.03
Opaque	Colemanite	0.04
	Hydroboracite	0.02

Table 3. *Particulate losses (% collected / sample).*

The results found are fairly low but still show distinctly that the use of colemanite will lead to a greater amount of particulate losses than the use of hydroboracite. This is due to colemanite's tendency to decrepitate upon heating. As hydroboracite does not decrepitate, it's presence will not lead to the same amount of batch movement as that of colemanite.

At these low levels, it could also be commented that a significant fraction of what is being collected on the filters is in reality condensed volatile losses and not particulate losses as such. For this purpose a chemical analysis has been done of filters with collected material on them.

The samples presented on glass fibre filters had a total weight of about 0.2 grams (sample + filter) and were fused in 2 grams of lithium metaborate. The fused samples were then leached in dilute nitric acid and analysed by ICP. Lithium metaborate has a 53.8% B2O$_3$ content which means that the B_2O_3 brought in by the sample and the filter is likely to represent less than 1% of the total B_2O_3 in the fused product. Therefore it was not possible to determine boron in the dust emissions.

Note: the results for CaO, SiO_2 and ZnO given in Table 4 may be inaccurate since the samples were presented on glass fibre filters which gave appreciable blank values.

		CaO	MgO	SiO2	ZnO	ZrO2
Transparent	Colemanite	16.2	3.5	54.6	6.5	n/d
	Hydroboracite	15.4	4.5	39.2	6.0	n/d
Opaque	Colemanite	15.5	5.8	38.6	7.0	9.5
	Hydroboracite	15.5	6.0	37.7	5.5	8.2

Table 4. *Composition of collected emissions (in % w/w).*

When comparing these results with the ones obtained with the volatile losses, it is easy to see that all the calcium, magnesium, silica, zinc and zirconium can only have come out in the form of particulate losses. The data in Table 4 also shows us that at least 70% of what has been collected on the filters results from particulate losses. Considering the uncertainty on some of the values, it appears that the composition of the particulate losses is fairly constant, richer in calcium and poorer in silica than the original frit composition (see Table 1). The levels of magnesium, zinc and zirconium appear to be similar to those of the frit composition.

CONCLUSION

Two pieces of laboratory equipment have been developed to study the behaviour of the batch during the fusion process by looking at the issue of emissions. One of these has been specifically designed to measure volatile emissions while the other allows us to collect and quantify the particulate losses.

This equipment has been used to compare the effect of two borates (hydroboracite and colemanite) commonly used in the frit industry, on these emissions. It has been established that borates can lead to quantitative and qualitative differences of both volatile and particulate emissions during the fusion process.

If this factor is taken into consideration when choosing a raw material benefits will include increased furnace life, improved frit quality and reduced emissions of elements into the environment.

ACKNOWLEDGEMENTS

It is easy to see that this paper is not the result of the work from just the three named authors, but rather from the work of a whole team of people. In particular, we would like to thank David Lever, Brian Robertson and John Simon without whom all this would not have been possible. We would also like to show our gratitude towards the team at Borax España whose work was crucial in the achievement of this paper.