SERIES ON CLEAN ENERGY TECHNOLOGY

Zhihua Wang · Kefa Cen
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Simultaneous Multi-Pollutants Removal in Flue Gas by Ozone

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Preface

Despite the rapid development in clean energy technologies, such as hydrogen fuel, wind and solar energy, the majority of the energy consumption in a foreseeable future will still rely on combustion technologies using fossil fuels, waste and biomass. It is well known that pollutant emissions including NO_x, SO_2, mercury, volatile organic compounds (VOCs), and dioxins from combustion and incineration processes of coal, biomass, municipal solid waste (MSW), and different kinds of waste, are extraordinary harmful to the atmosphere and human health. In China, coal has been traditionally the major primary energy source, and its role is expected to continue growing in the forecasted period. Under these circumstances, pollutant emissions derived from coal combustion have inevitably become prominent.

So far, a variety of possible options already existing to reduce these emissions individually are proposed and carried out, but unfortunately, each pollutant control method individually is turned out to be not only high investment, but also decreases the whole system reliability. Therefore, actively developing research on the coal-fired multi-pollutants removal and exploring an advanced, reliable, and cost-effective multi-pollutants removal technology are remarkably hot issues for Chinese sustainable development in light of the current use of coal as main energy source.

Ozone injection is one of the most promising multi-pollutants simultaneous removal technologies with high efficiency, energy saving, and low cost, because the strongly oxidizing radicals such as O_3, O, OH, and O_2^* are generated in flue gas after ozone injection. These radicals actively convert NO_x into NO_2 and transform elemental mercury into its oxidized form (such as HgO and $HgCl_2$), both of which are of thoroughly water-soluble. Integrated with the existing WFGD (wet flue gas desulfurization) system and special designed alkali absorption tower, pollutants including NO_x, SO_2, Hg, VOCs, and dioxin could be removed simultaneously.

By presenting a number of fundamental research findings, significant scientific breakthroughs, and novel advances in the research field of multi-pollutants removal by ozone during the last decades, this book will provide the readers with updated information in the field of air pollution control technology related to the coal-fired power plants. Furthermore, the fundamental research findings, comprised of the detail reaction mechanism between ozone and flue gas components, are obtained not only from chemical kinetics modeling but also from lab-scale experimental investigations. The demonstration case of the multi-pollutants removal by ozone will be attentively employed to conduct, with the help of the detailed reaction mechanism obtained. In short, this book remains at the fore front of research and development in this crucial area related with multi-pollutants removal by ozone injection.

The book is logically divided into the following five chapters.

Chapter 1 gives an overview of the state-of-art development of coal-fired pollution control technologies. It refers to various control technologies for sulfur dioxide, nitrogen oxides, mercury, VOCs as well as dioxin and flue gas multi-pollutants simultaneous removal technologies.

Chapter 2 presents the removal technology of multi-pollutants in flue gas by ozone oxidation. The physical and chemical properties of ozone are summarized. Ozone generation methods and overviews on the progress of ozone synthesis technologies with discharge plasma are described as well.

Chapter 3 elucidates in detail the chemical kinetics mechanism between O_3 and NO_x/SO_2/Hg, which stems from chemical kinetic modeling and lab-scale experimental invetigations. The chemical kinetics model considers 40 typical species in flue gas and refers to 121 elementary reactions in total.

Chapter 4 provides the simultaneous removal mechanism of multi-pollutants with ozone and wet scrubbing, which is obtained from lab-scale experimental work. It is attached extremely importance to the NO_2 absorption in a wet scrubber for achieving an optimal NO_x removal. Accordingly, key operational parameters that can affect the NO_2 removal are to take into account and effects of the pH value and initial NO/SO_2/S(IV) concentration are determined.

In Chapter 5, the work on the ozone multi-pollutants control associated with wet scrubber system has effectively led to the development of an oxidation-absorber system that is undergoing demonstration and commercialization. An economic analysis of the system is involved and highly needed for future commercialization.

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The authors have benefited enormously from the interaction and contributions of the other members of the group. Essentially, the book covers the experience and findings gained by the other working team in the related research field.

As a final note, we wish to thank all the authors for their participation in making this book possible. And we are especially grateful to the other members of our group. We also want to thank Dr. Zhengcheng Wen, Dr. Xiang Zhang, Dr. Min Kuang, Dr. Yong He, Dr. Shudong Jiang, Dr. Lv Yu, Dr. Xin Hu, Dr. Zhuo You, Dr. Xiaoye Liang, Dr. Pei He, Dr. Yajun Zhou, Miss Daili Li, Mr. Chaoqun Xu for contributions on managing and copy-editing the context of this special issue.

The authors
Hangzhou, China
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Development of Pollution Control Technology During Coal Combustion

1.1 Introduction

As we are moving ahead into the 21st century, our hunger for cost-effective and environmentally friendly energy continues to grow. The energy information administration of US has forecasted that only in the first two decades of the 21st century, our energy demand will increase by 60% compared to the levels at the end of the 20th century. Fossil fuels have been traditionally the major primary energy sources worldwide, and their role is expected to continue growing for the forecasted period, due to their inherent cost competitiveness compared to non-fossil fuel energy sources. However, the current fossil energy scenario is undergoing significant transformations, especially to accommodate increasingly stringent environmental challenges of contaminants like sulfur dioxide, nitrogen oxides or mercury, while still providing affordable energy [1]. In China, coal has been traditionally the major primary energy sources, and its role is expected to continue growing for the forecasted period, due to Chinese energy consumption structure and its inherent cost competitiveness compared to other fossil or non-fossil fuel energy sources [2].

The economy of China has been growing rapidly, and the living conditions of people have been improved significantly in the past three decades. However, with the development of the economy, the energy consumption has increased and the environmental pollution has inevitably become prominent.

As a primary source of energy, coal is mainly used for direct combustion. While, the traditional coal combustion is inherently plagued with a large amount of atmospheric pollutants, especially soot, SO_2, NO_x [3], CO/CO_2, volatile organic compounds (VOCs) [4], Hg and other trace toxic heavy metals [5,6], dioxins, and strong carcinogens. These pollutants irrefutably damage to the atmospheric and ecological environments and jeopardize human health.

On the basis of the statistics of National Environmental Protection Administration, 80% of soot emission, 90% of SO_2 emission, 67% of NO_x emissions, 90% of CO_2 emission and 40% of mercury emission of the total were extremely derived from the direct combustion of coal in China [7]. The state-of-date and the strictest emission limitations (GB13223-2011) in coal-fired power plant was promulgated and taken into force in 2012 in China. Thus, it is more likely that coal energy producers would adapt to the new requirements by developing and implementing emission control technologies.

1.2 Existing Air Pollution Control Technologies

It is well known that emissions including SO_2, NO_x, mercury, VOCs, and dioxins from coal combustion are extraordinary harmful to our atmosphere. In china, coal has been traditionally the major primary energy sources, and its role is expected to continue growing for the forecasted period, emission derived from coal combustion has inevitably become prominent. Thus, developing the existing air pollution control technologies and exploring the reasonable, high-effective alternative would be a hot issue and attached great importance.

So far, a variety of possible options already existing to reduce these emissions individually were proposed and carried out, whereas a simultaneous multi-pollutants removal technology during coal combustion in China is absent up to now and put forward in this book.

1.2.1 Desulfurization Technology

Approaches to control SO_2 emission of coal-fired boiler mainly include pre-combustion, combustion, and post-combustion desulfurization. A brief introduction to major desulphurization technologies is presented below.

1.2.1.1 Circulating Fluidized-Bed Technology

Fluidized-bed combustion (FBC) technology first appeared in the 1960s [8], followed by circulating FBC. Limestone or dolomite is mainly used as desulfurizer for this technology. During the coal combustion process, the limestone or dolomite is decomposed into CaO, which reacts with O_2 and SO_2 in the oxidizing atmosphere to form $CaSO_4$. Circulating Fluidized-bed technology is widely used in the world, because of the characteristics of fuel flexibility, high combustion efficiency, and low pollution emissions.

1.2.1.2 Wet Flue-Gas Desulfurization Technology

Wet flue-gas desulfurization (WFGD) technology, which is based on using limestone or lime as a reagent, is a wet scrubbing process and has been the most frequently selected flue-gas desulfurization (FGD) technology for SO_2 reduction from coal-fired utility boilers [9]. The WFGD flue gas treatment system is typically located after removal of particulate matter from flue gas either by a baghouse or an electrostatic precipitator (ESP). The cleaned flue gas is then discharged to the stack. SO_2 is removed by scrubbing flue gas with either a limestone or lime (reagent) slurry. Nowadays, WFGD, which is considered to be a commercially mature technology, has been applied widely in coal-fired power plants globally.

In most WFGD systems, the quantity of liquid sprayed relative to flue gas is related to the SO_2 collection efficiency needed and is referred to as liquid-to-gas (L/G) ratio. Higher L/G ratios improve SO_2 removal by exposing the gas to more absorbing liquid, implying that higher L/G ratios also consume more power.

Conclusively, the WFGD technology has such features as highly efficient desulfurization (achieving more than 95% SO_2 cleanup) and high operation cost.

1.2.1.3 Spray Dry Flue-Gas Desulfurization Technology

Alkaline solution or hydrated lime emulsion is usually employed as desulfurizer for the spray dry flue-gas desulfurization process [10]. Considering that the wet desulfurization agent is used but the dry final product is generated, this method is also called the semi-dry desulfurization technology. The rotary spray desulfurization technology is currently widely adopted by most countries especially municipal solid waste incineration power plants because of its reliable operation, no fouling and plugging, and easy handling of solid products. Moreover, this technology seems to be more economical and efficient in retrofitting the existing power plants than WFGD.

1.2.1.4 Calcium Injection/Humidification Desulfurization Technology in Furnace

Limestone, dolomite, and hydrated lime are typically used as desulfurizers, which are decomposed into CaO for SO_2 absorption [11]. The Alanco Company in the United States provides a charged spray dry absorbent device for dust removal and desulfurization system [12]. This device allows a high-speed absorbent flow through a high-voltage electrostatic-corona charging zone generated by the spray unit, so that the absorber carries strong electrostatic charge. As the absorber flows into the sooty flue gas, the electrical charges will exclude the particles with each another. Therefore, a uniform distribution with suspended state is then formed to produce a sufficient reaction between the absorbent and SO_2. This technology approves lower investment and small space needed, and is suitable for retrofitting old plants. However, the high technical demands and complex maintenance of this technology limit its application.

1.2.1.5 Electron-Beam (E-Beam) FGD Technology

The e-beam FGD technology is adopted for injecting NH_3 into flue gas, which is then irradiated by e-beam [13,14]. Therefore, SO_x and NO_x in flue gas react with NH_3 to generate $(NH_4)_2SO_4$ and NH_4NO_3. This desulfurization technology is competitive and has the following main features: (i) It is simple and can realize desulfurization and denitrification efficiently and simultaneously; (ii) The entire desulfurization process does not require post-treatment of wastewater; (iii) $(NH_4)_2SO_4$ and NH_4NO_3, which are the by-products of the reaction, are considered as raw materials of compound fertilizer production; (iv) This technology occupies small space and is a good alternative either for retrofitting old plants or newly-built units; (v) After treatment, flue gas can be directly released into the atmosphere; (vi) It requires relatively lower investment and operation cost.

1.2.1.6 Seawater FGD Technology

Seawater is commonly used as desulfurization agent for absorbing SO_2 through the seawater FGD technology [15]. The process of this technology is relatively simple, mainly including a spray absorber tower and an aeration tank. Flue gas reacts with seawater in the spray tower, which is then restored in the aeration tank. This technology has several advantages. For example, it does not require the preparation or addition of a desulfurizer and is reliable with low investment and operation cost, in addition to no wastewater and waste materials needed to be disposed. Consequently, this technology has received considerable attention all over the world and is now operating or under construction in Norway, Spain, Indonesia, United Kingdom, USA, and other countries.

1.2.2 Denitrification Technology

Methods for controlling NO_x emissions are usually classified into two categories: combustion deNO_x and post-combustion deNO_x technologies. The combustion deNO_x method is applied to diminish NO_x formation through the low-oxygen combustion, staged-air combustion, re-burning, and flue-gas recirculation by adjusting the primary air and secondary air distribution and changing the combustion conditions in the furnace. The post-combustion deNO_x method utilizes reagents to reduce NO_x in the flue gas. Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are usually used and involved in this category. The following content provides a brief introduction on denitrification technologies.

1.2.2.1 Low-Oxygen Combustion Technology

As to the low-oxygen combustion technology, combustion is kept at a low excess air coefficient, both limited oxygen fed into the reaction zone and relative low flame temperature can inhibit the generation of fuel NO_x and thermal NO_x on the basis of the oxygen-sensitive characteristics of fuel NO_x.

NO_x emissions can be reduced by 15% – 20% through this method. However, if the excess air coefficient is too low during the real operations, the combustion stability will be seriously jeopardized. Consequently, the flame center will moved up and emissions such as CO, soot, and fly ash will increase rapidly, which will irrefutably lead to dangerous boiler operation conditions.

1.2.2.2 Staged-Air Combustion Technology

The staged-air combustion technology obtains the minimum NO_x formation by forming oxygen-lean, fuel-rich regions in the main combustion zone through a multi-level air supply strategy. The injected over-fire air (OFA) makes the pulverized coal to be burnt out. The parameters which impact on the NO_x removal efficiency are the excessive air ratio, temperature, and residence time in the main combustion zone. The excess air ratio in the main combustion zone generally ranges from 0.7 to 0.95. The temperature and residence time mostly depend on the excess air ratio in the primary combustion zone.

This method is quite simple and effective for either the existing or newly built boilers. Compared with the outdated boiler models, the advanced, integrated-air staging combustion technology can reduce NO_x by 15% – 30% [16]. However, it may possibly cause corrosion and slag in the furnace, along with a reduction in the combustion efficiency.

1.2.2.3 Flue-Gas Recirculation

Flue-gas recirculation is one of a low-NO_x combustion technology, widely employed for gas-fired and oil-fired boilers. It introduces the re-circulate flue gas into the combustion zone by using a fan to lower the flame temperature and to dilute the oxygen concentration so as to reduce the NO_x formation.

Gas mixing and fuel combustion can be significantly improved by flue-gas recirculation. Thus, NO emissions can be reduced by about 20%. However, this method barely inhibits thermal NO_x generation. If the circulating flue gas exceeds to 15 wt.% of the combustion air, the NO_x reduction will eventually decrease a lot. The maximum flue gas recycled is limited by the flame stability. Recirculation fans must be added once retrofitting is necessary. Flue-gas recycling and modification is relatively easy and the retrofit investment is low.

1.2.2.4 Reburning Technology

Reburning [17] is an effective and promising alternative method for reducing NO_x emissions. Reburning technology can reduce NO_x emissions by 50% – 70%, which is inferior to SCR and SNCR. Reburning can keep a stable reductive atmosphere in the fuel-rich zone, low excess air ratio area, high concentrations of