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Review

# State-of-the-Art and Recent Advances in the Abatement of Gaseous Pollutants from Waste-to-Energy

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**Abstract:** Despite their key role in integrated waste management, direct (incineration) and indirect (gasification/pyrolysis) waste combustion processes are still opposed by some of the general public due to the past emission levels of air pollutants. In fact, although the release of air pollutants (especially dioxin) to the atmosphere from waste combustion processes has gradually decreased over the years, thanks to the introduction of stricter regulations and more advanced removal technologies, there is still an unsolved problem regarding the public acceptance of waste-to-energy facilities. The aim of this paper is to provide an overview of the state-of-the-art air pollution control (APC) technologies used in waste combustion facilities. Air pollution control technologies are designed to reduce or eliminate the emissions of harmful pollutants into the atmosphere. These technologies are important for safeguarding public health, protecting ecosystems, complying with regulations, and promoting a more sustainable and resilient future for both local and global communities. This paper will highlight the complexity behind emission control and the efforts made by this sector over the years. This paper will also propose suggested configurations based on the interactions/complementarity between different APC technologies and recent findings to improve their performance.

**Keywords:** waste-to-energy; pollutant emissions; flue gas depuration; environmental compatibility; cleaning technologies; air pollution



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## 1. Introduction

Waste-to-energy (WtE) refers to all kinds of processes for recovering energy from waste. Among all types of WtE processes, combustion processes have historically attracted more attention by the population than others because of the past levels of emissions of toxic compounds and because combustion processes take place in larger plants compared to other WtE processes due to the high investment costs that make small-scale plants economically unfeasible.

Although the release of air pollutants (especially dioxin) to the atmosphere from waste combustion processes has gradually decreased over the years [1], thanks to the introduction of stricter regulations and more advanced removal technologies, there is still an unsolved problem regarding the public acceptance of WtE facilities and the “not in my backyard” (NIMBY) syndrome [2]. Despite the chronic aversion to such processes, waste combustion still plays a key role in integrated waste management systems [3,4], responding to the fourth point of the Waste Hierarchy established by the European Union (“recovery”) and allowing for the reduction of the amount of waste sent to municipal solid waste (MSW) landfills. Regarding this last point, a recent revision of the European Union (EU) Landfill Directive established that the amount of MSW that can be sent to landfills will be limited to 10% of the total MSW produced by 2035 [5]. Thus, during the transition towards ambitious

“zero waste” targets, WtE processes based on direct or indirect combustion cannot be ruled out.

Waste combustion processes emit a large variety of air pollutants: dust and particulate matter (PM), nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), volatile organic compounds (VOCs), acid gases like sulfur oxides (SO<sub>x</sub>), hydrochloric acid (HCl) and hydrofluoric acid (HF), ammonia (NH<sub>3</sub>), heavy metals, polycyclic aromatic hydrocarbons (PAHs), dioxin (PCDD/Fs) and polychlorinated biphenyls (PCBs). Besides channeled emissions, which are the main emission sources of MSW combustion plants, diffuse emissions should also be considered in environmental impact assessment procedures and environmental monitoring [6,7]. Diffuse emissions are mainly related to the discharge, storage, and handling of waste and to operations related to the management of slags, bottom ashes, and fly ashes intercepted by dry dust removal systems. Furthermore, channeled emissions can be subdivided into two main categories: primary and secondary emissions. Primary emissions refer to the main stack(s) of a waste incinerator, i.e., the stack(s) that release(s) the flue gas coming from the combustion chamber and are treated by the air pollution control (APC) technologies installed.

From this viewpoint, the following technologies are available: mechanical collectors, such as cyclone separators and settling chambers, which use physical mechanisms to remove particulate matter from the air; and electrostatic precipitators (ESPs), which use an electric charge to attract and remove particulate matter from the air stream, for dust and PM removal. Wet scrubbers use a liquid (usually water) to capture and remove pollutants from the gas stream. Different types include venturi scrubbers, packed bed scrubbers, spray towers, and dry scrubbers for acid gas removal. The selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) systems are used to convert nitrogen oxides (NO<sub>x</sub>) into nitrogen, water, and carbon dioxide. It is commonly used in power plants and industrial facilities for the removal of NO<sub>x</sub>. The thermal oxidizers (these devices combust VOCs at high temperatures, converting them into less harmful substances) and the adsorption system (activated carbon or other adsorbents are used to capture and remove VOCs from the air) are used for the removal of VOCs. It is important to note that the effectiveness of these technologies depends on various factors, including the specific pollutants targeted, the industry or source of emissions, and local environmental conditions. Additionally, a comprehensive approach often involves a combination of these technologies and measures to achieve optimal air quality outcomes.

Secondary emissions include all the remaining channeled emissions related to the following main types of sources: the venting of silos containing ashes recovered by APC systems or reagents and the discharge of the air from waste storage compartments or other indoor environments. Secondary emissions have been recently estimated to account for up to 29% and 10% of the total dust and organic carbon releases, respectively, from channeled emissions [8]. Thus, their contribution is not negligible and should always be included in environmental impact assessment procedures, especially considering that their type of release may imply a weaker dispersion of air pollutants in the atmosphere.

In general, air pollution control technologies are crucial for several reasons, and their importance is underscored by the numerous benefits they offer to human health, the environment, and overall societal well-being. By analyzing the scientific literature, it is possible to find key reasons why air pollution control technologies are important. Orach et al. [9] highlight the importance of the protection of human health: air pollution is associated with a range of adverse health effects, including respiratory diseases, cardiovascular problems, and increased mortality rates. Implementing air pollution control technologies helps reduce the levels of harmful pollutants in the air, directly benefiting public health.

Alterio et al. [10] focus on the preservation of the environment: air pollution has detrimental effects on ecosystems, water bodies, and vegetation. Acid rain, for example, results from the release of sulfur dioxide and nitrogen oxides into the atmosphere, impacting soil and water quality. By controlling air pollution, we can mitigate these environmental impacts and protect biodiversity. Bianco et al. [11] highlight the necessity to improve air

quality: the implementation of pollution control technologies contributes to improving ambient air quality. Cleaner air enhances the quality of life for residents of urban and industrial areas, reducing the risk of respiratory illnesses and other health problems. Raff et al. [12] sharpen the necessity to meet regulatory standards: governments and environmental agencies establish air quality standards and regulations to protect public health and the environment. Air pollution control technologies are essential for industries to comply with these standards and regulations, avoiding legal consequences and penalties [13].

Zhanga et al. [14] and Unegga et al. [15] addressed the necessity of improving the global climate change phenomenon: some air pollutants, such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), contribute to climate change. Technologies that reduce greenhouse gas emissions play a crucial role in addressing global warming and mitigating the impacts of climate change. Other important points in this field are the benefits coming from waste source separation and the coupling between recycling and incineration.

Knox et al. [16] underline the question of sustainable development: implementing cleaner technologies aligns with the principles of sustainable development. By adopting more environmentally friendly practices, industries can reduce their ecological footprint and contribute to a more sustainable and resilient future. Panepinto and Zanetti [17] and Konga et al. [18] highlight the necessity of enhancing energy efficiency; many air pollution control technologies also contribute to increasing energy efficiency. For instance, technologies like combined heat and power (CHP) systems can simultaneously generate electricity and useful heat, reducing overall energy consumption and associated emissions. Dong et al. [19] promote the point of innovation and research: the development and deployment of air pollution control technologies drive innovation and research in environmental science and engineering. This fosters the creation of new, more efficient technologies and encourages continuous improvement in pollution control measures. Yang et al. [20] point out the aspect of public awareness and education: the existence and implementation of air pollution control technologies contribute to public awareness about the importance of environmental protection. This awareness, in turn, can lead to a more informed and engaged citizenry advocating for cleaner air and sustainable practices. Li et al. [21] and Ge et al. [22] underline the importance of global collaboration: air pollution is often a trans-boundary issue requiring international collaboration to address it effectively. By adopting and sharing best practices in pollution control technologies, countries can work together to tackle regional and global air quality challenges.

In summary, air pollution control technologies are designed to reduce or eliminate the emissions of harmful pollutants into the atmosphere. These technologies are important for safeguarding public health, protecting ecosystems, complying with regulations, and promoting a more sustainable and resilient future for both local and global communities.

The aim of this paper is to provide an overview of the APC technologies conventionally adopted in waste combustion plants (including incineration, gasification, and pyrolysis) and believed to guarantee the lowest environmental impacts at present. In addition, some novel APC options for the WtE sector will be discussed based on recent literature studies, and this is the real novelty of the paper, from which it is possible to draw some innovative measures within the topic covered.

## 2. Materials and Methods

The best available techniques (BATs) identified by the European Commission for waste incineration were considered a starting point for this work [23]. The BATs were reviewed to depict the current standard for APC technologies in waste incineration plants and to differentiate between consolidated techniques and novel processes/technologies/reagents that may represent advances in this field and opportunities to improve the abatement of emissions from the WtE sector.

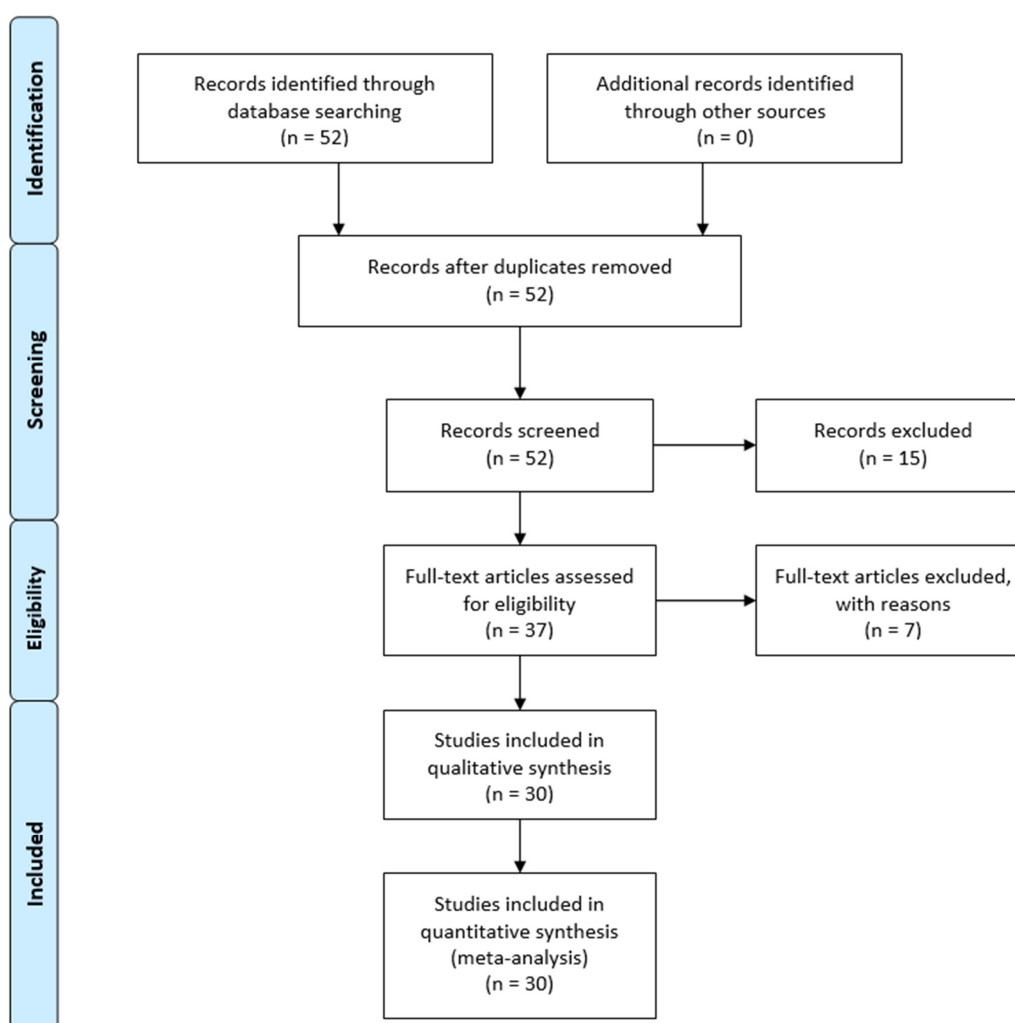
To keep track of the publications on novel processes for advanced APC in waste incineration plants, the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) was used. This methodology has been widely used to ensure transparency

and completeness in reporting the results of bibliographic research and literature reviews. PRISMA helps the reader reconstruct the process followed by researchers to include or exclude scientific articles and replicate the analysis.

In total, 52 publications were preliminarily selected based on the following search keywords, separated by logical operators “AND” and “OR”:

- waste AND incineration AND (air pollution control) AND NO<sub>x</sub>;
- waste AND incineration AND (air pollution control) AND ((acid gases) OR (HCl) OR (HF) OR (SO<sub>2</sub>) OR (SO<sub>x</sub>));
- waste AND incineration AND (air pollution control) AND VOCs, respectively, for the research on the removal of NO<sub>x</sub>, acid gases, and VOCs.

The PRISMA flow diagram is presented in Figure 1. The apparent low number of publications is due to the specificity of this topic (i.e., waste incineration) and the choice of limiting the search to novel strategies/techniques in a relatively narrow field (i.e., the abatement of gaseous pollutants).

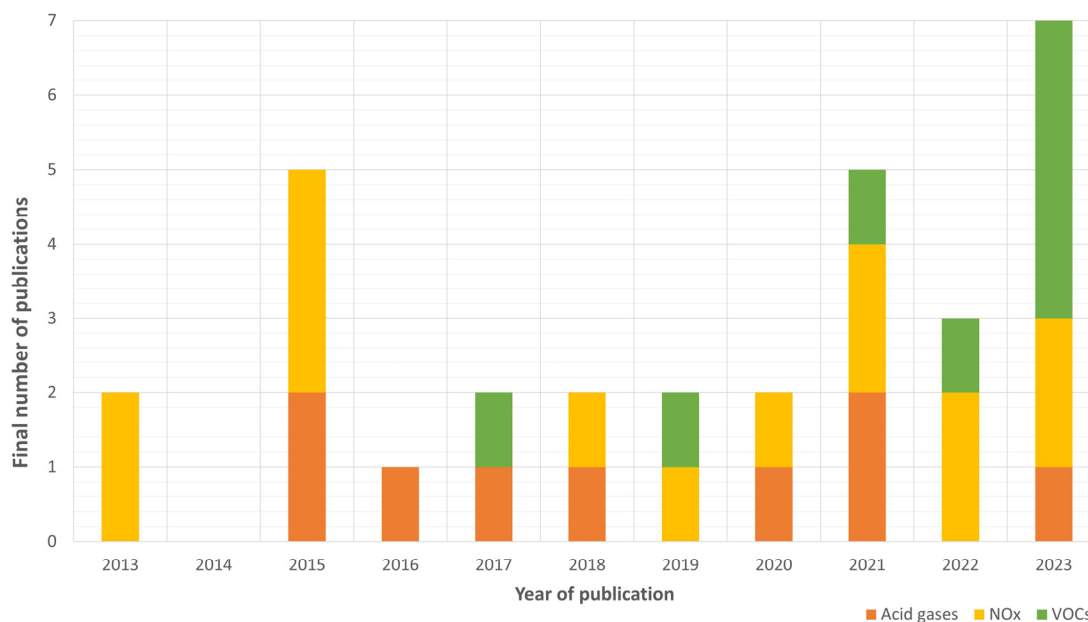


**Figure 1.** Flow chart of the PRISMA process for the selection of scientific publications on novel techniques for the abatement of gaseous pollutants in waste incineration processes.

The publications selected by the authors were identified in the Scopus database. Only publications written in English and published in 2013 were considered. The choice of limiting the research to recent publications is due to the need to identify novel options available for the abatement of gaseous pollutants. During this research, 15 publications were soon excluded as irrelevant to the topic. Thus, the publications considered to be eligible for read-

ing became 37. Seven publications were discarded after reading them because they were considered only marginally relevant to the research topic. The 30 remaining publications were considered and cited in this paper because they deal with either novel APC technologies for gaseous pollutants in waste incineration plants, modifications of conventional APC technologies, or novel reagents used in the abatement of gaseous pollutants.

The publications were considered eligible for reading primarily because of the relevance of their titles and, secondly, their abstracts. Finally, the selected papers were arranged into the following topic categories: (1) abatement of acid gases, (2) abatement of NO<sub>x</sub>, and (3) abatement of VOCs. Figure 2 shows the trend of publication year for the papers on novel abatement techniques cited in this work.



**Figure 2.** Distribution of the cited papers according to their topic and year of publication.

The literature review allowed for the evaluation of the possible adoption of novel techniques and their implementation in APC systems for waste incineration.

### 3. Air Pollution Control Technologies

#### 3.1. BATs

BATs are defined as “the most effective and advanced stage in the development of activities and their methods of operation, which indicates the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and, where that is not practicable, to reduce emissions and the impact on the environment as a whole” [24]. The concept of BAT was introduced by the European Council in 1996 when the directive on Integrated Pollution Prevention and Control (IPPC) was issued [25]. In 2010, the Industrial Emission Directive (IED) was published, updating and reinforcing the above concept [24]. Since their introduction, BATs have become a reference for industry. Operators and local environmental agencies are pushed to compare their installation performance with the specifications reported in these reference documents.

Three aspects are enclosed in the concept of BATs: the word “Technique” includes the “technology used and the way in which the installation is designed, built, maintained, operated, and decommissioned” [24]. This means that not only pollution abatement installations are considered, but also the environmental management of the whole production process. The term “Availability” indicates that the technique considered is “developed on a scale that allows implementation in the industrial sector under economically and

technically viable conditions” [24]. This definition implies that the technique is present on the market under accessible economic conditions. Finally, “Best” means that the technique considered is the “most effective for achieving a high general level of protection of the environment as a whole” [24]. The reference documents known as BREFs (Best Reference Documents) [26] analyze and describe BATs. The BAT-associated emissions limits, or BAT-AELs, are also listed in these publications. The procedure by which these BREFs are created and revised is known as the Sevilla Process, and it is governed by a specific Commission decision [27]. This method has been developed throughout the years, reaching a three-year revision process for BREFs. The determination of BATs is usually achieved through the identification of representative installations, data collection, performance analysis and comparison, and selection of the most appropriate solutions [28].

The original BREF on waste incineration was adopted by the European Commission in 2006. The review commenced in May 2014. The updated version was adopted by the European Commission in 2019, and the BAT Conclusions (BATC) were published on 3 December 2019. The Commission, EU Member States, the relevant industries, and non-governmental organizations that support environmental protection collaborated to produce the BREF document. The methods to prevent or (in cases where it is not feasible) limit the environmental impact of installations in this sector are described in Chapter 4 of this document. When applicable, this material also contains the environmental performance levels (such as emission and consumption levels) that can be attained through the application of the techniques, the costs and associated monitoring, as well as any cross-media effects. The BAT conclusions, as outlined in Directive Article 3(12), are presented in Chapter 5. Information on “emerging techniques”, as specified in Directive Article 3(14), is provided in Chapter 6. Chapter 7 reports concluding remarks and recommendations for future work [23,24].

The BATC for the waste incineration sector has been defined through an iterative process starting from the identification of the key environmental issues and the examination of the most relevant techniques to address these key issues. The next step in the analysis was to look at the circumstances that led to the achievement of significant environmental performance levels. Other important aspects, such as costs, cross-media impacts, and the positive/negative drivers for putting the strategies into practice, were also taken into account. The process terminated with the selection of BATs and their associated BAT-AELs. The main sources of information for the review process were [23]:

- scientific and technical literature;
- more than 300 questionnaires from operators of waste incineration and incineration bottom ash treatment plants;
- additional information from the technical working group (TWG) members;
- about 2900 comments on Draft 1 of the revised BREF;
- information gathered from site visits;
- outcomes of workshops and webinars.

BATs on flue gas control (FGC) in waste incineration systems are based on a combination of primary and secondary techniques [29]. Primary measures are defined as pollution prevention techniques to reduce or eliminate the generation of pollutants. Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants but serve as a means to contain and prevent emissions. These techniques must be integrated to provide an efficient system for the reduction of the pollutants present in the flue gases. To this end, multiple components and design approaches can be combined. In general, primary techniques include both optimization of the incineration process (e.g., advanced control systems or optimization of the furnace design) and optimization of the temperature, flow rates, and sites of injection for the primary and secondary combustion air, as well as the waste feed rate and composition, in order to efficiently oxidize organic compounds while lowering  $\text{NO}_x$  production. Although not listed as a BAT, the use of fluidized bed combustion technologies and rotary kilns is often mentioned in the BREF document for waste incineration as virtuous combustion technologies that enable lower contents of total organic carbon in slags and bottom ashes. Fluidized beds, in particular,

can accept various fuels, allowing for different co-incineration strategies, and also show relatively low NO<sub>x</sub> and SO<sub>x</sub> emissions [30,31]. The fluidized bed technology has also been conveniently employed for oxy-fuel combustion, i.e., by using oxygen instead of air [30]. Secondary techniques include a wide set of end-of-pipe technologies, which can be applied differently depending on the composition and features of the flue gas [32].

### 3.1.1. BATs for Acid Gas Reduction

For the neutralization of acid gases, three types of processes can be used individually or combined: wet systems, semi-dry systems, or dry systems. The main technologies are reported in Table 1. Each of the methods has its own advantages and disadvantages, depending on the conditions of the process and installations [33].

**Table 1.** Acid gas abatement technologies [34].

Technology	Principle	Advantages	Disadvantages
Boiler/Inline injection of sorbent (or duct sorbent injection, DSI)	A dry sorbent powder is dispersed by injecting it into the effluent gas stream (or combustion chamber). The sorbent reacts with the acid gas to form a solid, which is subsequently removed with dust suppression systems.	Simple technology; minimum amount of auxiliary equipment; low operating costs	Major consumption of sorbent; higher amount of residuals; possible dust pollution of heat exchange surfaces
Conditioned dry sorption	Separation of the pollutants is ameliorated by a hydrate shell, which is formed around the lime particles and results from the water contained in the flue gas. The separation is governed by the dissolution rate of the pollutants in aqueous solution.	Higher efficiency than no conditioned dry sorption	Flue gas must be conditioned to achieve higher relative humidity
Semi-dry scrubbing	A spray dryer is used to inject a suspension of lime and water (lime slurry) into the flue gas stream. When the suspension is injected into the flue gas stream, the water component evaporates, and only the solid lime particles remain in the flue gas.	50% less water consumption than wet methods; dry residuals	Worse use of sorbent in comp. to wet methods; Higher investment costs comp. to dry method
Wet scrubbing	Makes use of a liquid such as water or an aqueous solution capable of absorbing the acidic compounds present in the gaseous effluent.	Low consumption of sorbents; low sensitivity to fluctuation in flows	Higher complexity; higher corrosion; drop in flue gas temperature; large area needed
Flue gas desulphurization (FGD) with seawater	Wet non-regenerative type that makes use of the natural alkalinity of seawater to absorb the acidic contaminants present in the gaseous effluent.	No waste is formed; no reagents or additional chemicals; lower capital and operating costs.	Low efficiency; wet residues.

Wet systems are based on absorption through an aqueous solution containing alkaline reagents. The reaction products are in the aqueous phase; therefore, the system generates liquid effluents. The main wet technologies used include [23]:

- jet scrubbers;

- rotation scrubbers;
- venturi scrubbers;
- spray scrubbers;
- packed tower scrubbers.

The choice of the neutralizing agent is of fundamental importance. If milk of lime or limestone ( $\text{CaCO}_3$ ) is used, water-insoluble residues such as sulfates, carbonates, and fluorides may form. On the contrary, the use of sodium hydroxide ( $\text{NaOH}$ ) does not cause this problem since the products obtained are soluble. The use of  $\text{NaOH}$ , however, can lead to the accumulation of  $\text{CaCO}_3$  inside the scrubber [35]. Efficiencies vary depending on the type of scrubber used. For example, a single-stage venturi scrubber can achieve HCl removal efficiency of up to 95%, while a counter-current packed tower can deliver exceptionally high efficiency, up to 99.9%, and it is widely preferred in waste incineration plants [33].

In semi-dry systems, the absorbent is introduced into the gas stream in the form of a highly concentrated aqueous suspension or solution. When this solution comes into contact with acid gases, the water present in it evaporates. As a result, the reaction products are dry.

Dry systems are based on adsorption by means of an adsorbent agent, which is injected in the form of a powder. The dosage of the reagent depends on the temperature of the gases, the ratio between gaseous species, and the type of reagent. The reaction products are dry. These chemicals can then be collected along with the residual fly ash at the boiler exit using a baghouse filter or an electrostatic precipitator. Dry systems are mainly made up of two elements: a device for injecting absorbent material into the gas flow and a particle filtration device to remove reaction products [36]. The main technologies are:

- Techniques for injecting sorbent into the boiler: This approach involves introducing a dry sorbent into the combustion chamber or adding calcium- or magnesium-based sorbents to the bed of a fluidized bed boiler. The sorbent particles react with the acid gas present in the boiler effluents. Often, this technique is combined with a particulate emission control system;
- Circulating fluidized bed (CFB) dry purifier: the gaseous effluents coming from the air pre-heater in the boiler enter the lower part of the purifier and rise vertically through a venturi section, where a solid absorbent and water are injected separately. Also, in this case, this solution is usually associated with a technique for reducing suspended particles;
- Inline sorbent injection (DSI): This technique involves dispersing a dry powdered sorbent into the flue gas stream. The sorbent reacts with acid gases to form a solid, which is subsequently removed through particulate emission control systems. Usually, the use of bag filters is preferred;
- Atomizer, spray dryer absorber (SDA): a suspension or solution of alkaline reagent is introduced and dispersed in the flue gas flow. The material in contact with the gaseous contaminant reacts to form a solid, which is subsequently removed downstream through a particulate emission control system.

Dry systems are categorized as either sodium-based or calcium-based systems, depending on the additive employed. Table 2 lists the reactions that take place during the process of removing acid gas. The reaction process of calcium-based sorbents is explained by Equations (1)–(3). The reaction process of sodium-based sorbents is explained by Equations (4)–(6) [37].

The efficiency of adsorption processes is affected by the specific surface area of the solid ( $\text{m}^2/\text{kg}$  reagent), the degree of gas mixing, the concentration of the gas to be adsorbed, the temperature and humidity of the flow, and the concentration of the reagent (usually expressed in terms of stoichiometric ratio). Dry scrubbing systems need substantially more reagents than wet systems, requiring at least a partial recirculation of the separated solids in order to attain the same yields as wet systems [38]. Besides their higher cost, sodium-based sorbents generally provide higher collection efficiency than calcium-based sorbents. Regarding the latter, the substantial amount of additives that these processes

require is offset by their relatively low cost, which makes these processes appealing from an economic perspective. Furthermore, compared to single-stage bicarbonate-fed systems, calcium-based materials can result in significant operating cost savings when employed in efficient two-stage systems [39].

**Table 2.** Adsorption reactions for acid gases.

Calcium Hydroxide	Sodium Bicarbonate
$\begin{aligned} \text{Ca(OH)}_2 &\rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \\ \text{HCl} &\rightarrow \text{H}^+ + \text{Cl}^- \\ \text{Ca(OH)}_2 + 2\text{HCl} &\rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} \end{aligned} \quad (1)$	$\begin{aligned} 2\text{NaHCO}_3 &\rightarrow 2\text{Na}^+ + \text{HCO}_3^- \\ \text{HCO}_3^- &\rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} \\ 2\text{NaHCO}_3 &\rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \end{aligned} \quad (4)$
$\begin{aligned} \text{Ca(OH)}_2 &\rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \\ \text{SO}_2 + 2\text{OH}^- &\rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \\ \text{Ca(OH)}_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 &\rightarrow \text{CaSO}_4 + \text{H}_2\text{O} \end{aligned} \quad (2)$	$\begin{aligned} \text{Na}_2\text{CO}_3 &\rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \\ \text{HCl} &\rightarrow \text{H}^+ + \text{Cl}^- \\ \text{CO}_3^{2-} + 2\text{H}^+ &\rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} \\ \text{Na}_2\text{CO}_3 + 2\text{HCl} &\rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \end{aligned} \quad (5)$
$\begin{aligned} \text{Ca(OH)}_2 &\rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \\ \text{CO}_2 + \text{OH}^- &\rightarrow \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \\ \text{Ca(OH)}_2 + \text{CO}_2 &\rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \end{aligned} \quad (3)$	$\begin{aligned} \text{Na}_2\text{CO}_3 &\rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \\ \text{SO}_2 + 2\text{OH}^- &\rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \\ \text{Na}_2\text{CO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 &\rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 \end{aligned} \quad (6)$

Technologies or techniques designed for the abatement of other pollutants can also be used to remove acid compounds. For example, SCR and SNCR technologies were originally developed for the removal of nitrogen oxides in exhaust gases. Despite this, in SNCR, the ammonia used to reduce  $\text{NO}_x$  can also react with the HCl and HF present in the flying particles, forming ammonium chloride and fluoride [40].

### 3.1.2. BATs for $\text{NO}_x$ Reduction

In this study, nitrogen oxides ( $\text{NO}_x$ ) refer to the sum of nitrogen dioxide ( $\text{NO}_2$ ) and nitrogen monoxide (NO).  $\text{NO}_x$  may be formed in three ways [23]:

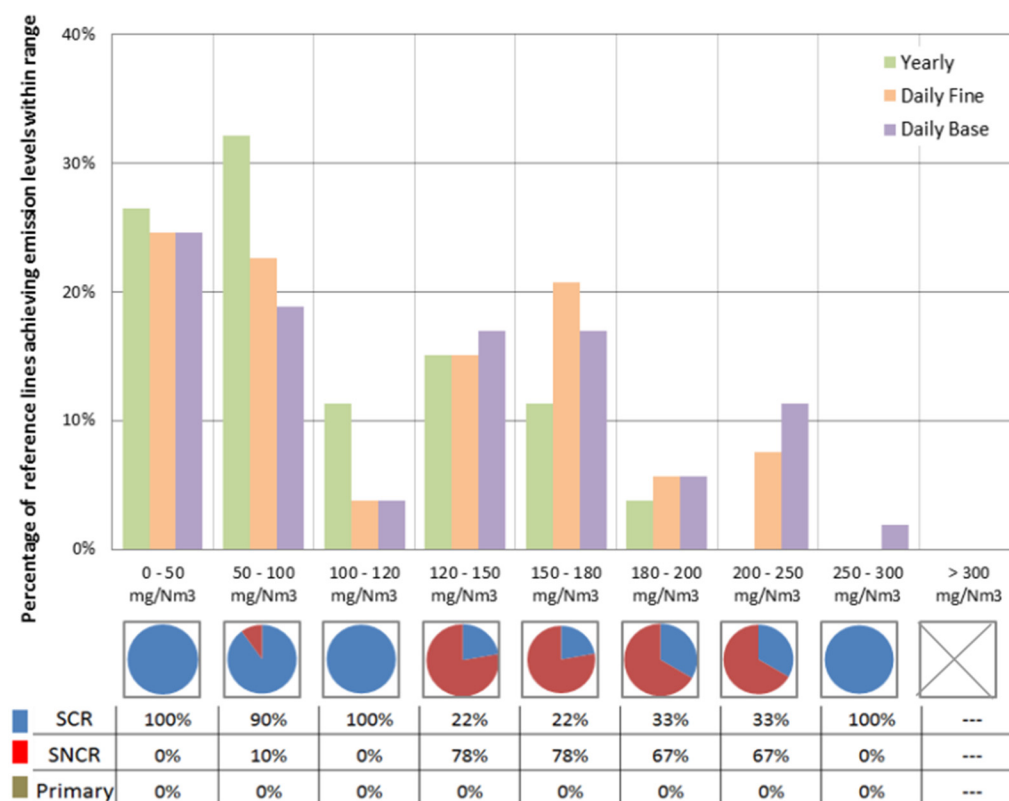
- Thermal  $\text{NO}_x$ : generated during combustion due to the oxidation of nitrogen contained in the air. This reaction is significantly triggered at temperatures above 1300 °C, and the rate of conversion depends exponentially on the temperature.
- Fuel  $\text{NO}_x$ : part of the nitrogen contained in the burning waste is oxidized to nitrogen oxides.
- Prompt  $\text{NO}_x$ : formation of  $\text{NO}_x$  via radical reaction; although this reaction cannot be stopped or mitigated, this mechanism has minor importance in waste incineration.

The average concentration of  $\text{NO}_x$  at the stack of European waste incineration plants, collected during the BREF revision process and based on continuous measurements, is reported in Figure 3.

For the reduction of  $\text{NO}_x$  emissions, primary techniques are of great importance. However, to reach an acceptable emission level, combinations of primary and secondary techniques are generally applied [41]. Considering primary techniques,  $\text{NO}_x$  production can be limited using measures that control the combustion process, preventing the oversupply of air or unnecessarily high combustion temperatures, and optimizing the control of the process for more homogeneous conditions. One widely used and significant primary strategy for reducing  $\text{NO}_x$  generation is the use of a well-distributed primary and secondary air supply to prevent uneven temperature gradients that lead to high-temperature zones and, consequently, higher  $\text{NO}_x$  production [42].

To this end, the control of gas mixing and temperature are important elements. Flue gas recirculation (FGR) is also a commonly used technique. With FGR, around 10–20% of the secondary combustion air is replaced with recirculated flue gases. The recirculated flue gases have a lower oxygen concentration, resulting in lower nitrogen oxide production. The injection of either pure oxygen or oxygen-enriched air also avoids the supply of additional nitrogen that may increase  $\text{NO}_x$  production [43]. Staged combustion is based on reducing the oxygen supply in the phase of the primary reaction and increasing the air supply in later

combustion zones to complete the oxidation of the gases. This approach requires effective air/gas mixing in the secondary zone to ensure that incomplete combustion products are maintained at low levels.



**Figure 3.** Continuously monitored NO<sub>x</sub> emissions into the air from reference lines incinerating predominantly MSW [23].

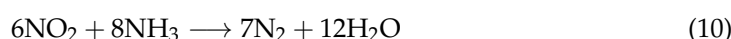
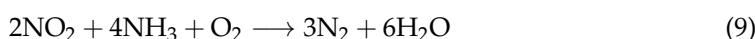
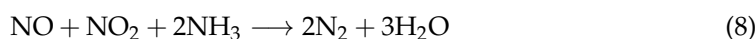
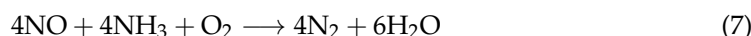
Advanced control options can also be applied to mitigate NO<sub>x</sub> production. For example, in existing installations, the detection of NO<sub>x</sub> precursors and their place of origin in the combustion chamber established the chance to reduce the oxidation of nitrogen compounds present in the fuel to NO by local control of the air flow [44]. A primary measure based on these findings is the Very Low NO<sub>x</sub> (VLN<sup>TM</sup>) process. In this process, combustion gas is drawn off from above the fuel bed at the rear of the grate. It is mixed with the secondary air and reduces the demand for combustion air [40].

To regulate NO<sub>x</sub> emissions from the combustor, natural gas can also be injected into the over-grate region of the furnace. Two methods can be used: methane de-NO<sub>x</sub> (i.e., by injecting natural gas directly into the primary combustion unit) or reburning (i.e., by injecting natural gas into a separate reburn zone situated above the primary combustion zone). Lastly, another option is to introduce water into the furnace. The hot spot temperatures in the primary combustion zone can be lowered with the use of an injection system that is correctly designed and operated [23]. One or more of the above primary techniques is implemented in the design of low-NO<sub>x</sub> burners. These burners are designed to delay but improve combustion and increase heat transfer. The conversion of fuel-bound nitrogen to NO<sub>x</sub> and the production of thermal NO<sub>x</sub> can be reduced by regulating the air/fuel mixing. In this way, the peak flame temperature and oxygen availability can be reduced while maintaining high combustion efficiency.

As mentioned above, secondary techniques are frequently needed to achieve compliance with NO<sub>x</sub> emission limits. For most processes, the application of ammonia or compounds releasing ammonia (e.g., urea) as a reduction agent is the proven standard method. The nitrogen oxides in the flue gas are reduced to N<sub>2</sub> and water vapor by the

reduction agent. Both  $\text{NH}_3$  and urea are applied as aqueous solutions. For safety reasons,  $\text{NH}_3$  is normally supplied as a 25% solution. Urea can also be applied in its pure, solid form. Two processes are important for the removal of nitrogen from flue gases: SNCR and SCR [45].

In SCR, an ammonia–air mixture (the reduction agent) is added to the flue gas and passed over a catalyst, usually a mesh (e.g., platinum, rhodium,  $\text{TiO}_2$ , zeolites). The most common SCR reactions, which are catalyzed, are reported in Equations (7)–(10):



SCR systems are frequently installed in low-dust positions (i.e., at the tail end, after de-dusting). However, in a few WtE plants, the SCR catalyst is installed as a so-called high dust catalyst directly downstream of the boiler [23]. Such an installation has the advantage, compared to a tail-end SCR, that it prevents energy losses by reheating the flue gas after the chemical gas cleaning stages. Nevertheless, the lifetime of the catalysts seems shorter compared to those in backend installations [40].

Most catalysts used in waste incineration processes operate in the range of 180–250 °C to limit the need for flue gas reheating. Lower operating temperatures, however, correspond to a larger catalyst surface. Also, a greater risk of fouling and catalyst poisoning is found at lower temperatures [46]. SCR allows high  $\text{NO}_x$  reduction rates (usually over 90%) considering stoichiometric (or close to stoichiometric) injections of the reduction agent. In waste incineration applications, SCR is mostly used in the low-dust configuration, that is, following the removal of acid gas and de-dusting stages. Zones of higher and lower response rates can be found within the 900–1000 °C temperature range where the SNCR process takes place. Using SNCR to reduce  $\text{NO}_x$  levels by more than 60–80% implies adding more of the reducing agent. Ammonia emissions, sometimes referred to as ammonia slip, may result from this. Recorded  $\text{NH}_3$  slip data are typically in the order of a few  $\text{mg}/\text{m}^3$  [44].

In SCR/SNCR systems, the operating temperature is a critical parameter. In SNCR, the temperature should be higher than 900–1000 °C and the residence times should be at least 0.2–0.5 s to keep the undesired nitrous oxide ( $\text{N}_2\text{O}$ ) emissions within the acceptable limits [47]. Conversely, it should be kept below 1050 °C to prevent the oxidation of  $\text{NH}_3$  and the formation of thermal  $\text{NO}_x$ . In SCR, low-temperature catalysts reached 90% removal efficiency already at 160 °C [48].

Another secondary alternative to BAT for  $\text{NO}_x$  abatement is catalytic filter bags. In order to produce the fibers utilized as the filter medium, either a catalyst is mixed directly with organic material or the catalyst is impregnated into filter bags. These filters have the ability to lower emissions of PCDD/F as well as  $\text{NO}_x$  when used in conjunction with an  $\text{NH}_3$  source [49].

### 3.1.3. BATs for the Removal of Organic Pollutants

Flue gas from waste incineration plants can contain trace quantities of a very wide range of organic species, including halogenated aromatic hydrocarbons, PAHs, benzene, toluene, and xylene (BTX), and PCDD/Fs [23].

As for  $\text{NO}_x$ , the limitation of organic pollutants is based on a combination of primary and secondary technologies. A well-controlled combustion process that prevents the formation of precursors is key to preventing incomplete combustion products in waste incinerators [50]. The primary techniques involve operational techniques, including the control and preparation of the waste before it is incinerated. Knowledge of the incoming waste, in fact, allows for better combustion control. Well-controlled combustion also aids in the destruction of PCDD/Fs and its precursors, which may already be in the waste.

In the energy recovery section of the process, the reformation of undesired by-products (PCDD/Fs in particular) must be prevented. Reducing the residence time of dust-laden gas in the 450 °C to 200 °C temperature zone reduces the risk of the formation of PCDD/Fs and similar compounds [51]. The potential for PCDD/F production is increased by dust removal devices (such as electrostatic precipitators and bag filters) operating at temperatures higher than 200 °C in high dust zones. As a result, temperatures at the dust removal stage should be kept below 200 °C. The ideal conditions for flue gas incineration, including the oxygen content, waste agitation, flue gas and waste residence time, and flue gas temperature and turbulence, allow a high destruction efficiency of the precursor compounds [52].

Regarding secondary techniques, adsorption on activated carbon reagents is one of the most commonly adopted processes. In an entrained flow system, activated carbon is injected into the gas flow. The carbon is filtered from the gas flow using bag filters. Activated carbon shows a high adsorption efficiency for many organic compounds, including PCDD/Fs [53]. Static or moving bed filters are also commonly used. These filter beds can be very efficient at adsorbing pollutants at low concentrations. In carbon-based systems, the spent carbon can be sent into the furnace, which will reburn the adsorbed pollutants [54]. The total pressure drop connected to the FGC system can restrict its use. Lack of space may limit the application in the case of existing plants [53]. The adsorption efficiency of different kinds of activated carbon varies. This has to do with the unique characteristics of the carbon particles, which are affected by the production process [55].

SCR systems that are commonly applied for NO<sub>x</sub> reduction can also destroy gaseous organic pollutants through catalytic oxidation. Abatement efficiencies of up to 99% can be reached for PCDD/Fs. In this case, the SCR system requires a deeper and multi-layered catalyst with respect to the de-NO<sub>x</sub>-only configuration.

As an alternative, catalytic filter bags can also be employed. Emissions of organic hydrocarbons can also be limited through the dust treatment stage since these pollutants tend to adsorb on fine particles. The same results can also be obtained by forced flue gas cooling (condensation) [56].

The BREF document on waste incineration also highlights some emerging techniques that could be considered for the removal of organic carbon pollutants. If wet scrubbing systems are used, oil instead of water (or other solvents) could be used as scrubbing liquor to absorb organic compounds. Some organic pollutants have low solubility in water, and therefore, they are not efficiently removed by water-wet scrubbers. If such pollutants (like PCDD/Fs) are more lipophilic, a high-boiling, partly unsaturated oil or an oil–water emulsion of such oil could provide suitable scrubbing media [23].

#### 3.1.4. Recommendations for Future Work

The intense knowledge exchange held during the BREF revisions revealed a number of issues that should be addressed in the future. The recommendations include the following [20]:

- More information and technology assessments of gasification, plasma, and pyrolysis plants incinerating waste should be included;
- More information on the incineration process of hazardous waste or sewage sludge should be collected, in particular for the characterization of the boiler efficiency and its variation depending, for example, on the use of auxiliary fuels or on the type and extent of sludge pretreatment in the case of the incineration of sewage sludge;
- With regard to the monitoring method for PCDD/F emissions, more information on PCDD/F emissions measured on the basis of short-term versus long-term sampling should be collected.

### 3.2. Novel Options for APC

#### 3.2.1. Acid Gas Removal

In the USA, Hunt et al. [57] studied the role of dry sorbent injection in the abatement of SO<sub>2</sub>, both as a retrofitting system and as a replacement of flue gas desulphurization

systems relying on wet and semi-wet systems that generate slurry products. The authors focused on the improvements in sorbents that have been achieved in the last two decades, specifically involving the production of enhanced hydrated lime sorbents with increased pore volume and surface area and with the addition of chemical treatment. The resulting material allows for lower reagent usage (about 50%) to obtain the same removal efficiency as conventional high-quality hydrated lime.

A wet scrubber combined with an ESP was studied by Park et al. [58] as a solution for the simultaneous removal of NO and SO<sub>2</sub> from the exhaust gas of thermal plants. Specifically, the wet scrubber used sodium chlorite (NaClO<sub>2</sub>) aerosol particles. Negatively charged aerosol particles obtained by the reaction of NO and SO<sub>2</sub> with NaClO<sub>2</sub> aerosol particles in an acidic solution (pH = 2) were collected at the anode of the ESP. Acidic conditions (pH = 2) were obtained by dosing an HCl solution onto the wet scrubber. The authors obtained a 100% SO<sub>2</sub> removal efficiency at an initial concentration of 500 mg/Nm<sup>3</sup>, an airflow rate of 60 Nm<sup>3</sup>/h, a contact time of 1.25 s, a NaClO<sub>2</sub> molar flow rate of 50 mmol/min, and an ESP power consumption of 68.8 W.

The simultaneous removal of NO<sub>x</sub> and SO<sub>x</sub> was also the subject of a recent study carried out in China by Zhu et al. [59]. In their work, 75% and 95% removal efficiencies were obtained for NO<sub>x</sub> and SO<sub>x</sub>, respectively, through the injection of de-NO<sub>x</sub> and desulfurization agents (respectively 0.4 g/Nm<sup>3</sup> and 0.6 g/Nm<sup>3</sup>) directly into the furnace, allowing for respective NO<sub>x</sub> and SO<sub>2</sub> stack concentrations of 80 mg/Nm<sup>3</sup> and 10 mg/Nm<sup>3</sup>. The de-NO<sub>x</sub> sorbent consists of urea, polypropylene, and sodium salt, while the desulfurization sorbent is made of sodium hydroxide and polypropylene. According to the authors, a shift from conventional desulfurization and de-NO<sub>x</sub> processes to sorbent injection would more than halve the operational costs and would reduce the investment costs by 21 times.

Wet technologies represent the majority (87%) of desulphurization systems worldwide [60] due to their low operational costs, high removal efficiency, and CaCO<sub>3</sub>, which is used as an absorbent. However, they are characterized by high investment costs, high space occupation, the production of waste sludge, and related treatment costs [38]. In contrast, semi-wet technologies like spray drying absorption may overcome many drawbacks of wet technologies in spite of disadvantages like the use of calcium hydroxide (Ca(OH)<sub>2</sub>) or sodium-based sorbents, which are more expensive than limestone, higher reagent rates required, and a higher exhaust gas temperature needed, which decreases the efficiency of the boiler. To reduce these drawbacks, alternative sorbents have been studied, like zeolites and silicates [38]. Zeolites and other clay minerals have been proven to be effective in terms of mercury removal from exhaust gas [61]. The addition of salts to Ca(OH)<sub>2</sub> may reduce water evaporation from the droplets due to their hygroscopic properties and, thus, increase the retention time of SO<sub>2</sub> on the droplet and its contact with Ca(OH)<sub>2</sub> [38].

A way to improve the removal of acid gases in dry sorbent injection systems is to optimize the residence time and the contact between the sorbent and the exhaust gas. For the removal of HCl in a real-scale reactor in the Republic of Korea, Kim et al. [62] studied a dry sorbent reaction accelerator, i.e., a reactor characterized by a peculiar layout: the exhaust gas enters the reactor from the bottom and comes into contact with Ca(OH)<sub>2</sub> particles, injected at a high speed in a narrow region of the reaction column; the column section then enlarges with a conic profile; sorbent particles fall by gravity laterally and are resuspended by the high-speed vertical flow of the exhaust gas at the center of the reaction column, to recreate the typical conditions of a fluidized bed. However, in spite of the improved contact between sorbent and exhaust gas, no quantitative comparison with a conventional dry sorbent injection system is made by the authors.

The removal of acid gases in dry sorbent injection and their cost-effectiveness may be improved by the use of two-stage dry systems, where Ca(OH)<sub>2</sub> and sodium bicarbonate (NaHCO<sub>3</sub>) are used, respectively, as sorbents in the first and second stages [36]. Both stages should be combined with bag filters to continue the reactions on the filter cake and to remove reacted sorbent particles, unreacted sorbent particles, and ashes. Unreacted sorbent particles can be reused in the adsorption processes, while calcium-based waste (e.g.,

gypsum) and sodium-based waste (e.g., sodium chloride and sodium sulfate brine) can be recycled in cement and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) production processes, respectively. Conversely, other calcium-based waste and ashes are usually disposed of. Dal Pozzo et al. [36] found that a two-stage calcium- and sodium-based dry sorbent injection process is more cost-effective than single-stage processes and may respond better to fluctuations in the composition of the input waste.

To improve the environmental sustainability of the thermal WtE sector, Kumar and Jana [33] suggested the use of marble waste as a substitute for limestone, recalling the work of Davini [63], who found that the  $\text{Ca}(\text{OH})_2$  synthesized by calcination and hydration of white-marble waste was more reactive than the  $\text{Ca}(\text{OH})_2$  obtained by processing commercial limestone because of its higher surface area. The use of marble waste would not require significant changes in the desulfurization systems using limestone, which cover most of the applications of acid gas removal technologies worldwide and allow for the recovery of gypsum from the reaction between limestone and  $\text{SO}_2$ . However, Kumar and Jana [33] suggest that also magnesium-based sorbents (specifically, magnesium hydroxide) in semi-wet processes could play an important role in  $\text{SO}_2$  abatement, thanks to the easy separation and drying of magnesium sulfite (the reaction product) for the generation of magnesium oxide ( $\text{MgO}$ ) and the possibility of using the released  $\text{SO}_2$  for sulfuric acid production ( $\text{H}_2\text{SO}_4$ ) with no production of waste.

### 3.2.2. $\text{NO}_x$ Removal

Improved flue gas recirculation, flue gas mixing, and heat recovery are considered preparatory steps to avoid  $\text{NO}_x$  formation in waste combustion processes [64–66]. Waldner et al. [44] stressed the importance of a correct design of furnaces to improve flue gas mixing, avoid regions where the flue gas is separated by secondary air, and thus reduce the air supply to reduce  $\text{NO}_x$  formation. The authors developed a model to optimize the gas flow and introduced a dynamic SNCR system in a real-scale grate combustion plant located in Switzerland, which is capable of injecting  $\text{NH}_3$  at different levels depending on the temperature of the flue gas. Indeed, to avoid  $\text{NH}_3$  slip, SNCR must be operated at temperatures  $> 850$  °C. Improved distribution and dosing of primary and secondary air reduced the  $\text{NO}_x$  concentration upstream of the SNCR from  $340 \text{ mg}/\text{Nm}^3$  to  $<190 \text{ mg}/\text{Nm}^3$ . The use of the dynamic  $\text{NH}_3$  injection system reduced  $\text{NH}_3$  slip by a factor of 2–8. Under such conditions, the stack concentration of  $\text{NO}_x$  was  $140 \text{ mg}/\text{Nm}^3$ . A higher  $\text{NH}_3$  yield further reduced the  $\text{NO}_x$  stack concentration to  $100 \text{ mg}/\text{Nm}^3$ , with only a slight increase in the  $\text{NH}_3$  slip.

Park et al. [58] previously mentioned  $\text{SO}_2$  abatement with an ESP combined with a wet scrubber and  $\text{NaClO}_2$  aerosol particles and obtained a 94.4% NO removal efficiency under the same conditions as the experiment carried out on  $\text{SO}_2$  abatement. Thus, an interesting NO removal efficiency was obtained without using conventional de- $\text{NO}_x$  systems like SNCR or SCR.

Focusing on the simultaneous removal of  $\text{NO}_x$  and PCDD/Fs, Lin et al. [67] studied an SNCR process with the injection of thiourea in addition to  $\text{NH}_3$  in a 2.9 volumetric ratio. This study focused on a real-scale MSW incinerator in China. Besides a 91% removal efficiency of PCDD/Fs, the use of thiourea reduced the  $\text{NO}_x$  concentration in the flue gas from  $140 \text{ mg}/\text{Nm}^3$  ( $\text{NH}_3$  injection only) to  $80 \text{ mg}/\text{Nm}^3$ .

Wang et al. [68] focused on the way to optimize the concurrent removal of PCDD/Fs and  $\text{NO}_x$  using  $\text{NH}_3$ -based SCR. Indeed, the removal of both types of pollutants with the same technology is limited by their competition in the catalytic reactions they are involved in and by the different optimal ranges of temperature for their removal (200–300 °C for PCDD/Fs and 300–400 °C for  $\text{NO}_x$ ). The authors investigated the benefits achievable from the use of manganese oxides–ceria oxides ( $\text{MnO}_x$ - $\text{CeO}_2$ ) composite catalysts modified by titanium oxide-based carbon nanotubes ( $\text{TiO}_2$ -CNTs). The authors set a Mn/Ti and a Ce/Ti ratio of 0.15 and 0.10, respectively, based on a previous study that focused on the simultaneous removal of dichlorobenzene and  $\text{NO}_x$  [69]. The larger surface area and the

higher ability to capture active components obtained with this modification seem to be the reasons behind the enhanced abatement of both pollutants. The removal efficiencies of ortho-dichlorobenzene (a substitute for PCDD/Fs) and NO increased from 27.9% and 51.3%, respectively, to >70% after the introduction of 20% wt. TiO<sub>2</sub>-CNTs.

Catalysis was also at the center of a study by Zhang et al. [70], but this time, it was used for the simultaneous abatement of NO<sub>x</sub> and dust. The aim is to understand if both categories of pollutants can be abated in one single stage since this would reduce the space occupied by the APC technologies in an MSW incinerator. The authors studied a modified PTFE bag filter with the addition of a cheap catalyst (V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> supported on TiO<sub>2</sub>) fixated on PTFE by a very simple method: immersion. The catalytic bag filter, preceded by NH<sub>3</sub> injection, would act as a catalyst for the SCR process and as a dust removal step at the same time. Based on a pilot-scale experiment on a real flue gas exiting the furnace of an MSW incinerator, the authors obtained simultaneous NO and dust removal efficiencies of >70.0% and 99.8%, respectively, starting from initial respective NO and dust concentrations of 150–180 ppm and 1800–2100 mg/Nm<sup>3</sup>, an NH<sub>3</sub> injection rate of 6–10 g/min, a gas flow rate of 25 Nm<sup>3</sup>/min, and a gas temperature of 180–195 °C. In their pilot-scale study, the authors used 48 bags with a filtration area of 24.4 m<sup>2</sup> and a catalyst loading of 16% wt. Two previous experiments carried out at lower temperatures (115–180 °C) showed better results in terms of NO removal (>80%) and similar results in terms of dust removal (>99.97%). In the first experiment, Pan et al. [71] used a MnO<sub>x</sub> catalyst on a TiO<sub>2</sub> sol-gel transition layer applied to a silicon carbide ceramic membrane to abate initial NO and dust concentrations of 300 ppm and 100–400 mg/Nm<sup>3</sup>, respectively, using an NH<sub>3</sub> concentration of 300 ppm. In the second experiment, Luo et al. [72] used a FeO<sub>x</sub>-MnO<sub>x</sub> catalyst applied to a PTFE/PPS membrane through hydrothermal methods, starting from 500 ppm and 800 mg/Nm<sup>3</sup> concentrations for NO and dust, respectively, and using NH<sub>3</sub> (500 ppm) as the reducing agent. At a higher temperature (200 °C), better results in terms of NO removal (95.3%) were obtained by Yang et al. [73], who used a Mn-Ce-Nb-Ox catalyst deposited on a P84 felt by foam coating. However, higher initial concentrations of NO and NH<sub>3</sub> were used (600 ppm in both cases).

As mentioned in Section 3.2.1, NO<sub>x</sub> and SO<sub>x</sub> could be simultaneously removed by direct injection of polymer-based sorbents in the furnace [59]. This would save space and reduce the investment and operational costs compared to dedicated SCR/SNCR and desulfurization units.

A life cycle assessment was undertaken by Wen et al. [74] to evaluate different scenarios for APC schemes in MSW incinerators. The authors compared three configurations: (1) a semi-wet adsorber, followed by activated carbon injection and filter bags; (2) a semi-wet adsorber, followed by dry alkaline sorbent injection, activated carbon injection, and filter bags; (3) an SNCR, followed by a semi-wet adsorber, dry alkaline sorbent injection, activated carbon injection, and filter bags. From the point of view of environmental impacts, the third scenario is preferable for NO<sub>x</sub> reduction. However, this configuration would lead to higher SO<sub>x</sub> stack concentrations (though below the limits set by many regulations worldwide) and, especially, to higher chromium emissions, for which concerns were raised in a recent study [75].

### 3.2.3. VOC Removal

As mentioned in Section 3.1.3, organic compounds, including VOCs, can be abated by different techniques, especially the optimization of the combustion process and the waste feed, dry sorbent injection, adsorption, and SCR. Alternative methods for VOC abatement were recently reviewed by Corbasson et al. [76]. One possible alternative is the use of membranes for the separation of VOCs from the gas flow. However, the operating temperature is an important factor influencing material resistance, VOC selectivity, and separation. Different materials behave differently with increasing or decreasing temperature, and this aspect should be considered when selecting membrane characteristics [77].

Non-thermal plasma has also been studied as a method to remove VOCs from gaseous effluents, but its application is still limited by the high energy consumption involved when dealing with high airflow rates [78] and the potential generation of unwanted by-products [79].

Zhang et al. [53] recently studied the use of biochar as an adsorber for VOCs and found that ball-milled biochar doped with hydrogen peroxide and ammonium hydroxide can capture 3 to 4 more times benzene and xylenes compared to pristine biochar, achieving high levels of reusability after thermal desorption. However, the ability of biochar to perform well at high temperatures was not proved because the authors tested biochar only at ambient temperature (25 °C).

SCR systems usually employ catalysts based on transition metals like vanadium (V), manganese (Mn), cerium (Ce), copper, and iron. Specifically, V-based catalysts ( $V_2O_5$ - $WO_3/TiO_2$ ) have shown the best catalytic activity in the temperature range of 300–400 °C. However, the usual operating temperature of SCR systems is lower than this range. Thus, there is a need to improve the conversion efficiency of catalysts at lower temperatures, possibly ensuring the simultaneous removal of  $NO_x$  and VOCs. The same problem exists for the simultaneous removal of  $NO_x$  and PCDD/Fs, as mentioned in Section 3.2.2. In recent experiments, Xu et al. [80] showed that  $V_2O_5$ - $WO_3/TiO_2$  doped with tungsten (W) and praseodymium (Pr) is capable of increasing the conversion efficiency of both  $NO_x$  and chlorobenzene significantly at lower temperatures (200–300 °C) compared to the undoped catalyst. In another recent study [81], different degrees of interaction (impregnation, physical mixing, co-precipitation, and sol-gel) between Mn- and Ce-based oxides were evaluated in terms of the removal capability of NO and dichlorobenzene. Co-precipitation and sol-gel resulted in the best formulations, enabling relatively high NO and dichlorobenzene removal rates (>80% and 60%, respectively) in the 200–300 °C temperature range.

When selecting catalysts for an SCR system, possible mechanisms of catalyst deactivation should be considered. In a recent review, Zheng et al. [82] discussed the potential risks involved in catalytic processes applied to industrial furnaces. For instance, heavy metals in the flue gas could clog active sites, preventing adsorption, or may induce electronic effects that reduce the adsorption of specific compounds. The presence of  $SO_2$  in the flue gas and of  $NH_3$  in SCR systems may form ammonium sulfites and sulfates, which may poison the catalysts. Finally, dissociated chlorine may react with ammonium to form ammonium chloride, which may deposit on the surface of catalysts, reducing the availability of active sites.

### 3.3. Suggested Configurations for an APC System, including Novel Removal Techniques

The tendency of the sector is to prefer dry removal technologies because of their easier management and absence of liquid waste streams [83]. However, wet removal technologies are preferable for the removal of  $NO_x$  (via SNCR or SCR) or specific substances that may induce environmental and/or health risks that are not compatible with the local context where the plant is located. For instance, Rada et al. [75] highlighted the potential impacts related to chromium (Cr) VI emissions from waste combustion plants, suggesting that wet removal technologies are more appropriate to reduce the emissions of Cr VI due to its relatively high water solubility.

In addition to these considerations, the possible location of the novel removal processes reviewed in Section 3.2 must be decided according to general rules adopted by current waste incinerators and related both to the technical and economic convenience of specific abatement processes and to the emission limits that waste incinerators must comply with. The choice of the location of novel abatement technologies/processes for gaseous pollutants must then consider the presence of other processes that are necessary to abate other regulated air pollutants, like PCDD/Fs, PCBs, PAHs, total suspended particles, and heavy metals.

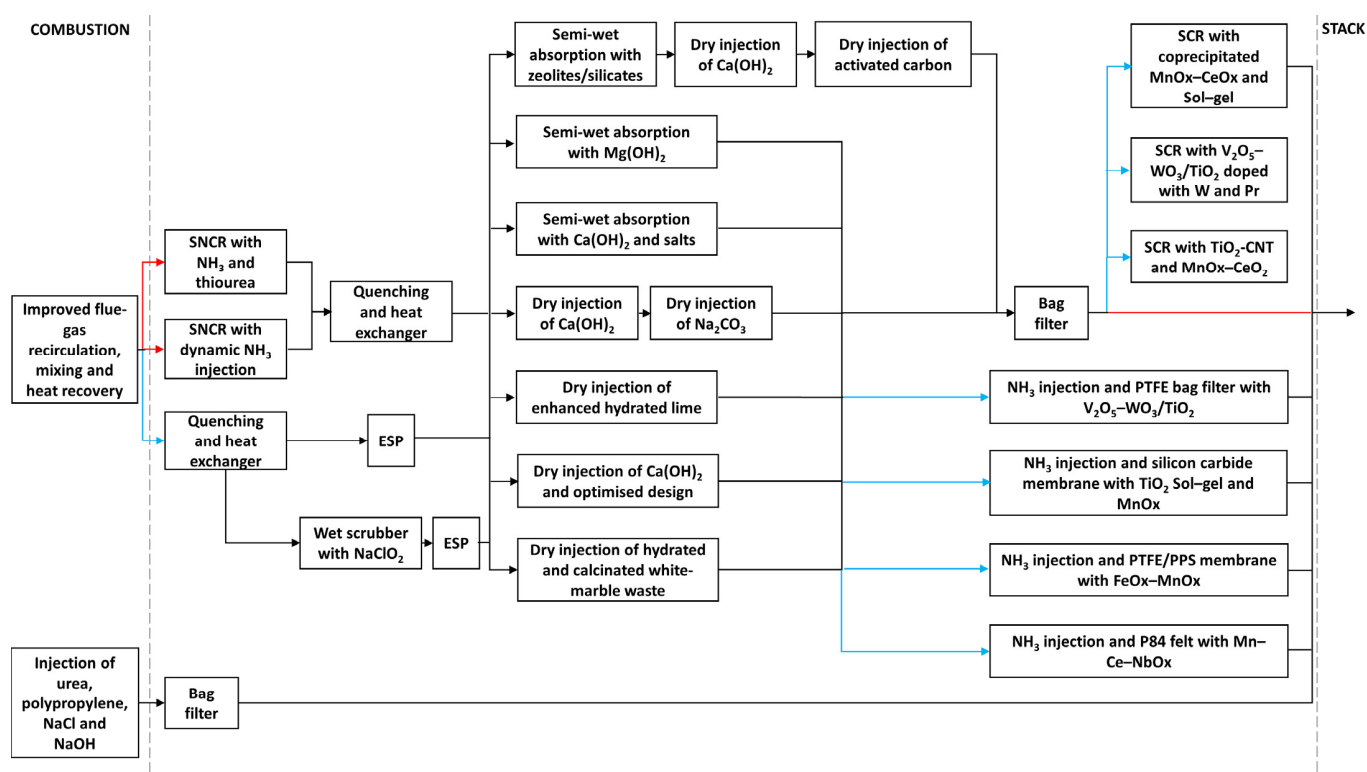
More in detail, Peng et al. [84] suggest that specific operating conditions of the combustion chamber (e.g., high flue gas turbulence, flue gas temperature > 1000 °C for at least

1 s or temperature  $> 850$  °C for at least 2 s, excess oxygen volume content of 3–6%) should be adopted to guarantee satisfying removal of PCDD/Fs formed during waste combustion. The choice of the de-NO<sub>x</sub> system also influences the location of other APC technologies; for example, if an SNCR is selected, it should be placed as close as possible to the combustion chamber to take advantage of the high temperature of the flue gas. Temperatures  $> 850$  °C are necessary to carry out NO<sub>x</sub> reduction without the aid of catalysts and prevent NH<sub>3</sub> slip.

If SNCR is not considered the de-NO<sub>x</sub> technology for a WtE plant, rapid quenching of the flue gas should be guaranteed through an appropriate design of the quenching tower and of the heat exchanger to avoid de novo formation of PCDD/Fs, which are formed by metal chlorides, fly ashes, and organochlorinated precursors that act as catalysts [85]. De novo formation of PCDD/Fs can be minimized by performing a rapid cooling of the flue gas to temperatures  $< 200$  °C and optimizing the design of the heat exchanger to reduce the chance of deposition of fly ashes on its surfaces [86]. The use of an SNCR system does not rule out the introduction of a downstream SCR system to abate NH<sub>3</sub> that may slip from the SNCR stage. In this case, the quenching stage should be placed soon after the SNCR stage. If SCR is used alone as a de-NO<sub>x</sub> process, this should be located preferably downstream of other abatement systems to avoid poisoning of the active catalyst sites by other pollutants [87] and, in any case, in a position where the flue gas temperature is low enough to ensure a satisfying removal efficiency of NO<sub>x</sub>. To avoid catalyst poisoning, SCR systems must be preceded by an efficient dust abatement technology, i.e., bag filters. The latter should be operated at relatively low temperatures, like SCR systems, to avoid moving the partition equilibrium of air pollutants to the gas phase rather than the particle phase. Indeed, high temperatures reduce the efficiency of bag filters. It is known that particle-phase pollutants may be generated from gas-phase pollutants undergoing nucleation, condensation, and coagulation, with gas temperature playing a key role in gas-to-particle conversion [88]. For instance, PCDD/Fs, originally formed in the gas phase, show the tendency to convert into particles with decreasing temperature and increasing the degree of chlorination [89]. As a result, the abatement of gas-phase contaminants may prevent the formation of particle-phase pollutants. Bag filters were found to give the best results at an operating temperature of 160 °C [90]. In addition, to make bag filters effective for the removal of heavy metals, PCDD/Fs, PCBs, and PAHs, they should be preceded by dry sorbent injection if dry abatement technologies are adopted for acid gas removal.

In light of the previous considerations, it is possible to suggest the introduction of the novel processes or materials reviewed in Section 3.2 within typical APC schemes for waste incinerators. Different possibilities for the implementation of novel techniques are proposed in Figure 4. The configuration proposed by Zhu et al. [59] was included in the scheme for completeness. However, such configuration does not include any techniques reported in the BAT Reference Document for Waste Incineration [23]. Thus, the applicability of this process should be further verified and evaluated case by case, depending on the country.

Similar configurations, with some minor changes, may be adopted for other thermal WtE processes like gasification or pyrolysis, i.e., indirect waste combustion processes. Indeed, both the air pollutants generated by syngas combustion and their emission rates are comparable with the typical emissions from waste incineration. The main difference is related to the lower emission rates of NO<sub>x</sub> and PCDD/Fs, which are generally lower because gasification and pyrolysis operate, respectively, with defects and the absence of oxygen [91,92].



**Figure 4.** Proposed configurations for the implementation of the novel techniques reviewed for the abatement of gaseous pollutants from waste incineration plants [33,36,38,44,57–59,62,64–68,70–73,80,81]. Paths specifically intended for configurations with SNCR and SCR are represented in red and blue, respectively.

#### 4. Conclusions

The present paper provides a review of treatments and APC technologies applicable to direct (incineration) and indirect (gasification and pyrolysis) waste combustion plants for the removal of gaseous pollutants, i.e., acid gases ( $\text{SO}_x$ , HCl, and HF),  $\text{NO}_x$ , and VOCs. State-of-the-art APC technologies were identified and reviewed according to the BREFs drafted by the European Commission for waste incineration. In addition, recent advances in the field were presented and discussed to suggest processes and technologies that go beyond the BATs presented in the BREFs. The focus on novel techniques aims to highlight the technological efforts that the WtE sector has made in the last decades to reduce the potential environmental and health impacts of high-temperature processes.

APC technologies allow for abating toxic and carcinogenic air pollutants (e.g., PCCD/Fs, PCBs, PAHs, VOCs,  $\text{NO}_x$ ,  $\text{SO}_x$ , CO, PM, and heavy metals) that may directly impact human health. Reducing HCl, HF, and  $\text{NH}_3$  emissions, as well as  $\text{NO}_x$  and  $\text{SO}_x$ , would prevent acid rains and soil acidification, which may negatively affect ecosystems. For these reasons, investing in research on novel abatement technologies is extremely important to continuously reduce the impact of the WtE sector and to go beyond the adoption of BATs, which already ensure high environmental standards.

The present paper showed the complexity behind the choice of optimal APC schemes due to the interactions between air pollutants, different APC technologies, and flue gas parameters (especially temperature). Suggested configurations were proposed based on recently published peer-reviewed papers and on the multi-year experience gained by this sector. As a matter of fact, such configurations include both well-known abatement technologies (e.g., ESPs, bag filters, SCR, and SNCR) and many of the new techniques reviewed in this paper.

Given the contribution of this sector to the emission of greenhouse gases (mainly due to the presence of waste with a non-biogenic origin), carbon capture technologies should be considered more insistently in the future, especially in reference documents like the BREFs. Such technologies are out of the scope of the present paper, which focuses on local air pollutants. However, reducing the carbon footprint of WtE technologies might help decrease the level of aversion and skepticism to such processes in public opinion.

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## Nomenclature

APC	Air pollution control	MgO	Magnesium oxide
BATs	Best available techniques	MSW	Municipal solid waste
BAT-AELs	BAT-associated emission limits	Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
BREFs	BAT Reference Documents	NaClO <sub>2</sub>	Sodium chlorite
BTX	Benzene, toluene, and xylene	NaHCO <sub>3</sub>	Sodium bicarbonate
CaCO <sub>3</sub>	Limestone	NaOH	Sodium hydroxide
Ca(OH) <sub>2</sub>	Calcium hydroxide	NH <sub>3</sub>	Ammonia
CFB	Circulating fluidized bed	NO	Nitrogen oxide
CH <sub>4</sub>	Methane	NO <sub>2</sub>	Nitrogen dioxide
CHP	Combined heat and power	NO <sub>x</sub>	Nitrogen oxides
CO	Carbon monoxide	PAHs	Polycyclic aromatic hydrocarbons
CO <sub>2</sub>	Carbon dioxide	PCBs	Polychlorinated biphenyls
DSI	Duct sorbent injection	PCDD/Fs	Polychlorinated dibenzo- <i>p</i> -dioxin and dibenzofurans
ESP	Electrostatic precipitator	PM	Particulate matter
FGC	Flue gas control	SCR	Selective catalytic reduction
FGD	Flue gas desulfurization	SDA	Spray dryer absorber
FGR	Flue gas recirculation	SNCR	Selective noncatalytic reduction
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid	SO <sub>2</sub>	Sulfur dioxide
HCl	Hydrochloric acid	SO <sub>x</sub>	Sulfur oxides
HF	Hydrofluoric acid	VOCs	Volatile organic compounds
IED	Industrial Emission Directive	WtE	Waste-to-energy
IPPC	Integrated Pollution Prevention and Control		

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