Emission Control while Firing Ceramics

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Volatile Organic Compounds (VOCs) define a broad range of compounds that are considered air pollutants and which are emitted by a variety of industrial processes. There are many national and international regulations regarding the emission of VOCs, given their photochemical reaction in the presence of atmospheric gases to form ozone, which has shown to be harmful to the environment. Most countries have their own regulations to limit the emission of VOCs, such as the 1990 Amendment of the Clean Air Act in USA and the TA Luft in Germany. There are also international regulations that limit these and other pollutants' emissions, such as the Gothenburg and Kyoto Protocols. In the case of the ceramic manufacturing industry, the emission of VOCs results from incomplete combustion and the volatilization of organic matter in the raw material, including binding agents, adhesives, and drying aids. The firing of ceramic products also results in the emission of other air pollutants, such as NO_x, SO_x, HF, HCl, CO, and CO_2, among others.

1 Introduction

Companies in the manufacturing industry have a growing interest in limiting the emission of VOCs because of their negative impact on the environment. Many are not only following government-imposed regulations, but creating their own policies in this regard. To ensure that these emissions are kept within the imposed limits, it is important to have an efficient system that is specially designed to the flow and composition of the combustion system's exhaust gases.
In this article, the authors further discuss the formation of VOCs and NO_x in combustion systems and some techniques that prevent or reduce these emissions.

2 Thermal oxidizers

VOC emission control technologies are designed to either recover, incinerate, or reduce the generation of VOCs present in exhaust gases. Because of their high VOC removal efficiency and capacity to process high flow rates and concentrations, thermal oxidizers, also known as incinerators or afterburners, are a widely used VOC abatement method in the ceramic manufacturing industry.

2.1 Basic operation and design

A thermal oxidizer or incinerator is a system that removes organic components from a stream by raising and maintaining their temperature above their autoignition temperature in the presence of oxygen to complete combustion. Fig. 1 shows a recuperative thermal oxidizer, while Fig. 2 shows a tunnel kiln with a thermal oxidizer.

Fig. 1 Recuperative thermal oxidizer

The main advantages of thermal oxidation systems over other types of VOC treatments are [1]:

- high VOC destruction rates (>99,99 %)
- less process components and an easier operation
- can be modified to operate with a variation of waste flow and composition
- there is no by-product disposal.

Thermal oxidizers can be used for a wide variety of VOC concentrations. However, to

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Fig. 2 Tunnel kiln with a recuperative thermal oxidizing system

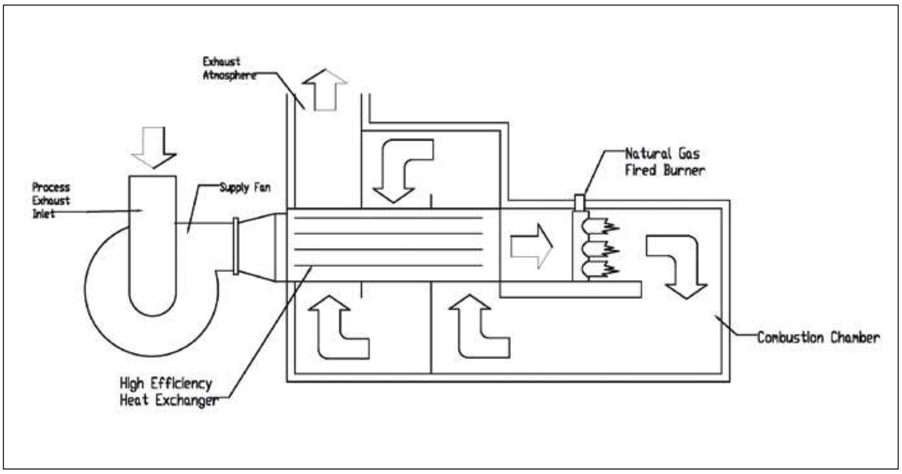

Fig. 3 Schematic of a recuperative thermal oxidizer

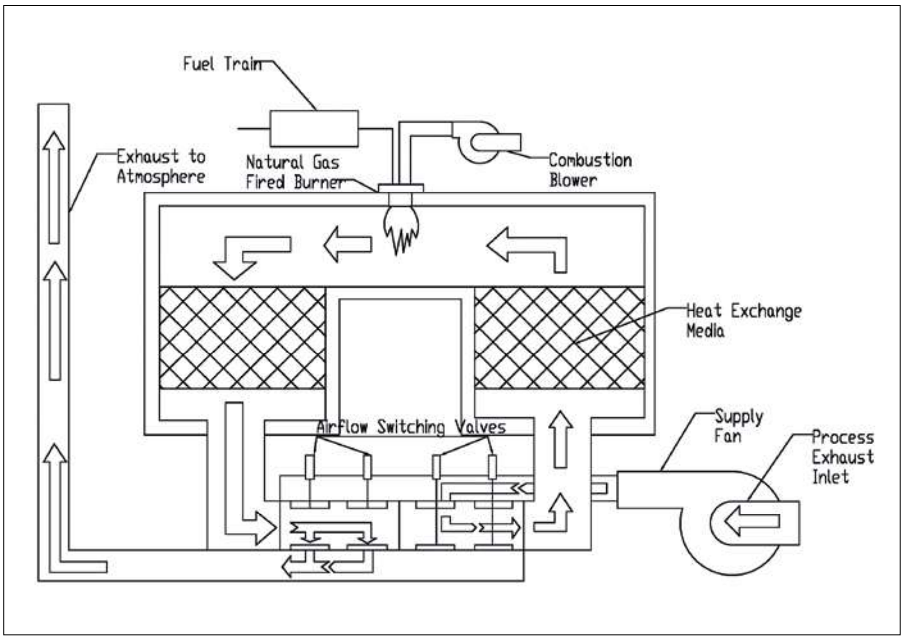

Fig. 4 Schematic of a regenerative thermal oxidizer

avoid any possibility of an explosion, the concentration of volatiles in the waste gas is usually limited to 25 % of the compound's lower explosive limit [2]. Some thermal oxidizers may work with higher concentrations, but due to safety regulations it is usually not the case.

2.2 Types of thermal oxidizers

A thermal oxidizer that uses direct firing is known as an afterburner. However, given the high operating temperature of these incinerators, it is common to include a type of heat recovery system to save on fuel costs. In these heat recovery systems, exhaust gases are used to heat the incoming gases prior to combustion.

Recuperative thermal oxidation systems use a heat exchanger to heat the incoming stream, and have the advantage of having a relatively short time span to reach operating conditions. A general schematic of a recuperative thermal oxidizer is shown in Fig. 3.

Regenerative systems work with pairs of ceramic beds that alternate between heating up with exhaust gases and cooling down by transferring the captured heat to the incoming flue gases before combustion. These systems have a very high efficiency, recovering up to 95 % of the thermal energy of both the fuel and VOC combustion. [3]. Fig. 4 shows a diagram representing a regenerative thermal oxidizer.

Regenerative thermal oxidizers are best suited for medium to high concentrations, since the heat of combustion of the volatiles can then be enough to maintain the operating temperature. In a flow with low volatile concentration heat recovery no longer becomes economically viable and, in these cases, direct-fired thermal oxidizers or afterburners are preferred.

Afterburners can be equipped with specialized burners that are mounted in the kiln's exhaust duct and are designed to combust incoming flue gases. These burners use the oxygen content present in exhaust gases for combustion instead of requiring combustion air.

2.3 Design parameters

The efficiency of thermal oxidizers is directly affected by the 3 T's: Temperature, Time, and Turbulence, as well as the amount of oxygen present. Operating temperature is the most critical parameter when designing a thermal oxidizer. The temperature at which the incinerator operates depends on the components of the VOCs being treated, more specifically, their auto-ignition temperature. This is the minimum temperature at which combustion will be completed. Most thermal oxidizers operate at a temperature of about 650 °C to 1100 °C [4]. The importance of operating temperature when designing an incinerator has two main reasons: it has the greatest impact on the incineration efficiency of VOCs, and a high combustion temperature will increase the production of unwanted pollutants such as nitrogen oxides.

Residence time also impacts VOC destruction efficiency, since the incoming gas should be enough time inside the incinerator for complete combustion to occur. Most organics can be completely oxidized with residence times of 0,5–2,0 s [1].

Turbulence inside the thermal oxidizer is important since it affects the proper mixing of VOC and oxygen molecules as well as the temperature uniformity. To ensure a high degree of turbulence, the Reynolds number (Re) for the gas flowing inside the incinerator should be greater than 10 000 [1]. If a satisfactory level of turbulence is not reached, the volatiles will not be completely eliminated from the airstream since the oxygen and/or temperature required for combustion will not be available throughout the whole incinerator. Another important parameter to be considered is that there is enough oxygen present to combust all the VOCs in flue gases entering the incinerator. Typically, the minimum oxygen concentration required in thermal oxidizers is 3 % [1]. This may be achieved by mixing the incoming stream with excess combustion air or pure oxygen.

Tab. 1 shows a table published by Donley and Lewandowski showing general guidelines for the destruction efficiency of a thermal oxidizer for different operating temperatures and residence times. An oxygen level of at least 3 % is assumed, as well as enough turbulence (Re >10 000) to provide sufficient mixing.

Although the efficiencies listed in Tab. 1 can be applied to the combustion of most VOCs, the design of an incinerator must be specifically designed considering the flow rate and composition of the incoming exhaust gases. It is especially important to ensure that the gases have a high velocity to create enough turbulence for proper mixing while maintaining time residence and gas temperature at an acceptable level and uniformity to oxidize all organic material.

2.4 Effect of design parameters in afterburner efficiency

When designing a thermal oxidizer, it is extremely important to consider the operating parameters listed in the previous section to maximize VOC destruction efficiency and prevent any safety or environmental hazards.

Tab. 1 Destruction efficiency vs. temperature and residence time in a thermal oxidizer; adapted from [1]

Destruction Efficiency [%]	Degrees Above Autoignition Temperature [°C]	Residence Time [s]
95	150	0,5
98	200	0,5
99	250	0,75
99,9	300	1,0
99,99	350	2,0

One of the methods used to design an effective afterburner is using a Computational Fluid Dynamics (CFD) simulation. Fig. 5 a–c show three different afterburner designs. All three designs use direct firing and have two burners. Design in Fig. 5 c has deflector plates to redistribute the incoming airflow.

A CFD simulation was run for all three designs, using the same burner power, operating temperature and flue gas flow rate. Fig. 6 a–c show the temperature contours in the middle of the afterburner for all three designs. In this case, a temperature of 760 °C was deemed enough to combust all VOCs in the flue gas. It can be seen that for designs in Fig. 6 a–b, the gases reach enough temperature for combustion more than halfway through the afterburner, which results in less residence time and thus an incomplete combustion.

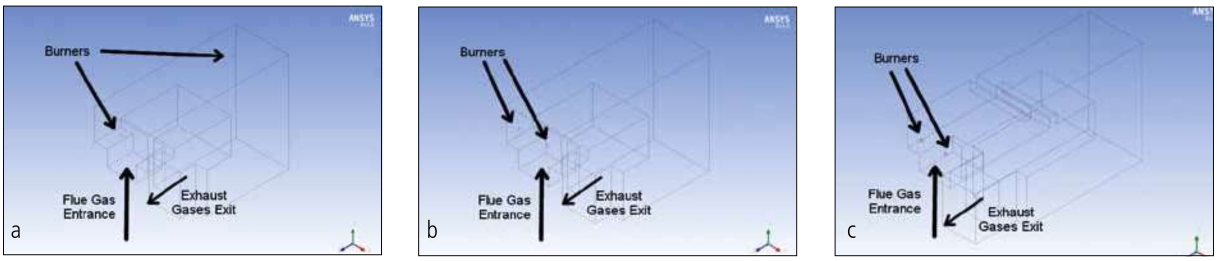

Fig. 5 a–c **Geometry for three different designs of a thermal oxidizer**

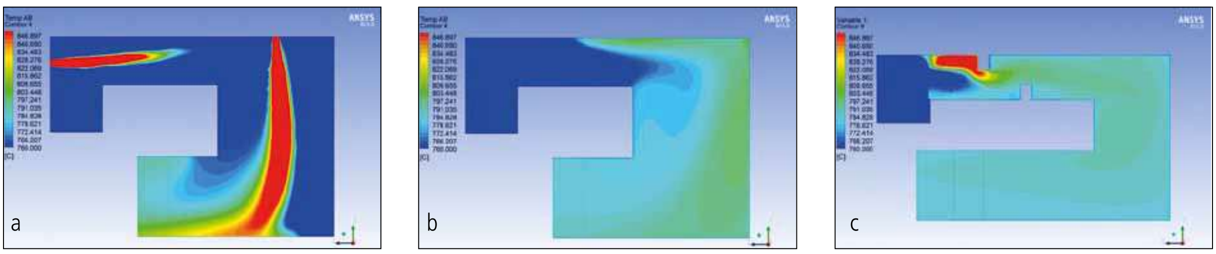

Fig. 6 a–c **Temperature contours for three different designs of a thermal oxidizer**

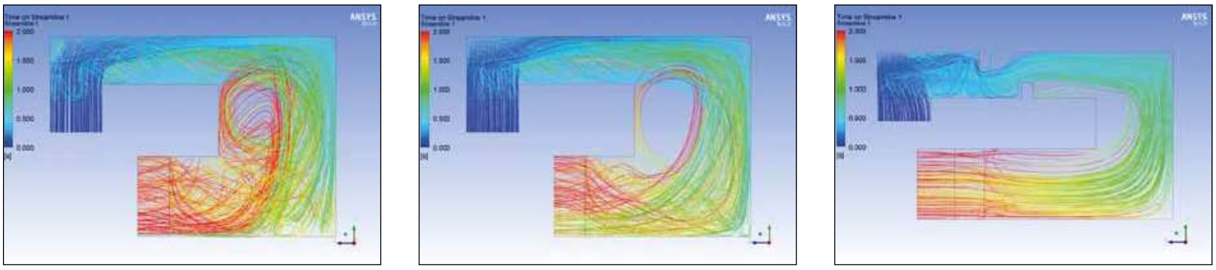

Fig. 7 a–c **Residence time for three different designs of a thermal oxidizer**

Fig. 7 a–c show the residence time of streamlines inside the afterburners. Even though all three designs show an acceptable residence time on average, design Fig. 7 c presents more uniformity.

This is important, since a design with low uniformity means that there will be zones inside the afterburner where VOC combustion will not be complete. A residence time that is not uniform throughout the thermal oxidizers implies that there is not enough turbulence to achieve a proper mixing of oxygen and fuel, resulting in incomplete combustion and a lower VOC destruction efficiency.

The importance of afterburner design and its effect on VOC combustion can be seen in Fig. 5 through Fig. 7. The 3 T's (temperature, time, and turbulence) must always be considered to maximize the thermal oxidizer's efficiency.

3 NO_x emission during ceramic firing

Nitrogen oxides (NO_x) are formed as a by-product of the combustion of organic material. NO_x emissions, like VOCs, are regulated, since they form a part in the atmospheric photochemical reactions that produce ozone.

NO_x refers to two different chemicals: nitric oxide (NO) and nitrogen dioxide (NO_2). They are formed in all combustion processes, and can come from one of three sources: thermal NO_x, fuel NO_x, or prompt NO_x. In the case of ceramic kilns, most NO_x emissions will be formed by the thermal dissociation of nitrogen and oxygen present in combustion air at high temperatures (thermal NO_x) [1]. However, a smaller part of NO_x emissions can be attributed to the oxidation of nitrogen with the fuel (prompt NO_x) or nitrogen compounds present in fuels before combustion (fuel NO_x).

Given that most NO_x produced during combustion is thermal, operating with a high temperature or with excess combustion air will increase emissions significantly.

Another factor that has a great impact on the formation of NO_x is the preheat temperature of combustion air, since this increases flame temperature. Because of this, most NO_x reduction techniques seek to reduce flame temperature since below 760 °C, thermal NO_x formation is significantly reduced [5].

4 NO_x abatement techniques

As mentioned earlier, NO_x, like VOCs, are unwanted by-products of the ceramic manufacturing process. Because of this, most kilns are equipped with abatement methods that reduce NO_x emissions, to minimize the need to post-process exhaust gases to comply with NO_x regulations. Some of the most popular technologies are discussed in the following section.

4.1 Flue gas recirculation

This method consists of recirculating exhaust gases to be mixed with the burner's combustion air. This works in two ways: the relatively cool flue gases lower peak flame temperatures, and when mixed with combustion air they lower its oxygen concentration. Recirculating 20 % of flue gases has been reported to reduce around 65–80 % of NO_x emissions in natural gas burners [5]. Some low NO_x burners are designed to recirculate products of combustion.

4.2 Staged combustion

Low-NO_x burners with staged combustion can work with air staging or fuel staging, both involving the strategic delay of mixing fuel with combustion air.

In air staging burners, around 75–85 % of the air is mixed with all of the fuel in the primary combustion zone, creating fuel-rich combustion. This reduces NO_x emissions by both reducing flame temperature and limiting the availability of oxygen to form NO_x.

In the second stage, the remainder of the combustion air is injected with the unburned fuel from the first stage.

Air-staged low-NO_x burners working with natural gas may achieve NO_x reductions of up to 40–50 % [7]. Fig. 8 shows an air-staged burner.

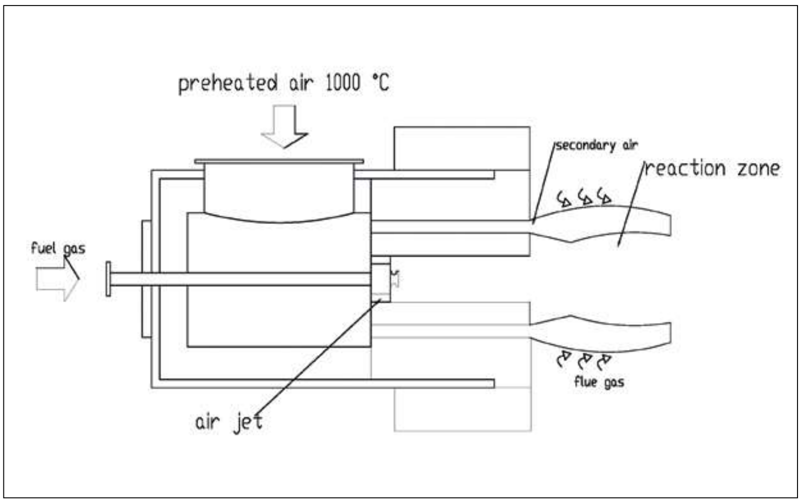

Fig. 8 **Staged-combustion burner with air staging, adapted from [6]**

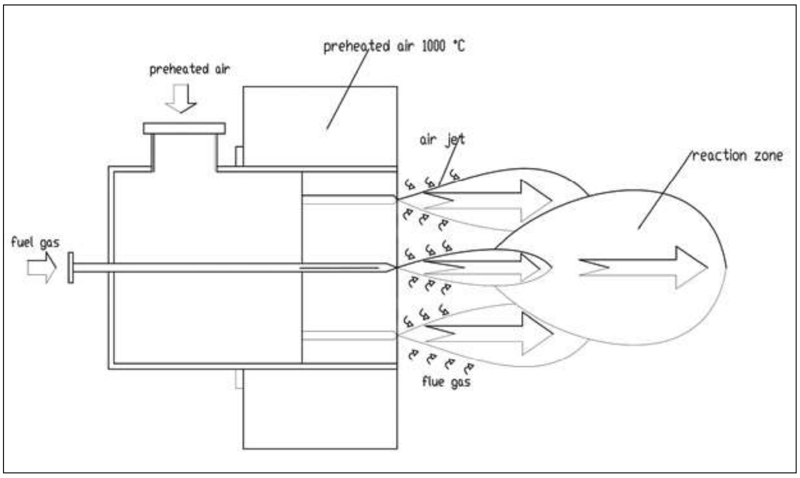

Fig. 9 Flameless oxidation burner, adapted from [6]

Fig. 10 Kiln with self-recuperative burners, capable of firing in flameless oxidation mode

Fuel staging works in much the same way. In the first stage, about 60–70 % of the fuel is mixed with all of the combustion air. Due to the high level of excess air, flame temperature is lowered, thus reducing the formation of NO_x. The remainder of the fuel is then injected. Low-NO_x burners that use fuel staging can reduce NO_x emissions by up to 60 % [7].

4.3 Flameless oxidation

In flameless oxidation, both fuel and air are injected directly into the kiln chamber instead of being premixed, and combustion happens inside the chamber. This leads to a low flame temperature and low oxygen partial pressures, which results in reduced thermal NO_x formation.

Fig. 9 shows a flameless oxidation burner. Since the fuel and combustion air are recirculated along with exhaust gases, the temperature is relatively uniform throughout the whole chamber instead of there being a temperature peak around the flame. Chamber temperature must be above the fuel's auto-ignition temperature for flameless combustion to occur. Because of this, kilns must be operating at around 800–900 °C for flameless oxidation to occur [6]. Fig. 10 shows a kiln with self-recuperative burners, which can be operated in flameless oxidation mode.

5 Conclusions

The emission of VOCs and NO_x, in some cases by-products of thermal processes in the ceramic industry, is restricted by government bodies or company policies, because of their negative impact on the environment.

Thermal oxidizers, when properly designed, can substantially reduce VOC emissions. The design of a thermal oxidizer is mainly based on the operating temperature, residence time, and turbulence, all of which must be carefully considered to ensure an efficient removal of VOCs from exhaust gases.

NO_x emissions are mostly reduced by altering the combustion process to reduce flame temperature and thus prevent their formation. Some techniques used for this are low-NO_x burners, which may work using a combination of staged combustion, flue gas recirculation, or flameless oxidation.

References

[1] Donley, E.; Lewandowski, D.: Optimized design and operating parameters for minimizing emissions during VOC thermal oxidation. Metal Finishing **98** (1996) [6] 52–58

[2] Newsholm, G.: The safe use of thermal oxidizer (incineration) systems for potentially flammable mixtures. British HSE **12** (2004) 13

[3] Khan, F.I.; Ghoshal, A.K.: Removal of volatile organic compounds from polluted air. J. of Loss Prevention in the Process Industries **13** (2000) [6] 527–545

[4] Moretti, E.C.: Reduce VOC and HAP emissions. Chem. Engin. Progress **98** (2002) [6] 30–40

[5] Skalska, K.; Miller, J.S.; Ledakowicz, S.: Trends in NO_x abatement: A review. Science of the total Environment **408** (2010) [19] 3976–3989

[6] Flamme, M.: Low NO_x combustion technologies for high temperature applications. Energy Conversion Management **42** (2001) [15] 1919–1935

[7] Bell, R.D.; Buckingham, F.P.: An Overview of technologies for reduction of oxides of nitrogen from combustion furnaces. MPR Associates, Inc, 2002, 23