INTEGRATED POLLUTION PREVENTION AND CONTROL IN THE CERAMIC TILE INDUSTRY. BEST AVAILABLE TECHNIQUES (BAT)

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ABSTRACT

A document has been drawn up setting out Best Available Techniques (BAT) in ceramic tile manufacture, based on Directive 96/61/CE. The content of the document is applicable to glazed and unglazed, redware and whiteware floor and wall tile manufacturing processes, involving wet and dry raw materials preparation methods, using pressing and extrusion as forming techniques, and surface finishes with or without machining.

The ceramic tile manufacturing processes referred to in the present document only consider single or twice firing of ceramic tiles, but always by using single-deck roller kilns or similar techniques.

The limiting values for emissions, energy and water consumption, etc. are at least those set out in the Environmental Recommendation of the European Ceramic Tile Manufacturers' Federation (CET).

To establish the nature and concentration of the substances present in each stream, the origin of each substance has been analysed in detail, and the substances that may be found have been identified; after identification, the corresponding analysis methods have been established and adjusted.

The document includes Best Available Techniques (BAT) for cleaning gas emissions, Best Available Techniques for reducing consumption, preventing and reducing emissions, treatment of the wastewater arising in the process, and Best Available Techniques for the prevention, reduction and treatment of the waste arising in ceramic tile manufacture.

1. INTRODUCTION

Based on the guidelines set out in Directive 96/61/CE, a document has been drawn up of Best Available Techniques (BAT) in ceramic tile manufacture. The objective of the present paper is to provide the ceramic technician with practical information on the cleaning systems that can be used in gas emissions, discharges and wastes arising in the ceramic tile manufacturing process[1].

A current issue of concern in the ceramic industrial branch, and matter of considerable economic importance, is the possible industrial interaction with the environment, especially if the high concentration of companies and growing demands of the international market are taken into account.

Directive 96/61CE of the EU Commission issued on 24 September 1996 concerning integrated pollution prevention and control (DO no. L257, of 10 October 1997), represents the first initiative at EU level to establish measures for preventing or, whenever this is not possible, reducing emissions into the air, water or land, and therefore also includes wastes.

Directive 96/61CE indicates that all the industrial facilities covered by the Directive need to have a permit for running the industrial facility under certain conditions, ensuring compliance with the Directive. Moreover the Directive defines Best Available Techniques (BAT) as the most efficient and advanced stage (state of the art), for conducting the activities and process modes, which in principle have demonstrated their technical capacity to constitute a basis for emission limits, in order to prevent, or whenever this is not possible, to generally reduce emissions and their impact on the whole environment.

[1]. *Directive 96/61/CE*. DOCE nº L257, of 10 October 1997.

In Annex IV, the Directive sets out the aspects to be taken into account of a general nature, or in a specific case when Best Available Techniques (BAT) are determined, defined in Point 11 of Article 2, taking into account the costs and profits possibly stemming from an action, and the principles of precaution and prevention.

Use of minimum waste producing techniques.

Use of least hazardous substances.

Development of recovery and recycling techniques of substances produced or used in the process, and of arising waste should this be the case.

Comparable processes, facilities or operating methods that have yielded satisfactory results on an industrial scale.

Technical advances and evolution of scientific knowledge.

Nature, effects and volume of the emissions involved.

Starting up dates of new or existing facilities.

Term required for implementing the best available technique.

Consumption and nature of the raw materials (including water) used in efficient energy methods.

Need to prevent or minimise the overall impact of the emissions and risks to the environment.

Need to prevent any risk of accident occurring or minimising their consequences for the environment.

Information published by the Commission, in virtue of Section 2 of article 16, or by international organisations.

Taking into account the above Directive, and especially the contents referred to above, the present document has been drawn up to provide the ceramic tile industry with information concerning best available techniques, whose exchange amongst Member States and the relevant industrial branches is to be organised by the Commission in observance of the provisions set out in Section 2 of Article 16.

The content of the document is applicable to glazed and unglazed, redware and whiteware floor and wall tile manufacturing processes, involving wet and dry raw materials preparation methods, using pressing and extrusion as forming techniques, and surface finishes with or without machining.

The ceramic tile manufacturing processes referred to in the present document only consider single or twice firing of ceramic tiles, but always by using single-deck roller kilns or similar techniques.

The techniques put forward in this document meet the following requirements:

- Effectively available for development on a scale allowing application in the ceramic tile branch under economically and technically feasible conditions, taking into account resulting costs and benefits, and possibilities of access under reasonable conditions.

- Being the best techniques, in the sense of most effective for achieving a high overall degree of general environmental protection.

The limiting values on emissions, energy consumption, water consumption, etc., are at least those contemplated in the Environmental Recommendation of the European Ceramic Tile Manufacturers' Federation (CET), hereinafter termed CET Recommendation[2], [3].

A study of any system of prevention, reduction and treatment of emissions, discharges and industrial waste requires:

Determining the substances contained in the various streams, with their concentrations and the characteristics of the stream.

Starting out, at least initially, from set limit values. In this paper, the limit values for emissions, water and energy consumption etc. set in the Environmental Recommendation of the European Ceramic Tile Manufacturers' Federation (CET) (Annex I)[3] were used as starting limit values.

Identification of Best Available Techniques, indicating wherever convenient, the most suitable ones for each given situation.

2. BEST AVAILABLE TECHNIQUES FOR CLEANING GAS EMISSIONS ARISING IN CERAMIC TILE MANUFACTURE.

To establish the nature and concentrations of the substances present in each stream, the origin of each has been analysed in detail, identifying the substances that might be present; after identifying these, the corresponding analysis methods were established and adjusted[4], [5], [6].

Once the pollutants to be treated and their initial and end concentrations had been determined, it was necessary to establish the characteristics of the stream. The better the stream to be treated is known, the greater will the possibilities of success be on choosing the cleaning system; for each stream the following data must at least be determined: flow rate, temperature, moisture content, presence of problem compounds (acids, melted or corrosive materials, etc.), and in the emissions from a combustion process, the oxygen percentage.

2.1. GAS EMISSIONS IN THE RAW MATERIALS PREPARATION STAGE

2.1.1. CONCENTRATION OF SUBSTANCES PRESENT AND CHARACTERISTICS OF THE GAS STREAM

The arising emission in this stage involves particulates from the raw materials used

[2]. *Environmental Requirements of the European Ceramic Tile Manufacturers.* (CET). Brussels, November 1996.
[3]. PROBST, R.; *Environmental Requirements Recommendation of the European Ceramic Tile Manufacturers.* V World Congress on Ceramic Tile Quality. Qualicer, Castellón, March 1998.
[4]. ASSICERAM. *Inquinamento da fumi nell'industria ceramica.* Ceramica Informazione, 133, 407 - 415, 1977.
[5]. BLASCO, A.; ESCARDINO, A.; BUSANII, G.; MONFORT, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.
[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

in preparing the bodies. The constituents involved are mainly clay particles, quartz, feldspar and carbonates and the characteristics of the particulate or dust emissions are the same as those of the raw materials used[5].

In dry milling, the emission flow rate is about 6Nm^3 air/kg , and particulate concentration lies at about 50g dust/kg processed raw materials.

In wet milling, particulate emissions drop significantly compared to the dry method, since the milled product appears as a slip. The emission flow rate is similar to the previous one, lying at about 6Nm^3 air/kg, with a particulate concentration of around 15g/kg[6]).

2.1.2. BEST AVAILABLE TECHNIQUES (BAT) FOR TREATING GAS EMISSIONS IN THE RAW MATERIALS PREPARATION STAGE

Based on the foregoing data, bag filters are the most suitable cleaning systems for reducing particulate concentrations from emissions arising in raw materials preparation to the limits set in the CET Recommendation

Wet cleaning systems of a Venturi type are not recommendable, since to obtain satisfactory yields, these must operate at high speeds (50-100 m/s), entailing very high charge losses and water consumption.

Dry emission cleaning systems have the advantage of obtaining the waste in a solid form, facilitating recovery and handling. These are therefore the most suitable treatment procedures in facilities where bodies are prepared by the dry method, and in those in which spray-dried powder is used which comes from external facilities via wet milling (spray dryers).

As both cases involve emissions of particulate matter with a low moisture content, the best technique is a local suction system with filter bag cleaning.

If this equipment is correctly sized, they run at "filtration rates" of less than 2 m/min (air flow rate/filtering surface area ratio), and if filters of suitable material are used, very high yields are produced (98-99.8%).

With a view to limiting the spread of dust inside the workplace, a suction system needs to be installed to ensure an appropriate particulate capture rate at every point.

2.2. GAS EMISSIONS IN SPRAY-DRYING THE BODY SLIP

2.2.1. CONCENTRATION OF SUBSTANCES PRESENT

The following substances were determined: particulates (P_v), nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2) and oxygen (O_2). In the emissions arising on drying slips to which aqueous suspensions were added containing ceramic materials from cleaning operations run in the glazing section, the following elements were also determined: boron (B), chlorine (Cl) and lead

[5]. BLASCO, A.; ESCARDINO, A.; BUSANII, G.; MONFORT, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.

[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

(Pb)[6]. Table 1 presents the variation ranges of the concentrations obtained for these substances.

Substance	Variation range	Substance	Variation range
P_v (mg/Nm^3)	150 –1500	B (mg/Nm^3)	< 0.3
NO_x (ppm)	3 – 15	Cl (mg/Nm^3)	1 – 5
CO (ppm)	1 – 15	Pb (mg/Nm^3)	< 0.15
CO_2 (%)	1.5 – 4		

***Table 1.** Concentration of the substances present.*

The particulates found in spray-dryer emissions come from the dust and finest spray-dried granules being dragged along by the gases. Boron, chlorine and lead come from the water used in cleaning the glaze application sections. Most of these compounds are held in the spray-dried granules, and the remainder, which are detected in the emissions, are drawn along with the water that evaporates in spray drying[5].

With regard to carbon monoxide, a substance arising in combustion, the values found are low as the fuel used is natural gas

Boron and lead concentrations are low, because the concentrations of these elements in the cleaning water used in slip preparation is low, since their presence is due to the dissolution of these elements in the waste glaze contained in the cleaning water. The chlorine concentration is the highest, as its content in the cleaning water is the largest.

On comparing the concentrations of the substances detailed in Table 1 with the concentration limits set in the CET Recommendation, it can be observed that the only substance that needs cleaning is particulate matter.

2.2.2. CHARACTERISTICS OF THE GAS STREAM

The parameters that were determined to characterise the gas streams in the spray dryer stack were: flow rate (Q), temperature (T), moisture (H) and oxygen content (O_2)[6]. Table 2 shows the variation ranges found in different facilities for these parameters.

Parameter	Variation range	Parameter	Variation range
Q (Nm^3/h)	15000 –125000	H (m^3 water/m^3 total)	0.13 - 0.20
T (°C)	90 – 115	O_2 (%)	16 - 20

***Table 2.** Characteristics of the gas stream.*

The variation range of the flow rates is very wide, as the evaporation capabilities of spray dryers range from 4000 l/h for a spray-dried powder production of 10 t/h, to 15000 l/h for a 39 t/h production.

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[5]. Blasco, A.; Escardino, A.; Busanil, G.; Monfort, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.

[6]. Busani, G.; Palmonari, C.; Timellini, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

Temperature and moisture content in the stream are critical parameters, which need to be carefully taken into account when it comes to selecting a cleaning system. The values of these two parameters will produce water condensation when the temperature drops below the dew point.

2.2.3. BEST AVAILABLE TECHNIQUES (BAT) FOR CLEANING GAS EMISSIONS IN SPRAY DRYING THE SLIP BODY

Based on the data from the above sections, bag filters and wet cleaning systems are the most suitable treatment systems for lowering particulate concentrations in the emissions from the spray-drying stage to the limits set in the CET Recommendation. This section describes the specific technical characteristics required for each of these systems to allow using them in this stage. All these parameters have been defined for different emission source flow rates.

2.2.3.1. BAG FILTERS

Bag filter design for this emission source should take into account the arising water condensation when the temperature drops below dew point. If this condensation is not avoided, the material will stick to the material at the outer surface of the bag and produce clogging. To avoid such condensation, bag filters are thermally insulated and fitted with a heating system so that on starting up the equipment, they have a temperature exceeding 120°C, before the stream to be treated is fed in. Moreover, these systems need to be equipped with a control system to ensure that when the gases at filter entrance have a temperature below 120°C, these gas will be released without going through the cleaning system[6].

The parameters to be defined in bag design are: type of bag fabric, material used to build the filter and bag holder, and filtration rate.

Bag fabric is conditioned by stream temperature and moisture content. The fabric may be polyester, whose dust intake face is prepared to facilitate peeling of the retained cake, or may be acrylic (Dralon T) or tefloned nomex.

The material used to build the filter and bag holders needs to be corrosion-proof, and to withstand possible water condensation. The filtration rate used in designing these systems ranges from 1.2 to 1.5 $m^3/m^2/min$.

These systems yield particulate concentrations in the treated stream of less than 30 mg/Nm^3.

2.2.3.2. VENTURI-TYPE WET SCRUBBERS

In Venturi-type scrubbers, after the gases have entered into contact with the water, they enter an expansion chamber where part of the water drops are separated from the gas stream.

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[6]. Busani, G.; Palmonari, C.; Timellini, G., *Piastrelle ceramiche & Ambiente*. Sassuolo (Italy), Edi.cer, S.p.a. 1995.

In such systems, the key parameter controlling particulate removal is the ratio between the gas rate and water droplet rates in the Venturi throat.

If a spray dryer is available, the use of wet gas scrubbers is feasible, as the water used in treatment can be reused in slip preparation.

These systems yield particulate concentrations in the treated stream of between 50 and 75 mg/Nm^3, depending on Venturi charge loss.

2.3. GAS EMISSIONS IN THE TILE FORMING STAGE

2.3.1. CONCENTRATION OF SUBSTANCES PRESENT AND GAS STREAM CHARACTERISTICS

In forming the tiles by pressing, the moisture content of the ceramic powder body lies at around 5-6%, which is sufficiently dry to reduce sticking and facilitate dispersion, especially in the finer fractions or those with a lower moisture content.

Dust dispersion in the environment is attributable to:

Raw materials transport from the bins to the press hoppers.

Pressing operation (sliding filler feed, die filling, etc.).

Scraping or machining the compact.

Suction systems should be installed to ensure suitable particulate capture.

The chemical characteristics of the collected powder are those of the raw materials used, since no type of transformation has occurred.

In forming the pieces by pressing, the emission flow rate is around 5Nm^3 air/kg, and particulate concentration lies at about 7g/kg.

In extrusion processes, as mixing takes place with water prior to extrusion, this stage yields no particulate emissions.

2.3.2. BEST AVAILABLE TECHNIQUES (BAT) FOR CLEANING GAS EMISSIONS IN THE FORMING STAGE

In this case, as in the raw materials preparation, bag filters are the most suitable cleaning system for reducing particulate concentrations in the emissions during raw materials preparation to the limits set in the CET Recommendation.

2.4. GAS EMISSIONS IN DRYING GREEN CERAMIC BODIES

The drying of green tile bodies has traditionally and still does take place in vertical dryers, though the use of horizontal dryers is becoming quite widespread. The data corresponding to the substances present and stream characteristics correspond to vertical and horizontal dryers.

2.4.1. CONCENTRATION OF SUBSTANCES PRESENT

The following substances were determined: suspended dust (P_s), carbon dioxide

(CO_2) and oxygen (O_2)[6]. Table 3 shows the variation ranges of the concentrations found.

Substance	VARIATION RANGE
P_s (mg/Nm^3)	5 -25
CO_2 (%)	1 - 3
O_2 (%)	16-20

Table 3. *Concentration of substances present.*

The particulate matter found in dryer emissions is the result of dust particles stuck to the body and dust arising from breaking tiles in the dryers being drawn along by combustion gases. Particulate concentrations in this gas stream are moderate.

The CO concentration is very low, owing to the high excess air used in these facilities with fuelling by natural gas. The widespread use of natural gas in this process stage has lowered potentially polluting substances considerably in this emission source. The low temperatures usually employed in these facilities (< 300°C) impede nitrogen oxide (NO_x) formation in this process stage.

Comparing the concentrations detailed in Table 3 with the limits set in the CET Recommendation reveals that no cleaning system is required for this stream.

2.4.2. CHARACTERISTICS OF THE GAS STREAM

The following parameters were determined to characterise gas streams: flow rate (Q), temperature (T), moisture content (H) and oxygen content (O_2).

Parameter	Variation range	Parameter	Variation range
Q_{dry} (Nm^3/h)	2000 –7000	H (m^3 water/m^3 total)	0.04 - 0.11
T (°C)	50 – 190	O_2 (%)	17 – 20

Table 4. *Characteristics of the stream.*

The gas stream arising in drying green ceramic materials is characterised as being a stream with a lower flow rate than that of other manufacturing process stages, especially compared to spray drying.

2.4.3. GOOD PRACTICE FOR MINIMISING PARTICULATE EMISSIONS IN THE DRYING STAGE OF GREEN CERAMIC BODIES

Good management of a dryer, keeping particulate emissions in the exhaust stream to a minimum, is sufficient to render implementing a cleaning system unnecessary.

[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente*. Sassuolo (Italy), Edi.cer, S.p.a. 1995.

Particulate emissions can be minimised basically by the following good practice:

- Periodically cleaning the dryer to remove possible scrap inside.
- Keeping the cleaning equipment at the dryer entrance in good condition.
- Periodical revision of tile handling systems in the dryer, to avoid breakage.
- Minimising gas flow rate, etc.

2.5. GAS EMISSIONS IN THE GLAZING AND GLAZE PREPARATION STAGES

The characteristics of the emissions in these stages will depend on the glaze application technique used.

2.5.1. CONCENTRATION OF SUBSTANCES PRESENT AND CHARACTERISTICS OF THE GAS STREAM

During the glazing and glaze preparation process, particulates are released in the following operations:

- Milling or mixing of the materials making up the glaze formulation. The finest materials tend to spread out in the surroundings during the mill loading step.
- Machining of stick-ups on the body and scraping of unfired glaze from the tile edges. This produces dry or semi-dry dust, as most of the water contained in the glaze slip has been removed by absorption in the body y/or evaporation.
- Glaze application in disking or airbrushing booths that produce a more or less intense haze from the slip, in the former case by centrifugation and in the latter by spraying with compressed air. In both cases, the glaze tends to hang in the air as droplets or a fine mist.
- Dry glaze application as granulars or in powdered form. As they are directly applied to the bodies, dust is produced in the surroundings; the finer the material involved the greater the dust.

The physico-chemical characteristics of these emissions are highly variable as a result of the great diversity in glazes used. In this case, the emission flow rate is around $5Nm^3$ air/kg and particulate concentration is about 0.5g dust/kg processed glaze[6].

The dust arising in glazing and glaze preparation is characterised by the presence of compounds exhibiting network forming cations (silicon, boron, zirconium, etc.), compounds exhibiting network modifying cations (sodium, potassium, lead, lithium, barium, calcium, magnesium, zinc, etc.) and compounds exhibiting intermediate cations (aluminium, etc.).

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[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

Thus the arising dust released in glazing is intrinsically much more toxic than the particulates released in preceding production stages.

2.5.2. BEST AVAILABLE TECHNIQUES (BAT) FOR CLEANING GAS EMISSIONS FROM THE GLAZING AND GLAZE PREPARATION STAGES

Based on the data set out above, the most suitable cleaning systems for reducing particulate concentrations in the emissions arising in the glazing and glaze preparation stages to the limits set in the CET Recommendation are wet cleaning systems, mainly of the Venturi type.

Wet systems are the most widely used systems as the particulate matter to be treated generally contains appreciable quantities of water at room temperature. As very fine particulates are to be captured, systems that produce droplets of water or large air bubbles, and/or do not achieve the necessary turbulence to bring the liquid phase and the solid phase into contact, will not produce good yields.

To ensure that these conditions are met, in Venturi-type scrubbers this requires reaching high rates in the Venturi throat (50-100 m/s).

The water produced in cleaning these gases usually joins the water from the washing operations of the glazing and glaze preparation facilities, and both streams undergo the same treatment.

2.6. GAS EMISSIONS IN THE FIRING STAGE

Firing ceramic tile usually takes place in single-deck roller kilns.

These kilns exhibit two potential pollutant emission foci; the flue gas exhaust stack and the cooling air intake stack.

The gases arising in the tile heating zone exit the exhaust stack. These gases mainly consist of gases produced in the combustion of natural gas, as well as gases released in the chemical decomposition that occurs in the body during heat-treatment.

The hot gases produced in cooling the tiles from peak temperature down to kiln exit temperature (usually higher than room temperature) leave via the cooling stack. As no chemical breakdown takes place during cooling, and the gas used for cooling is air, the stream arising in this stack consists of hot air. Therefore, the concentrations of potential pollutants in the emissions from the cooling stack are very low and no cleaning treatment is required.

The data on the nature and concentrations of the substances present, as well as stream characteristics, only refer to the exhaust stack emissions in which pollutants may need to be cleaned.

There is a great variety in firing facilities, each of which has its own peculiarities with regard to production, type of product, heat-treatment cycle, width and design of the kiln, etc. The principal differences in these emission foci concerning the presence and concentration of substances are basically due to the composition of the body and size of the pieces being fired.

Tile size affects the concentration of the substances present in the exhaust stack, because tile thickness is generally associated with tile size. As the gas flow rate in the kiln does not change significantly with size, and the absolute quantity of broken-down matter rises owing to increased tile mass, raising tile size raises pollutant concentrations.

2.6.1. CONCENTRATION OF SUBSTANCES PRESENT

The following substances were determined: particulates (P_s), fluorine (F), boron (B), chlorine (Cl), lead (Pb), nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2) and oxygen (O_2)[6].

The suspended dust in the kiln exhaust stack is drawn along by the gases inside the kiln, and comes from particulates deposited on the tiles (granulars, dirt or grit, etc.) and/or scrap from the first areas in the kiln. As the quantities of such particulates and scrap are not very high, the suspended dust concentration in the exhaust stack stream is usually low.

Substance	Variation range	Substance	Variation range
P_s (mg/Nm^3)	5-50	Pb (mg/Nm^3)	< 0.15
F (mg/Nm^3)	5-40	NO_x (ppm)	15 – 60
B (mg/Nm^3)	< 0.5	SO_2 (mg/Nm^3)	< 10
Cl (mg/Nm^3)	20-90	CO (ppm)	1 – 15
		CO_2 (%)	1.5 – 4

Table 5. *Concentration of substances in the exhaust stack.*

The fluorine detected in the gas stream comes from the decomposition of the clay minerals contained in the raw materials of the body[8]. The emission of fluorine depends on the firing cycle and characteristics of the raw materials used[9]. In general, when faster firing schedules are used and when clays containing considerable proportions of calcium compounds are involved, the fluorine emissions are reduced as a result of stable calcium fluoride formation. The fluorine concentration in the clays used as ceramic raw materials ranges from 500 to 800 ppm (mg/kg).

The boron and chlorine present in the emissions mainly come from the water contained in the tile when it enters the kiln, which is subsequently evaporated in the first firing stages. The water involved has remained in the tile after drying the body or was incorporated into the body and/or glaze during the glazing operation.

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[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

[7]. BUSANI, G.; LANCELLOTTI, F.; TIMELLINI, G.; PIAZZA, F.; *Il controllo delle emissioni dagli impianti ceramici.* Modena (Italy). Edi.cer, S.p.a. 1987.

[8]. GAZULLA, M.F.; GÓMEZ, P.; CABRERA, M.J.; MONFORT, E.; *Determinación de fluor en las arcillas utilizdadas en la fabricación de baldosas cerámicas.* Técnica Cerámica, 243, 298-302, 1996.

[9]. MAZZALI, P.; FOGLIANI G.; ORLANDI, L.; BUSANI, G.; *Effetto della temperature e del contenuto di calcio e magnesio sulla cessione di fluoro nella cottura delle piastrelle ceramiche.* La Ceramica, 33(2), 1 (1980).

Boron concentrations are low as the boron concentration in the cleaning water is low. With regard to chlorine, the concentration depends on the type of water used.

The stream's lead content is quite small and basically comes from vaporisation of the quite minor group of glazes containing this element.

2.6.2. CHARACTERISTICS OF THE GAS STREAM

The parameters that were determined in order to characterise the gas stream, and which are needed for designing a suitable cleaning system are: flow rate (Q), temperature (T) and moisture content (H). Table 6 sets out their variation ranges.

Parameter	Variation range	Parameter	Variation range
Q_{dry} (Nm^3/h)	5000 -15000	H (m^3 water/m^3 total)	0.05 - 0.10
T (°C)	130 - 300		

Table 6. *Characteristics of the stream.*

The stream of gases exiting the kiln via the exhaust stack as a result of the firing process is a stream with a low flow rate, especially on comparing it to other production process stages like spray drying. The measured flow rates at the different facilities were found to lie within a relatively narrow range, although production in the different facilities differed considerably.

The temperature values measured were variable and mainly depended on the type of product being fired and firing curve design in each case.

The moisture content of the gases was lower than the value found in the spray dryer emissions and came mainly from the water that formed during combustion, and from the moisture removed from the body and the glaze in the first stages of the firing process.

2.6.3. BEST AVAILABLE TECHNIQUES (BAT) FOR CLEANING THE GAS EMISSIONS ARISING IN FIRING CERAMIC TILE

The cleaning system to be implemented in a tile firing kiln needs to fulfil a double task: capturing the fluorine in the gas phase and separating the particulate matter suspended the gases, thus cleaning the gases.

Taking into account the data set out in the foregoing sections, the most suitable cleaning systems for cutting back particulate concentrations in firing stage emissions are bag filters, electrostatic precipitators and wet filters.

This section describes the specific technical characteristics required by each of these types of cleaning systems to allow using them in this stage.

2.6.3.1. DRY KILN GAS CLEANING SYSTEMS

In these systems, to capture the fluorine present in the gas phase as hydrofluoric acid, this is made to react with a solid reagent. After the reaction between the fluorine present in the gas phase and the reagent, the reaction is usually separated from the gas stream by a system that separates suspended particulates.

The efficiency of the different reagents used for capturing fluorine in the gas stream depends on many factors. The following are particularly to be highlighted:

- Starting fluorine concentration in the gas stream
- Contact time between gases and reagent
- Gas temperature
- Specific surface area of the reagent used
- Level of turbulence reached in the reaction region, etc.

The reagents normally used to capture fluorine are calcium hydroxide ($Ca(OH)_2$) and sodium bicarbonate ($NaHCO_3$), which form calcium and sodium fluoride respectively. Calcium fluoride is a flocculating salt, so that minor additions to the clay slip raise slip viscosity. This then requires increasing the deflocculant addition to be added to the slip, in turn lowering slip solids content. On the other hand, sodium fluoride has a very slight flocculating effect on the slip's rheological behaviour, so that it can be added in small proportions.

If calcium hydroxide is used as a reagent to retain fluorine the following chemical reaction arises:

$$Ca(OH)_2 + 2\,HF \longrightarrow CaF_2 + 2\,H_2O$$

According to the literature[9], for a HF concentration in the gas stream of a single-deck roller kiln (4-40 mg/Nm^3), the quantity of calcium hydroxide to be used is 6.48g $Ca(OH)_2$/g FH. The final amount of substance thus produced is the sum of the excess calcium hydroxide and the calcium fluoride that is produced.

If sodium bicarbonate is used to retain fluorine the following chemical reaction arises:

$$NaHCO_3 + HF \longrightarrow NaF + H_2CO_3$$

The product that really reacts with HF is sodium carbonate, which forms when the sodium bicarbonate loses a water molecule above 180°C (10). The sodium carbonate that is thus formed has a high specific surface area and therefore great efficiency in fluorine retention.

The quantity of substance that is thus ultimately produced is the sum of the excess

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[9]. Mazzali, P.; Fogliani G.; Orlandi, L.; Busani, G.; *Effetto della temperature e del contenuto di calcio e magnesio sulla cessione di fluoro nella cottura delle piastrelle ceramiche*. La Ceramica, 33(2), 1 (1980).
[10]. NEUTREK Process. E.P. 0603218 (29/1/97).

sodium bicarbonate and the sodium fluoride that forms, therefore being 4.20g $NaHCO_3$ / g HF[11].

2.6.3.1.1. BAG FILTERS

Bag filter design for this emission source must especially take into account the high temperatures of the gases to be treated. The fact will mainly affect bag filter operation and the type of bag to be used.

The flue gases from the single-deck roller kiln are drawn to the bag filter, as shown in Figure 1. In flue gas travel to the bag filter, the solid reagent ($Ca(OH)_2$ or $NaHCO_3$) is injected into the stream to retain fluorine. This powdered reagent is injected into the flues by a pneumatic spraying system. It is important to add the reagent as far away as possible from the bag filter, to obtain the longest contact time between the gas phase and the solid phase.

The bag filter is designed to work at a given temperature, normally below kiln gas exiting temperature. If necessary, these hot gases need to be cooled by bleeding in air at ambient temperature or by using an air-air heat exchanger.

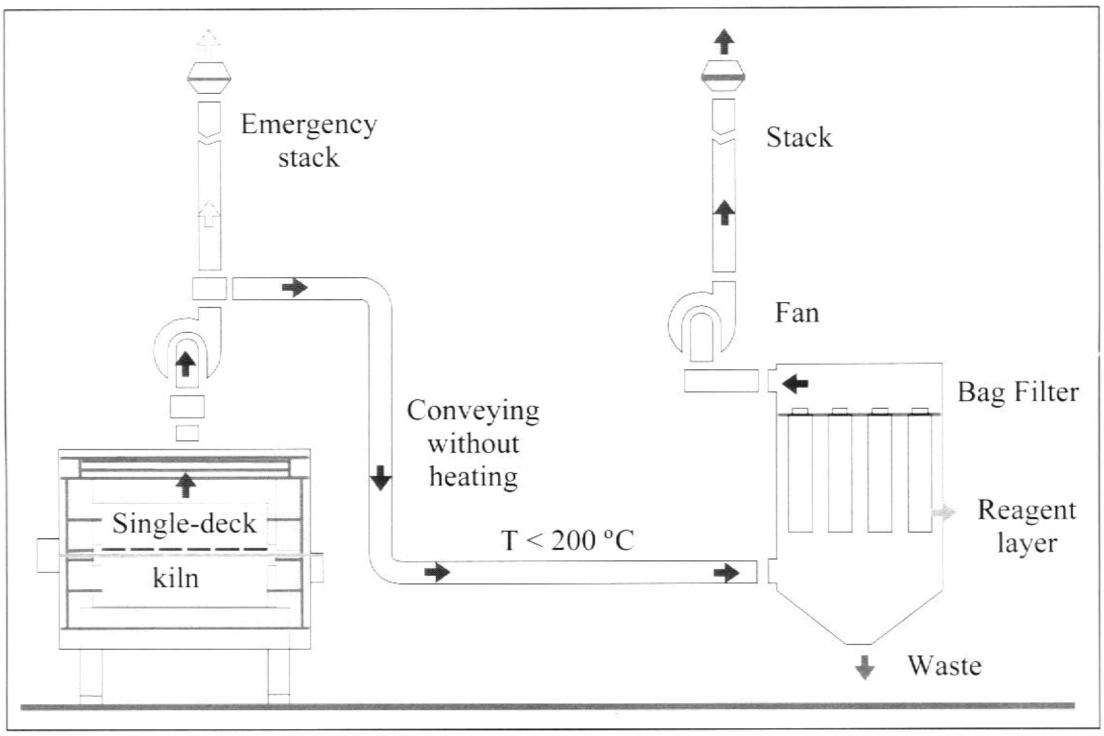

Figure 1. *Schematic of the kiln exhaust gas cleaning system with a bag filter.*

The bag fabric is defined by the temperature of the gases to be treated, and may be of polytetrafluoride ethylene (Teflon or gorotex), aromatic polyamide (tefloned nomex), polyester (dracon), acrylic (dralon T) or polyamide material.

A bag filter facility allows achieving fluorine concentrations in the treated stream of

[11]. VICENT, R.; ARANGUREN, J.; MONFORT, E.; *Acid emission cleaning system with sodium bicarbonate for ceramic tile kilns*. V. World Congress on Ceramic Tile Quality. Qualicer, Castellón, March 1998.

less than 5 mg/Nm³ and suspended dust concentrations of less than 20 mg/Nm³. The cleaning efficiency of these systems is estimated at 99% for retention of suspended particulates, and 95% for fluorine retention[5], [6].

2.6.3.1.2. ELECTROSTATIC PRECIPITATOR

The flue gases from the single-deck roller kiln are drawn to the electrostatic precipitator, as shown in Figure 2. All the aspects relating to the reagents and their use are the same as in cleaning with bag filters.

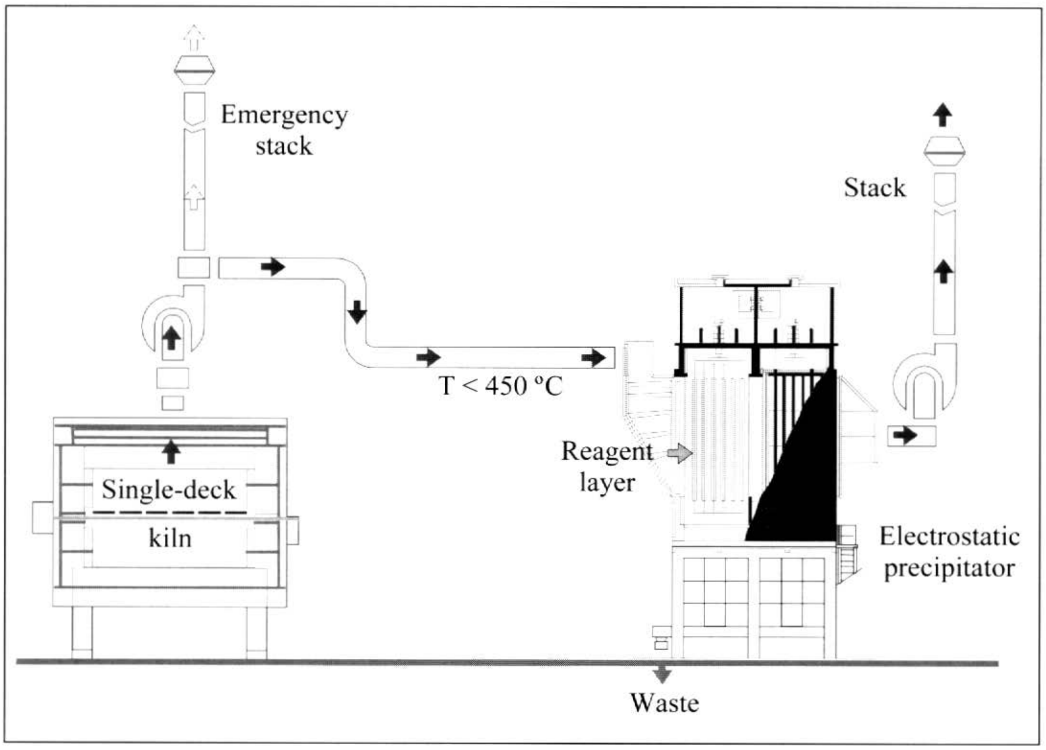

Figure 2. *Schematic of the kiln exhaust gas cleaning system with an electrostatic precipitator.*

This cleaning system has the advantage of being able to run at high temperatures, easily exceeding 400°C, so that no cooling of the exhaust flue gases is required prior to cleaning, and energy recovery from the clean gases is facilitated[11].

2.6.3.2. WET CLEANING SYSTEMS OF KILN EXHAUST GASES

Figure 3 presents a schematic of the wet gas scrubbing facility for kiln exhaust gases. In these facilities the following points should be taken into consideration:

The need to work at temperatures of 70-80°C can determine whether to use heat exchangers, as the gases exit the stack at temperatures of around 200°C.

The equipment needs to be built with materials and systems that are corrosion-

[5]. BLASCO, A.; ESCARDINO, A.; BUSANII, G.; MONFORT, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica*. Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.

[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente*. Sassuolo (Italy), Edi.cer, S.p.a. 1995.

[11]. VICENT, R.; ARANGUREN, J.; MONFORT, E.; *Acid emission cleaning system with sodium bicarbonate for ceramic tile kilns*. V. World Congress on Ceramic Tile Quality. Qualicer, Castellón, March 1998.

proof, as the gas pollutants on entering the liquid phase usually form a corrosive medium. To counteract this effect, in some systems water pH is monitored and reagent additions are used to neutralise and/or enhance the scrubber's yield for specific pollutants.

In particulate removal, to obtain suitable yields high-speed Venturi systems should be implemented. Other types of wet scrubbers usually exhibit very low yields.

As in dry gas cleaning, the system used depends on the reagent employed to capture fluorine, i.e., whether the substances in the water are sodium or calcium compounds.

In this case, sodium hydroxide and sodium carbonate are employed as sodium compounds, although sodium compounds of a deflocculating nature could be used for the body slip, such as sodium metasilicate and sodium tripolyphosphate.

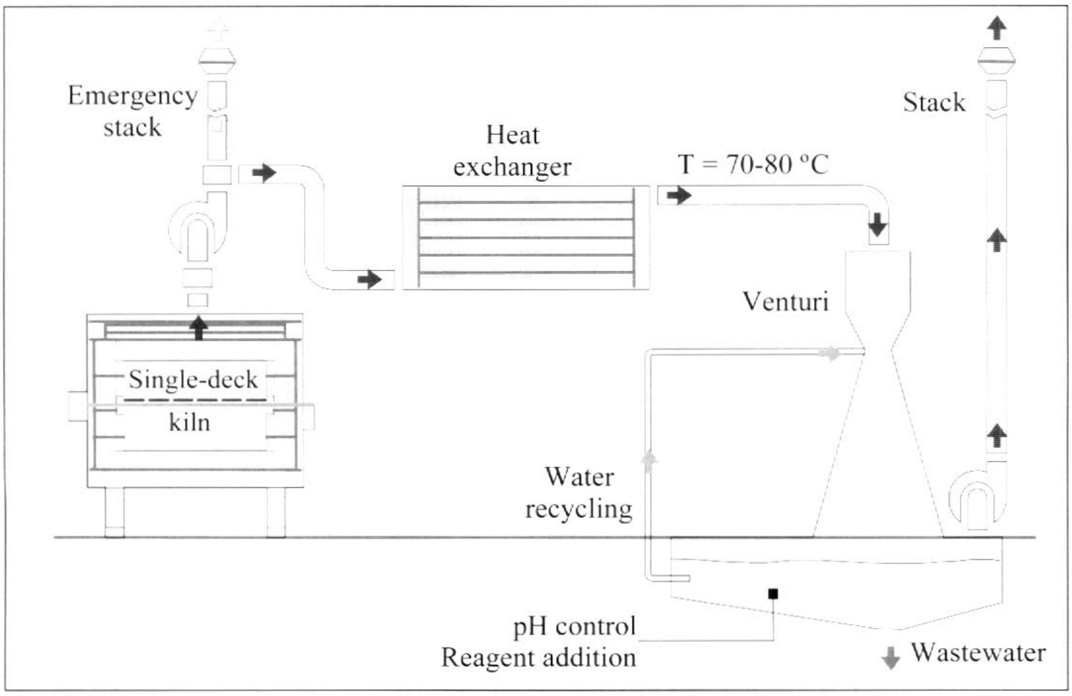

Figure 3. Schematic of the kiln exhaust gas cleaning system with a wet scrubbing Venturi-type facility.

3. BEST AVAILABLE TECHNIQUES FOR REDUCING CONSUMPTION, PREVENTING AND REDUCING EMISSIONS, AND TREATING WASTEWATER ARISING IN CERAMIC TILE MANUFACTURE

3.1. CHARACTERISTICS OF THE FACILITIES AFFECTING WASTEWATER MANAGEMENT

There is no single solution in the ceramic tile branch when it comes to designing an industrial wastewater management plan. This depends on the specific characteristics of each facility and type of product involved. The characteristics affecting such management are as follows:

As the solutions adopted in one company cannot be extrapolated to another with apparently similar characteristics, it is important to establish alternative management processes[5], [6], [12].

3.1.1. TYPE OF BODY PREPARATION PROCESS FOR POWDER PRESSING

In dry body preparation, the raw material for the body is dry milled in a hammer mill or a pendular type of mill. The mixture is then wetted to 7-12% on a dry weight basis. In this last case, the granulated material is dried to a moisture content of 6-7%.

In wet body preparation, the raw material of the body is wet milled in a ball mill by mixing with water to a moisture content of 42 % on a dry basis. Granulation subsequently takes place using a spray-drying process and the granulated material is dried to a moisture content of 5-6%.

It can be observed that when a wet process is used, water consumption is about four times higher than in the dry process. This means that the quantity of water employed, which can be reused in the same body preparation process, is greater in the wet method than in the dry method.

3.1.2. TYPE OF PLANT

Plant types involve those with a body preparation process, i.e., having a full manufacturing cycle, and those without a body preparation process, i.e., whose spray-dried powder comes from an outside supplier.

In the case of a ceramic tile manufacture with a full manufacturing cycle, wastewater management is easier, as all the arising wastewater can be reused in the body preparation process.

In the second case, wastewater management is limited. The recommended solution is returning the wastewater to the milling and spray-drying facility that supplies the spray-dried powder.

3.1.3. WORKING ARRANGEMENTS

In every factory the various sections can have different working arrangements. The sections that produce most wastewater and whose working arrangements can therefore most affect wastewater management design are body preparation and spray drying, and glaze preparation and application.

The working arrangements of the body preparation and spray drying sections influence the design of the wastewater storage tank, which must have sufficient capacity to store all the arising wastewater when the section is not running.

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[5]. BLASCO, A.; ESCARDINO, A.; BUSANII, G.; MONFORT, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.

[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

[12]. AA.VV. *La depurazione delle acque nell'industria ceramica.* Edi.cer, Sassuolo (Italy), 1987.

The working arrangements of the glaze preparation and application section can involve one, two or three daily shifts. In the first and second case, wastewater production will be greater because at the end of the day, all the application systems need to be cleaned.

3.1.4. SURFACE FINISH AND TYPE OF PRODUCT

The appearance or surface finish of the product determines the type and number of glaze applications. The applications used influence wastewater management, as the greater their number, the larger will the arising amount of water be.

3.1.5. NUMBER OF MODELS AND PERIOD OF UNINTERRUPTED PRODUCTION

The number of models and period of uninterrupted production affect the arising amount of wastewater to be managed. The quantity of wastewater increases with each change in model in production, as the glazing lines and glaze preparation mills need to be thoroughly cleaned.

3.2. WATER USE AND REQUIREMENTS IN THE CERAMIC TILE MANUFACTURING PROCESS

In all the ceramic tile manufacturing process stages, water plays a very important role with specific technological functions, in which it is used as a raw material or in auxiliary functions. This therefore requires analysing the manufacturing process, determining the stages in which water is used, its required characteristics, and which stages produce wastewater.

The main uses and qualitative requirements of the water used in the process are:

3.2.1. AS A RAW MATERIAL

Water is used for ceramic body preparation, glaze preparation and wetting the bodies[5], [6]).

To prepare the body by a wet process, untreated wastewater can be used, taking the necessary precautions with regard to the risk of slip deflocculation problems. In dry processes, wastewater can be used, which has been treated by a physical process (settling), to avoid clogging the nozzles of the wetting equipment.

Clean water must be used in glaze slip preparation. If treated water is used, problems can arise as a result of dissolved elements in the water.

The water used as a raw material does not create any wastewater emissions, as it is evaporated into the air in the various process stages: spray drying, drying, glazing and firing.

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[5]. Blasco, A.; Escardino, A.; Busani, G.; Monfort, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.
[6]. Busani, G.; Palmonari, C.; Timellini, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

3.2.2. AS A HEAT EXCHANGE VEHICLE

Water performs this function in cooling press oil and compressors, etc. The water used for this purpose must be clean and exhibit low hardness to prevent scaling in the heat exchangers.

The water used can recirculate in closed circuits after simple cooling and/or cleaning operations. Thus, water consumption corresponds to the amount of evaporated water, and wastewater is only produced on cleaning the circuit, which can then be incorporated into the wastewater for subsequent recirculation or treatment.

3.2.3. AS A CLEANING AGENT

Water is used to clean the facilities, especially mills and glazing lines, etc. Cleaning water consumption is quite variable.

This is the operation in which most water is used and requires suitable management to achieve savings in a scarce commodity and avoid waste. Water consumption can be reduced if the water is treated and reused several times in cleaning. Wastewater needs adequate treatment to avoid smells.

3.2.4. AS PART OF A GAS SCRUBBING SYSTEM

Water is also used in gas scrubbers. In these systems wastewater can be used, which has been treated by a simple physical procedure (settling with or without prior chemical treatment), and can be recirculated or treated again.

3.3. CHARACTERISTICS OF THE WASTEWATER ARISING IN THE MANUFACTURING PROCESS

As set out above, most wastewater arising in the process comes from washing the glaze preparation and application sections[5], [6]. All the wastewater arising in the process is usually brought together in a basin, thus producing a single stream for each plant.

However the flow rate and characteristics of this single stream can vary highly across time, especially owing to manual washing operations (of an intermittent nature), and the wide range of applications that are typically used.

The arising wastewater in the process usually exhibits turbidity and colour owing to the very fine suspended particles of glaze and clay mineral. From a chemical point of view these are characterised by the presence of:

Suspended solids: clays, frits rests, insoluble silicates in general.

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[5]. Blasco, A.; Escardino, A.; Busanil, G.; Monfort, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.

[6]. Busani, G.; Palmonari, C.; Timellini, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.

Dissolved anions: sulphates, chlorides, fluorides, etc.

Dissolved or suspended heavy metals, mainly lead and zinc

Boron in more or less variable quantities.

Traces of organic matter: screen-printing vehicles and glues used in glazing operations.

The concentrations of these elements depend on the type and composition of the glazes used and of the water flow rate.

Table 7 details the standard composition of untreated wastewater arising in ceramic tile manufacturing facilities.

Substance	Variation range	Substance	Variation range
pH	7-9	Calcium (mg/l)	5-500
Suspended matter (mg/l)	1000-20000	Magnesium (mg/l)	10-100
Settleable matter (mg/l)	5-30	Sodium (mg/l)	50-500
Chlorides (mg/l)	100-700	Potassium (mg/l)	1-50
Sulphates (mg/l)	100-1000	Aluminium (mg/l)	<2
Fluorides (mg/l)	<2	Silicon (mg/l)	5-30
COD (mg/l)	100-400	Iron (mg/l)	<0.5
BOD5 (mg/l)	40-160	Zinc (mg/l)	<2
Boron (mg/l)	1-60	Lead (mg/l)	<5

Table 7. *Mean chemical analysis of untreated wastewater.*

3.4. BEST AVAILABLE TECHNIQUES (BAT) FOR PROCESS WASTEWATER ARISING IN CERAMIC TILE MANUFACTURE

In accordance with the available information on the typology of the processes involved in ceramic tile manufacture, and characteristics of the wastewater arising in these processes, the most suitable systems for complying with the limits on water consumption and water component concentrations set in the CET Recommendation are reuse of the water employed in the process and wastewater treatment, including in this latter case at least physico-chemical treatment and boron removal by inverse osmosis or ion exchange[5], [6], [13], [14].

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[5]. Blasco, A.; Escardino, A.; Busanil, G.; Monfort, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.
[6]. Busani, G.; Palmonari, C.; Timellini, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.
[13]. Busani, G.; Timellini, G.; Salvatori, S.; Zoli, M.; *La depurazione del boro nelle acque di scarico da industrie ceramiche: valutazione tecnico economica e gestionale.* Cer. Acta, 3(4-5), 35 (1991).
[14]. Busani, G.; Timellini, G.; *Boron removal in wastewaters from ceramic tile factories.* Ceram. Eng. & Sci. Proc., 14 (1-2), 457 (1993).
[15]. Blasco, A.; Ginés, F.; Jarque, J.C.; Monfort, E.; *Adición de fangos reciclados a composiciones de pavimentos and revestimientos cerámicos (I).* Técnica Cerámica, 195, 470-483, (1991).
[16]. Blasco, A.; Ginés, F.; Jarque, J.C.; Monfort, E.; *Adición de fangos reciclados a composiciones de pavimentos and revestimientos cerámicos (II).* Técnica Cerámica, 196, 578-585, (1991).

3.4.1. OBJECTIVES AND SOLUTIONS

Application of the best available techniques for treating the water arising in the industrial tile manufacturing process involves lowering water consumption and achieving minimum wastewater emissions[5], [15], [16].

On tackling the problem of treating the wastewater arising in the manufacturing process, minimising consumption is fundamental. To achieve this reduction, the following practical courses of action can be implemented:

- Acting on the water circuit, installing automatic valves that prevent leaks when water is no longer needed.
- Installation of a high-pressure system in the plant for cleaning purposes.
- Switching from current wet cleaning systems to alternative, non-water consuming systems (cleaning by air suction, dry gas cleaning, etc.)
- Installation of "in situ" waste glaze collection systems.
- Installation of slip piping systems.
- Repeated reuse of the cleaning water from the glaze sections after suitable treatment.

The optimum solution involves reusing the arising wastewater in the same production process[5], [15], [6].

To determine the maximum amount of reusable wastewater in the plant, and design such use, a water balance must be drawn up setting out all the possible uses of wastewater[6].

Thus, if the wastewater is to be used in the body preparation process, no treatment will in principle be required. A homogenising tank will just need to be built to ensure keeping the most consistent possible characteristics. If water is to be employed in cleaning the facilities, water quality will need to be higher, so that settling is needed followed by aerating, with or without subsequent chemical treatment to remove smells. When all the possibilities of reuse have been exhausted, excess wastewater shall be chemically treated to comply with legal emission limits.

Figure 4 depicts a schematic of wastewater reuse in the wet body preparation process.

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[5]. BLASCO, A.; ESCARDINO, A.; BUSANII, G.; MONFORT, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.

[15]. BLASCO, A.; GINÉS, F.; JARQUE, J.C.; MONFORT, E.; *Adición de fangos reciclados a composiciones de pavimentos and revestimientos cerámicos (I).* Técnica Cerámica, 195, 470-483, (1991).

[16]. BLASCO, A.; GINÉS, F.; JARQUE, J.C.; MONFORT, E.; *Adición de fangos reciclados a composiciones de pavimentos and revestimientos cerámicos (II).* Técnica Cerámica, 196, 578-585, (1991).

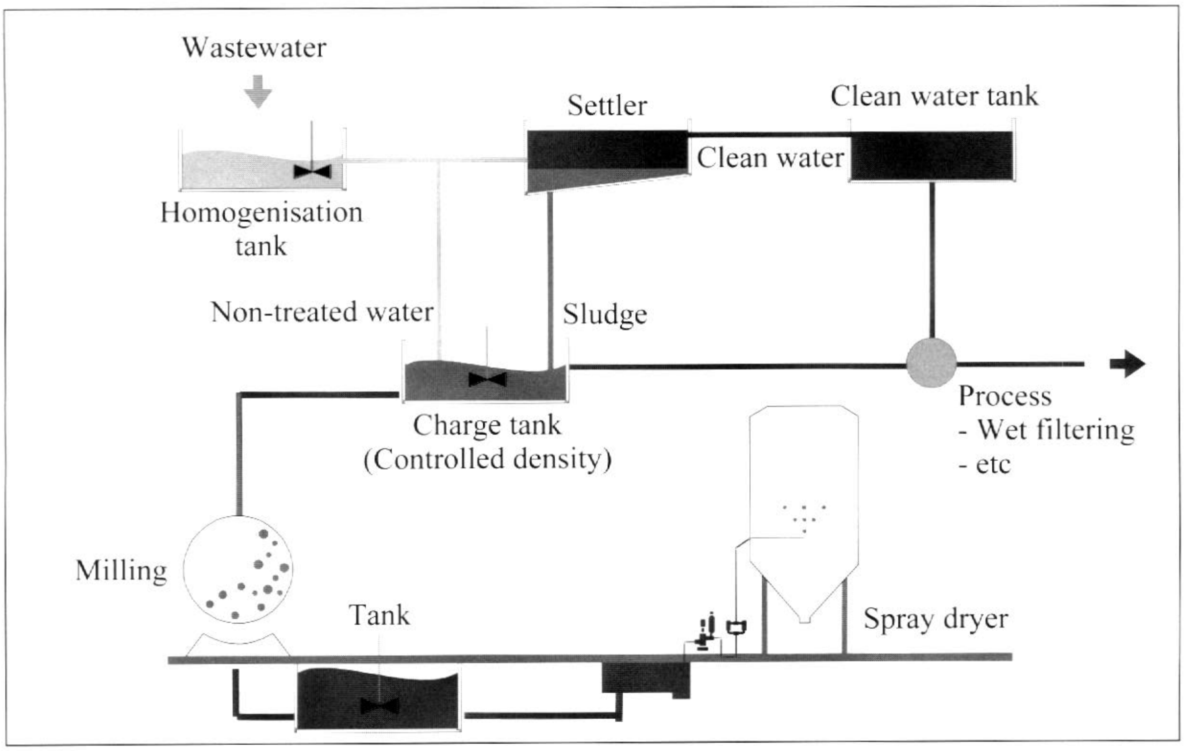

Figure 4. *Schematic of process wastewater reuse in wet body preparation.*

3.4.2. SYSTEMS OF PROCESS WASTEWATER TREATMENT

The main wastewater treatment systems in the ceramic tile manufacturing process are as follows:

Homogenisation. Homogenisation tanks are used to obtain a consistent composition in the water to be treated, and suppress as far as possible problems relating to variations in the constituents. Using such tanks yields improvement in all subsequent treatments, as the resulting homogeneity facilitates control of product additions and consistency in the operating facilities.

Aeration. This is a physical process that is frequently used in water treatment for different purposes, such as oxidation of the materials to facilitate subsequent flocculation, oxygenation of the organic compounds present in the wastewater, eliminating smells, etc. Aerating equipment may involve surface stirrers or turbines.

Settling. This is the partial separation of solid particles in a liquid by gravity. There are various types of settlers: these may be rectangular, round or lamellar.

Filtration. Filtration involves the separation of suspended solids in a liquid, by putting the suspension through a porous medium that retains the solids and allows the liquid through. The types used in the ceramic industry are in-depth filters, filterpresses, and rotating filters.

Active carbon absorption. This is based on carbon's ability to fix organic molecules

[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente*. Sassuolo (Italy), Edi.cer, S.p.a. 1995.

at its surface in water. This is a very suitable system for separating out non-biodegradable organic substances.

Chemical precipitation. This is a process for eliminating different dissolved elements by precipitation as insoluble compounds.

Coagulation and flocculation. The purpose of this treatment is to break up colloidal suspensions and produce particle agglomeration.

Ion exchange and inverse osmosis. These processes serve to remove boron from the cleaning water coming from the glaze preparation and application sections.

4. BEST AVAILABLE TECHNIQUES FOR THE PREVENTION, REDUCTION AND CLEANING OF WASTE ARISING IN CERAMIC TILE MANUFACTURE

4.1. POTENTIAL WASTES IN THE CERAMIC TILE MANUFACTURING INDUSTRY

In the ceramic tile manufacturing process industrial wastes exhibiting different characteristics can be produced, depending on the process stages involved, the technology used and products made[5], [6], [17].

Potential wastes are:

- Waste that can be incorporated in urban refuse (used office materials, refuse or rubbish from company kitchens and canteens, etc.).
- Packing and wrapping materials, subject to the relevant legal requirements for this type of waste.
- Industrial waste common to many industrial processes (heating or hydraulic oils, etc.), whose disposal is the general one for this type of waste.
- Wastes arising in the ceramic tile production process, which are subject to special examination below.

4.2. WASTE SPECIFICALLY ARISING IN THE CERAMIC TILE MANUFACTURING PROCESS

4.2.1. UNFIRED WASTE (GREEN SCRAP)

This waste arises in the stages prior to firing, i.e., non-processed raw materials, or green materials that were broken during or after forming, or that are defective. These materials exhibit the same composition as the body with variable amounts of glaze.

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[5]. BLASCO, A.; ESCARDINO, A.; BUSANII, G.; MONFORT, E.; *Tratamiento de emsiones gaseosas, efluentes líquidos and residuos de la industria cerámica.* Ed. AICE-ITC. ISBN:84-604-1114-1. Castellón (Spain), 1992.
[6]. BUSANI, G.; PALMONARI, C.; TIMELLINI, G., *Piastrelle ceramiche & Ambiente.* Sassuolo (Italy), Edi.cer, S.p.a. 1995.
[17]. MONFORT, E.; ENRIQUE, J.E.; GAZULLA, M.F.; BLASCO, A.; *Caracterización de residuos de la industria azulejera.* Técnica Cerámica, 224, 395-403, (1994).

These materials can usually be easily reused in the same production process, by incorporating them in the body composition, so disposal is generally not required.

4.2.2. FIRED WASTE (FIRED SCRAP)

This waste arises after firing, either as a result of breakage, or because of rejection on not complying with specification requirements. Reuse is currently concentrated in certain building products.

These materials are generally inert but their use in the same production process is relatively difficult and not always satisfactory, usually requiring at least one preliminary milling. Possible uses are as inert materials in producing certain building products or disposal without any treatment.

4.2.3. WASTE FROM GAS CLEANING

These wastes are obtained in the various gas cleaning systems. According to whether the system involved is a wet or dry one, subsequent treatment will be quite different, i. e. either directly as a dry solid or as an aqueous suspension.

Most of the materials obtained in gas cleaning can be reused in body preparation as they generally consist mainly of matter having the same composition as the body.

In the case of hot emissions, the widespread use of natural gas has virtually done away with emissions of sulphur compounds, so that only dust and fluorine emissions have to be taken into account.

Depending on the fluorine removal process used, and in particular the additive employed to capture fluorine, the resulting fluorine capture compounds can be incorporated with greater or lesser ease in the body preparation stage.

4.2.4. WASTES ARISING IN WATER TREATMENT (SLUDGES)

These wastes come from the wastewater treatment facilities of the wastewater arising in the process involved in cleaning glaze preparation and application equipment. These wastes will hereinafter be referred to as wastewater treatment sludges or just as sludges, regardless of their water content.

4.2.4.1. SLUDGE QUANTITY AND COMPOSITION

The quantity and composition of these sludges vary considerably since, besides arising in the different production processes, a great variety of raw materials tends to be used (different glazes, frits, etc.) even in the same facility, which produce significant fluctuations in sludge composition. It is therefore not possible to define a specific set of characteristics for all the arising sludges, although variation ranges can be set.

These sludges are made up of glaze production waste, so that their standard chemical composition resembles that of a glaze.

Table 8 sets out the typical sludge composition variation ranges (in oxide percentage of the corresponding element).

Substance	Variation range
SiO_2	40-60 %
Al_2O_3	5-15 %
B_2O_3	0-10 %
Fe_2O_3	0.1-5%
CaO	5-15 %
MgO	0.5-3%
Na_2O	0.5-3%
K_2O	0.5-3%
TiO_2	0-7%
ZnO	1-8%
BaO	0.1-3%
PbO	0.1-15%
ZrO_2	1-15%
Loss on ignition	1-12%

Table 8. *Mean sludge chemical composition (wt%).*

4.2.4.2. BEST AVAILABLE TECHNIQUES (BAT) FOR TREATMENT OF THE WASTE ARISING IN GLAZE PREPARATION AND APPLICATION IN CERAMIC TILE MANUFACTURE

The recycling options for sludges produced in wastewater treatment are as follows:

4.2.4.2.1. RECYCLING IN THE RAW MATERIALS PREPARATION PROCESS

Recycling involves sludge reuse in the bodies as is the case with aqueous suspensions and slips containing ceramic materials, as set out in Section 3.4.1.

The quantity of dry sludge produced in a ceramic tile facility ranges from 0.09-0.15 kg/m^2 finished product, which, for a product with a body mass of 15-20 kg/m^2, involves 0.4-1.0% (kg dry sludge/kg body).

The addition of sludges produced in wastewater treatment relative to the body's raw materials is therefore around 0.4-1.0% on a dry basis, i.e., all the sludge arising on treating the wastewater produced in the process can be reused in manufacturing glazed tile.

On the other hand, it has been found that 1% sludge additions, together with the wastewater in the bodies prepared for tile manufacture, do not generally affect the behaviour of the products during the production process.

These systems can be easily implemented in facilities with raw materials preparation by wet milling, as the sludges can be directly used without needing any subsequent treatment, or just simple physical or physico-chemical treatments, with the additional advantage of being able to use the water that they contain as milling water. If a dry body preparation process is involved, although the sludge addition is no problem, management is more complicated as the sludge needs to be dried first.

Consequently, both in terms of the mass balance and the resulting change in behaviour, the complete incorporation of sludges in wet milling processes is technically feasible and facilitates the management of wet milling processes, in which water and aqueous suspensions from cleaning operations in the glaze preparation and application sections can be incorporated together.

In the case of wet processes in which the body preparation plant is an independent facility, or stands separate from the tile production facility, the sludges can be transported by road making sure that there are no spills; in these cases the aqueous suspensions and sludges can be transported by tankers or conveyed by pipeline.

4.2.4.2.2. RECYCLING IN FRIT AND GLAZE MANUFACTURE

The sludges from wastewater treatment are made up of glaze waste from production, so that their reuse as glaze constituents would in principle seem to be the most suitable option. Moreover, from an economic point of view, it is the most interesting ceramic sludge reuse option, as this allows considerably raising the value of the sludge.

The use of sludge in glaze manufacture can be set up by directly reusing the sludge or after putting it through a fritting process.

The main drawback in both processes is the considerable heterogeneity across time of the sludge compositions, owing to the diversity of glazes usually found in production in most companies, which largely conditions the number of glazes that can be produced. On the other hand these sludges cannot be the sole glaze constituent, but must be considered additives.

Therefore, although it may be a very good solution in some cases, the use of these sludges in frit and glaze manufacture cannot be considered a general solution.

4.2.4.2.3. SLUDGE REUSE AS AN ADDITIVE IN OTHER PRODUCTS

Sludges may be reused in other types of industries from the branch generating them, as they may involve technically interesting or economically advantageous solutions. In this sense, very satisfactory results have been obtained by using sludge in brickmaking and producing expanded clay.

At present, given the rise in refractoriness of the glazes commonly used in ceramic floor and wall tile manufacture, sludge reuse in producing building products does not represent any substantial advantage.

With regard to the contribution of fluxing constituents, as these sludges provide no benefits, they find no ready acceptance in these manufacturing processes. Moreover, for this to be a real option, industrial facilities must be available for making these products in an area close to ceramic tile manufacture, which highly constrains such possible reuse.

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The importance is also to be highlighted of the literature produced by Italian and Spanish Organisations and companies, detailed in the References.

ANNEX I

ENVIRONMENTAL RECOMMENDATION OF THE EUROPEAN CERAMIC TILE MANUFACTURERS' FEDERATION (CET)

The requirement limits set in the Environmental Recommendation of the European Ceramic Tile Manufacturers' Federation (CET),) were adopted, in accordance with best available techniques (BAT), as limits on emissions and waste arising in the ceramic tile manufacturing process. The CET also recommends using EMAS (Environmental Audit System) as a recognised system of Environmental Management with a view to improving company environmental performance.

These limits are as follows:

Air emissions

Process stage	Polluting substance	Concentration	Test method
Milling, Forming, etc.	Particulates	≤ 100 mg/m^3	BS 3405
Spray drying	Particulates	≤ 75 mg/m^3	BS 3405
Glazing	Particulates	≤ 20 mg/m^3	BS 3405
Firing (Kilns)	Particulates	≤ 25 mg/m^3	BS 3405
Firing (Kilns)	Fluorine	≤ 10 mg HF/m^3 (*)	VDI guide 2286

(*)relative to 18% O_2

Discharges

Characteristics	Concentration	Test method
pH	5.5-9.5	NF T 90-008
Suspended solids	≤100 mg/l	pr EN 870
COD	≤150 mg/l	BS 6068 Section 2.34
Boron	≤5 mg/l	DIN 38406 Part 22
Lead	≤0.5 mg/l	DIN 38406 Part 22
Cadmium	≤0.1 mg/l	DIN 38406 Part 22
Zinc	≤5 mg/l	DIN 38406 Part 22

Specific energy consumption:

≤12GJ/t; Total primary energy consumption ((fuel oil, gas and electricity) relative to ceramic tile production) divided by total production turnover in a year.

Specific water consumption:

≤30 litres of (non-recycled) water/m^2 of produced product, over a period of a year.

Reuse relationship:

Water: ≥50% wastewater recycling, over a period of a year.

CERAMIC WASTE: ≥50% recycling by weight (dust, sludge, scrap (fired and unfired); including recycling fired scrap in other building products), over a period of a year.