STUDY, CONTROL AND CHARACTERISATION OF EMISSIONS IN FRIT PRODUCTION. ADAPTATION OF INTEGRAL PRODUCTION PLANNING TO ENVIRONMENTAL VARIABLES

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ABSTRACT

Particulate emissions are the main source of environmental pollution of ceramic frit production systems.

The work undertaken reflects the influence of the composition of the kiln material feed, its production parameters and the desired characteristics of the end product on air emissions.

This study was conducted by selecting four different compositions corresponding to two types of traditional industrial frits, two white zirconium frits and two transparent boric frits, which because of their compositions were considered appropriate for developing the study.

The experimental method followed required a probe capable of sampling the particulates isokinetically, an exhaust gas analyser, as well as simultaneous access to the chemical characteristics of the fritted material, the combustion parameters of the kilns involved, and controls performed on the resulting frit. The exhausted particulate solid waste was characterised by SEM, XRD, and XRF.

The influence of the raw materials on the chemical composition of the exhausted solid waste was established by characterising this waste.

This study can entail a series of advantages for the frit and glaze industry, as it can contribute technical ideas for assessing alternatives for implementing secondary emission abatement measures in melting kilns, i.e., the installation of cleaning systems and their subsequent maintenance.

1. INTRODUCTION

The main environmental problem associated with frit production is that a high-temperature, energy-intensive process is involved. This entails the emission of combustion products, and the high temperature causes the nitrogen in the air to oxidise.

The melting output with regard to the raw materials input is about 75-80%, depending on each formulation. Most of this loss is due to CO_2 emissions during melting.

The emissions also contain particles (from volatilisation and the subsequent condensation of the volatiles) and traces of chlorine, fluorine and metals present in the raw materials. The frits produced for glazes release a large amount of fluorine owing to the quantity of materials containing this element, which are used in the kiln. Technical solutions are in principle possible for all these emissions, but each technique has its related economic and environmental implications.

If a cleaning system is used for each kiln, recovery of the treated material in the same process is simple and the effect of the cleaning system on kiln operation is very low, so that the required control tasks and systems are fewer. However, the investment and space needed are much greater. If a single cleaning system is used for several kilns, the capital outlay and space required are smaller, but the problems of materials management and kiln and cleaning system operation increase.

2. OBJECTIVES

The following objectives were set in this study:

I. Quantification of the solid waste produced by air emissions.

II. Characterisation of the exhausted solid waste.

III. Relationship of the air emissions to the different industrial frit production process variables.

IV. Raising the issue of considering the environmental variable in integral production planning.

3. EXPERIMENTAL DEVELOPMENT

3. 1. EXPERIMENTAL TECHNIQUES FOR EMISSION SAMPLING

The gas analyser used was a Testo 350 analyser, with an automatic control unit that allows recording data intermittently or continuously (Figure 1).

The isokinetic probe used was the Model 31-200TC probe with a semi-automatic, computerised control unit for sampling control with isokinetic or constant flow (Figure 2).

Figure 1. Testo 350 gas analyser.

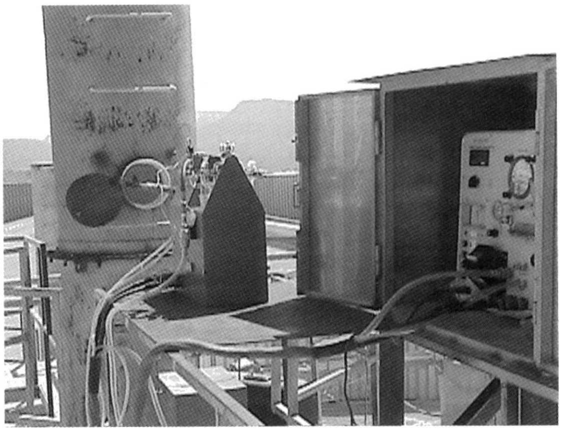

Figure 2. 31-200TC isokinetic probe.

3.2. CHARACTERISATION TECHNIQUES

The waste obtained was analysed by X-ray fluorescence (XRF), using a SIEMENS spectrometer for determining the chemical composition. The crystalline phases were also analysed, using a SIEMENS, Model D5000, diffractometer (DRX). The scanning electron microscope (SEM) fitted with an energy-dispersive X-ray analysis (EDXA) LEO-Oxford spectrometer, provided the microscopic and micro-analytical study of the samples.

3.3. STUDIED MATERIALS AND PRODUCTION PARAMETERS

3.3.1. Input material composition

Four different compositions (O1, O2, T1, T2) were chosen to conduct the study, corresponding to two types of traditional industrial frits: a zirconium white frit (O) and a transparent boric frit (T), which because of their characteristics were considered appropriate for the objectives set.

The compositions in oxides of the materials fed into the melting kiln to produce these four frits are detailed in Table I.

FRIT	Al_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	SiO_2 (%)	Na_2O (%)	ZrO_2 (%)	B_2O_3 (%)	ZnO (%)
O1	4.5 - 7	7 – 9	1 - 2.5	3.5 - 6	53-57	0.5 - 2	6 - 8	4.5 - 6	11.5 - 14
O2	4.5 - 7	8.5 - 10.5	2 - 3.5	2.5 - 5	56 - 59		6.5 - 9	2.5 - 5	11.5 - 14
T1	6.5 - 8	10.5 –12	1 - 2.5	3.5 - 6	56 - 59	0.5 - 2		5 - 7.5	11.5 - 14
T2	6.5 - 8	12.5 – 14	1 - 2.5	3.5 - 6	58 - 62			1 - 3.5	11.5 - 14

Table 1. Composition in oxides of the studied frits.

The raw materials used to obtain the oxide contribution for each test composition are set out in Table II.

The relative grading of the raw materials quantities used and their impurities, which can give rise to differences in the type of emissions, are presented in Table III.

O1	O2	T1	T2
Quartz	Quartz	Quartz	Quartz
K feldsp.	K feldsp.	K feldsp.	K feldsp.
H_3BO_3			
ZnO	ZnO	ZnO	ZnO
$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$
Dolomite	Dolomite	Dolomite	Dolomite
K nitrate	K nitrate	K nitrate	
Zr flour	Zr flour		
	Colemanite	Colemanite	Colemanite
		Kaolin	Kaolin

Table 2. *Raw materials composition of the estudied frits.*

Raw material	Grading
K feldspar	O1 >> O2 > T2 > T1
K nitrate	T1 > O2 >> O1
$CaCO_3$ / Dolomite ratio	T2 > O1 ≅ O2 ≅ T1
Impurity	**Grading**
Fe_2O_3	Kaolin >> $CaCO_3$ ≅ K feldspar ≅ Dolomite ≅ ZnO
SO_3	Colemanite >> H_3BO_3

Table 3. *Relative grading of raw materials compositions and impurities introduced.*

3.3.2. Melting kiln parameters.

One of the traditional considerations in production planning is control of kiln operating parameters. The characteristic values of these parameters for the compositions studied during isokinetic sampling are given in Table IV.

	O1	O2	T1	T2
Gas (%)	89	82	86	82
Air (%)	87	91	90	91
O_2 (%)	10	0	5	0
Gas (m^3/h)	187	173	180	173
Air (m^3/h)	1835	1910	1880	1910
O_2 (m^3/h)	45	0	23	0
P (mmwc)	-1	-1	-1	-1
T kiln (ºC)	1530-1540	1510-1520	1500-1510	1470-1480
T exh. gases (ºC)	543	560	400	415

Table 4. *Kiln parameters for each formulation.*

The quantity produced per kiln was also controlled by weighing the bags that were being filled. The average production of each test material on the sampling days is shown in Table V.

Composition	Production (Ton/day)
O1	16
O2	16.5
T1	15.5
T2	16

Table 5. *Average kiln production for each test material.*

3.3.3 Product control

Another traditional consideration to be taken into account in production planning is product control through analysis by hot-stage microscopy. The characteristics of the material obtained, simultaneously to the sampling performed, are presented in Table VI.

Frit	Type	HOT-STAGE MICROSCOPE				
		T sintering (°C)	T soften (°C)	T sphere (°C)	T 1/2 sphere (°C)	T melting (°C)
O1	Control	891	1050	1095	1185	1220
	STD	915	1065	1105	1195	1220
O2	Control	920	1090	1135	1165	1200
	STD	915	1090	1135	1165	1200
T1	Control	915	1045	1085	1155	1180
	STD	930	1060	1095	1155	1190
T2	Control	930	1050	1110	1175	1210
	STD	940	1075	1110	1180	1210

Table 6. *Hot-stage microscopy data.*

On the other hand, the formulations used have a certain output in industrial kiln production, which is studied and controlled by the company laboratory. The values for the studied compositions are detailed in Table VII.

Composition	Output (wt%)
O1	≈ 87
O2	≈ 87
T1	≈ 87
T2	≈ 86

Table 7. *Output in wt% of the compositions fed into the melting kiln.*

RESULTS AND DISCUSSION

4.1. GAS ANALYSIS

Exhaust gas analysis, with the Testo 350 analyser, yielded a set of data as a function of the relative sampling time.

Figure 3 shows that composition T1 had higher temperature point values than compositions O1 and O2, while T2 exhibited the lowest value. The direct relationship is

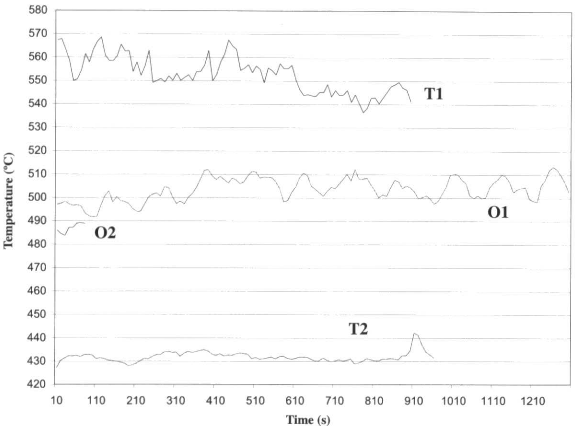

Figure 3. Exhaust gas temperature.

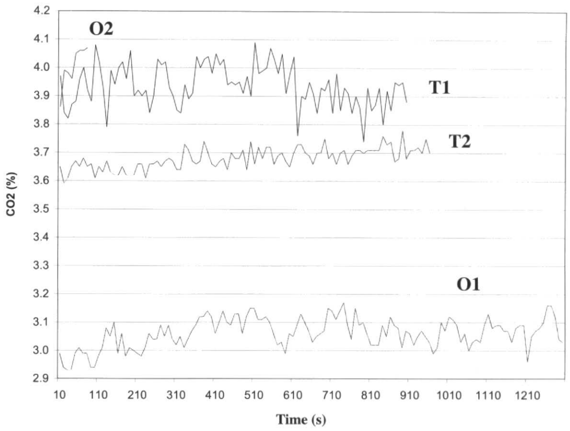

Figure 4. *CO_2 in the exhaust gases.*

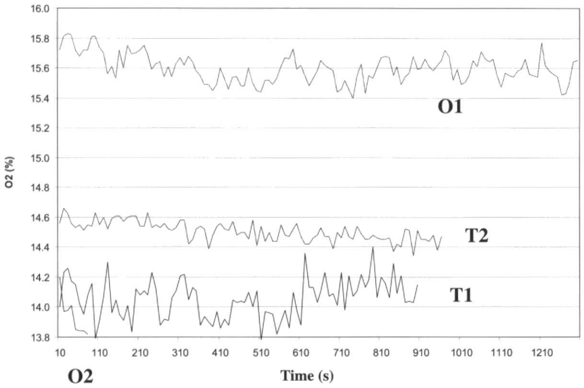

Figure 5. *O_2% in the exhaust gases.*

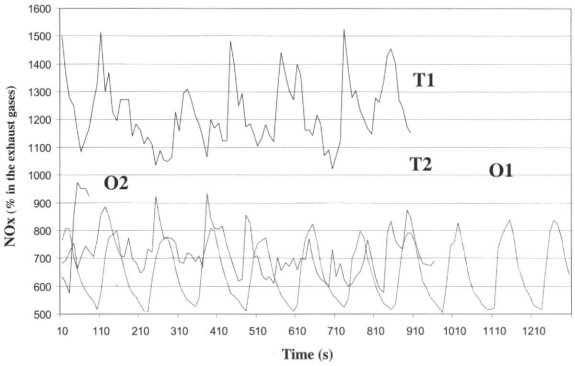

Figure 6. NO x % in the exhaust gases.

to be sought in the temperature inside the melting kiln. Table IV indicates that the expected exhaust gas temperature grading is: O1>02=T1>T2. However, the air flows at ambient temperature must be taken into account, which are introduced in each of these streams, to understand the change in the grading.

Figure 4 shows that compositions T1 and O2 generated a higher percentage of CO_2 in the exhaust gas composition, followed by T2. Composition O1 had a much lower percentage of CO_2 in the gases, and was also the one that contained the least CaO in the batch charge, adding this as carbonate and dolomite. (Table III).

Figure 5 indicates that composition O1 had a higher O_2 percentage in the emission gases than the other compositions. The explanation can be found in Table IV, where this kiln is observed to work with the greatest O_2 percentage enriching the combustion mixture.

Figure 6 contains the plots of NO_x evolution for different compositions over a period of time. They show that composition T1 produced a greater emission of this pollutant, presenting a heterogeneous waveform, whereas a composition such as O1 had a lower emission rate and presented a waveform with a certain regularity. The explanation lies in Table I, Table II and Table III, which show that composition T1 has a greater K_2O content, added mainly as potassium nitrate, followed by T2, O2, and finally O1, which also has a lower K_2O content, added mainly as potassium feldspar.

Finally, as a common consideration, it can be said that the trends are only clear in Figure 6 for NO_x. The explanation for the alterations in the compositions in the other figures without a clear origin lies in the importance of the ambient air flow introduced before the measuring point, which affected three of the foregoing variables: exhaust gas temperature, CO_2 and O_2, but did not affect NO_x, in the same way, which are not contributed by this stream.

4.2. VELOCITY AND GAS FLOW RATE

Table VIII sets out the results obtained from isokinetic sampling with the probe of the emission flow according to Method 5 of the Environmental Protection Agency.

	O1	O2	T1	T2
P din. Average (mmH_2O)	8.821	10.575	9.349	10.326
T abs. Stack. Average (K)	828	716	728	663
P abs. Stack. Average (mm Hg)	745.4	740.4	737.4	736.4
PM h (g/mol)	28.386	28.509	28.352	28.341
Moist. Fract.	0.070	0.062	0.071	0.074
Average Velocity (m/s)	**17.26**	**17.60**	**16.77**	**16.83**

Table 8. *Calculation of average velocity (m/s) in the stack.*

Introducing the calculated value of the moisture fraction yields the dry gas flow rate under standard pressure and temperature conditions (Figure 7).

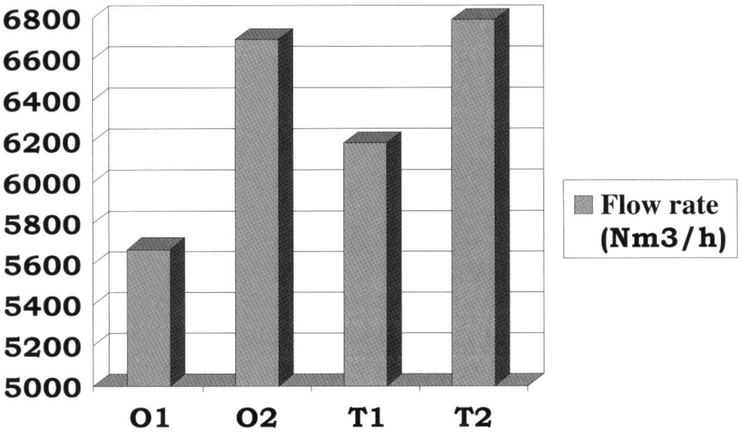

Figure 7. *Calculation of in-stack average dry flow rate (Nm^3/s).*

4.3.. PARTICLE EMISSIONS

The levels of particulate emissions for the different types of materials fed into the melting kiln are shown below. To enable comparing the emissions, all the results are based on a reference oxygen value of 15% (according to Equation 1).

$$Cref = Cm \cdot \frac{(21 - O2ref)}{(21 - O2m)} \qquad \text{Eq (1)}$$

These emission concentrations are shown in the commonest and most appropriate way (Figures 8,9,10).

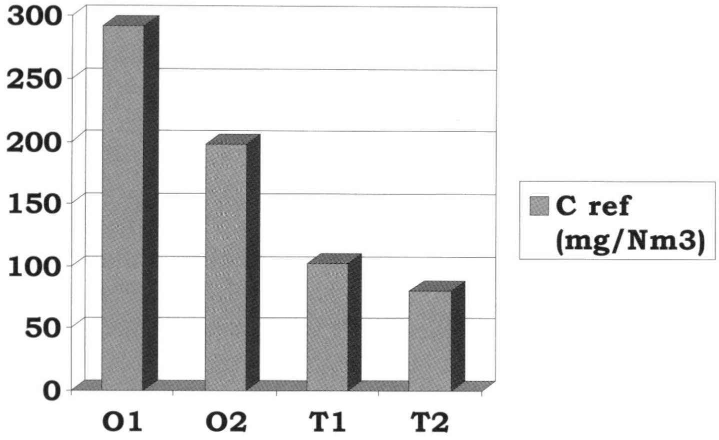

Figure 8. *Emission concentration under isokinetic conditions, with regard to 15% oxygen in the exhaust gases.*

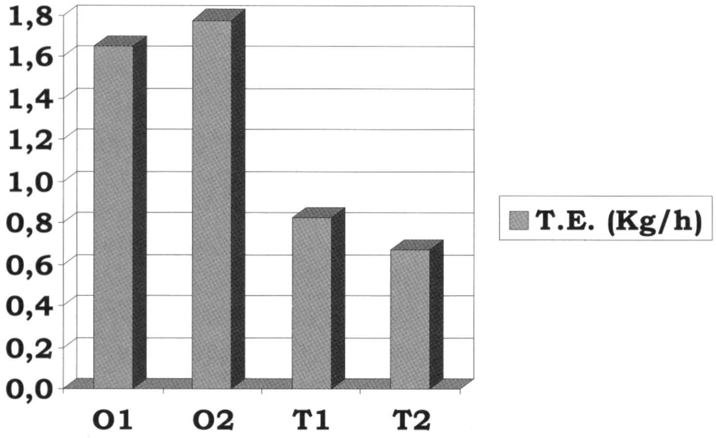

Figure 9. *Emission rate under isokinetic conditions.*

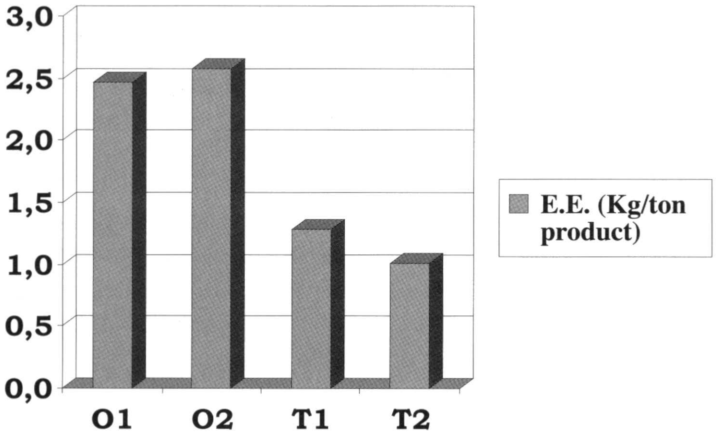

Figure 10. *Specific emission (kg exhausted particles / ton of produced material).*

Observation of the different emission concentration indices which can be compared, such as specific emission (E.E.), emission rate (T.E.) or reference concentration (C ref), shows that the zirconium white frits exhibited a higher emission than the transparent boric frits.

Owing to the different exhaust gas flow rates, depending on the O_2 enriched air percentage in the kiln and the influence of ambient air to keep the kiln atmosphere at a certain pressure, hindering gas exhaust, the specific emission was considered to be the best way to compare the emissions.

Based on this comparison, O2 is the composition with the greatest emission in relation to the same quantity of material produced by the kiln, closely followed by O1, evidencing a clear difference with types T1 and T2, respectively.

With regard to the raw materials composition, O2 provides all the B_2O_3 as colemanite and K_2O as potassium nitrate and feldspar.

The composition of the exhausted waste will provide information on the raw materials that contribute relatively more to the emission concentrations.

4.4. CHARACTERISATION OF THE EXHAUSTED PARTICLES

Analysis of waste adhered to the filters (RF).

By sampling with the isokinetic probe, microparticles that circulate together with the gas stream or aerosol adhere to the filter. These particles have a smaller average diameter than the other particles that do not circulate in the dynamics of the gas flow. The micrograph in Figure 11 shows the waste adhered to the filter during O1 material emission sampling.

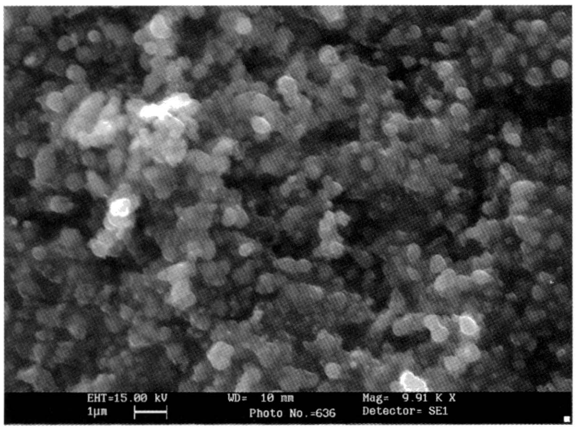

Figure 11. *SEM micrograph, 9910 x, EHT= 15. 00kV. Focal distance= 10 mm, Detector= SEI.*

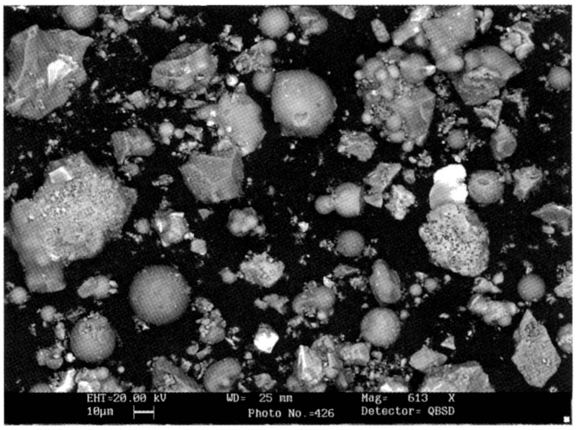

Figure 12. *SEM micrograph, 613 x, EHT= 20. 00kV. Focal distance= 25 mm, Detector= QSBD.*

Interpreting the spectrum in Figure 13, it can be stated that the material retained in the isokinetic probe filter exhibits an amorphous phase, i.e., without any crystalline phase in its composition.

Table IX sets out the results obtained by XRF analysis of the filters with the adhered material. It can be observed that K_2O rose in the waste composition as a greater quantity is added as potassium feldspar (Table III).

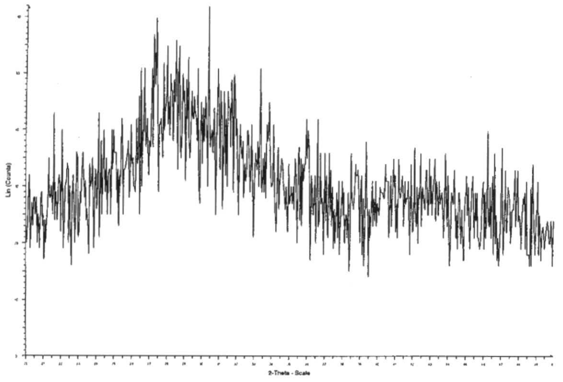

Figure 13. *XRD spectrum of sample RF O1.*

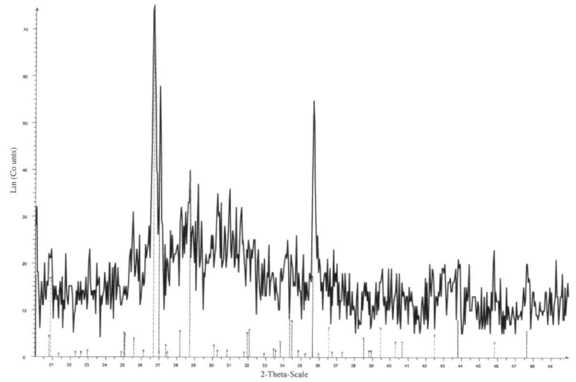

Figure 14. *XRD spectrum of sample RCh O1.*

SO_3 also follows a logical order, as a smaller amount was found in the O1 waste, where the boric acid is introduced as colemanite. In any case, the presence of B_2O_3 is the waste was greater on using H_3BO_3 as a raw material, according to Table X.

Analysis of waste adhered to the stack (RCh).

The material is collected at the stack opening where the isokinetic probe is introduced for sampling. The main differences in the material that reaches the filter can be expected to be the composition and particle size, as it does not circulate in the gaseous stream. The micrograph in Figure 12 shows the waste collected from the stack for composition T2 residing in the kiln.

Component	O1 Composition %	O2 Composition %	T1 Composition %	T2 Composition %
B_2O_3	48.30	42.90	54.60	-
K_2O	26.30	18.80	13.70	3.31
ZnO	12.60	18.80	6.30	6.90
SiO_2	5.48	0.09	6.53	61.90
Na_2O	4.49	14.40	9.54	15.96
BaO	1.20	0.96	1.72	1.84
Cl	0.64	0.88	0.62	0.04
CaO	0.43	0.39	0.89	1.65
SO_3	0.42	2.58	5.37	-
Fe_2O_3	0.27	0.27	0.29	0.27
MnO	0.14	0.09	0.15	0.09
ZrO_2	-	-	-	-
Al_2O_3	-	-	0.50	7.55

Table 9. *Chemical composition of the RF analysis by XRF (%)*

Figure 10 presents another spectrum, in this case of material T2, with crystalline phases present such as $ZrSiO_4$, SiO_2 and $KAlSiO_4$.

With these interpretations, the waste collected from the stack can be considered to contain material drawn off the raw materials by the exiting gas stream itself, as is the case of SiO_2 and $ZrSiO_4$.

Component	O1 Composition %	T2 Composition %
K_2O	20-25	15-20
ZnO	15-20	10-15
SiO_2	20-30	20-30
CaO	15-20	20-30
SO_3	0-3	0-5
ZrO_2	5-10	0-1
Al_2O_3	1-5	1-5
PbO2	0-2	0-2
MgO	0-2	1-5

Table 10. *Chemical composition of the RCh analysis by XRF (%).*

Table X lists the results obtained by XRF analysis of the waste collected from the stack walls for a zirconium white composition (O1) and for a transparent boric composition (T2).

5. CONCLUSIONS.

5.1.SPECIFIC CONCLUSIONS

In accordance with the objectives set, the study allowed drawing the following conclusions:

I. Quantification of the solid waste produced by air emissions.

It was determined that the input compositions of the type classified as an opaque white zirconium frit produced greater particulate concentrations than another composition classified as a transparent boric frit.

The explanation lies in the interrelationship between the type of waste found and the process variables.

II. Characterisation of the exhausted solid waste.

Waste was obtained adhered to the filter with very different characteristics from the waste collected from the stack or deposited in the isokinetic probe. The filter waste had a diameter smaller than 10 μm and was mainly made up of B_2O_3, ZnO and K_2O, without exhibiting any crystalline phase. This waste is thus exhausted as an aerosol and becomes part of the air quality.

Stack waste exhibited isolated particles with a varying diameter depending on their melting state and composition. It was made up of volatile material such as B_2O_3, K_2O, and unmelted material such as ZnO or $ZrSiO_4$, which appear as a result of turbulence inside the kiln drawing this material along with the gas flow. Emission of this material causes problems of sticking on the stack walls and clogging of the exhaust gas duct inside the stack.

Cyclone waste had a similar morphology to the stack waste but did not reach the filter, as it had a larger size than the waste in the filter.

The explanation of the morphology and composition of the different wastes that were characterised lies in the interrelationship of the emissions with the rest of the variables.

III. Relationship of the air emissions to the different industrial ceramic frit production process variables.

The influence of the raw materials in the chemical composition of the exhausted waste is presented in Table XI.

Raw material	Particle emission	Relative importance	Main oxide	O_2 %	CO_2 %	NO_x
K feldspar	↑	1	K_2O	-	-	↓
Potassium nitrate	↓	1	K_2O	-	-	↑
Colemanite	↓	1	B_2O_3	-	-	-
H_3BO_3	↑	1	B_2O_3	-	-	-
ZnO	↑	2	ZnO	-	-	-
Dolomite	↓	3	CaO	↑	↓	-
$CaCO_3$	↑	3	CaO	↓	↑	-

Table 11. *Conclusions regarding the relative contributions of the raw materials to air emssions.*

This table shows the tendencies of the relative contribution of certain raw materials to the final concentration of exhausted particles. The different operating parameters of the kiln and their different states of appearance should also be kept in mind as part of the raw materials input into the kiln.

IV. Raising the issue of considering the environmental variable in integral production planning.

The conclusion was reached that the quantity of waste adhering to the stack walls was sufficiently important to warrant considering the environmental variable in integral production planning.

Considering the best option of a cleaning system installation to be the grouping of the exhaust streams from three or four kilns, it is important to take into account the possibility of solid waste recovery, as part of the economic output of the cleaning facility.

In view of the results of this study, it would be compatible to have a group of melting kilns containing zirconium white compositions and transparent boric compositions similar to the ones studied, the zirconium white frits being the ones that contribute the largest relative emissions.

Finally, it is necessary to plan the materials that are to be fed into the melting kilns in relation to the cleaning system, and control the homogeneity of the resulting waste, if this waste is to be reused in formulating new ceramic frits.

5.2. GENERAL CONCLUSIONS

To end this study, three final conclusions are presented from three different points of view regarding the benefits obtained from the study of air emissions, i.e., the aerosol (gas plus submicron particles) and micron-size particles.

From an environmental standpoint it was found that although the submicron particles can have a negative effect on the overall environment, the micron-size particles can have negative effects on a local scale, which becomes greater with larger concentrations of similar facilities in the same area. As the micron-size particles are basically drawn along by the aerosol, this conclusion relates directly to the following one.

With regard to the economic aspects, it appears clear from the study of the emissions collected in the stack that the frit production process can be optimised in to two ways: i) reduction of the losses of useful material (fundamentally micron-size particles), this raising production yield, ii) avoiding as far as possible the number of production stoppages for conditioning the stacks owing to problems of obstruction.

Finally, in relation to the conclusions regarding science applied to the environment, it is evident that the approach must be interdisciplinary and multidisciplinary to be able to understand the emission phenomena as a whole, as specialisation in some of the different aspects (i.e., gases, sub-microparticles, microparticles) only provide partial views. The study conducted has shown the intercorrelation between the various aspects dealt with. This type of study can therefore only be performed by teams of different specialists from the university and/or scientific community as well as from the field of industrial production.

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