Review

배출가스의 질소산화물과 이산화황 동시 저감 기술

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Various Technologies for Simultaneous Removal of NOx and SO₂ from Flue Gas

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초 록

석탄화력발전소를 포함한 다양한 산업설비에서 유해 대기오염물질이 배출되고 있으며, 이러한 오염물질은 인체 건강과 자연 생태계에 영향을 준다. 특히, 질소산화물(NO_x)와 이산화황(SO_2)은 인체 건강에 악영향을 주는 미세먼지($PM_{2.5}$) 형성에 원인물질로 알려져 있다. 이러한 NO_x와 SO_2 배출을 저감하기 위해서 선택적 촉매 환원(SCR)과 습식 탈황 공정 (WFGD)으로 결합된 혼합 시스템이 사용되고 있으나, 높은 설치비용 및 운전비용을 필요로 하며, 유지보수의 문제점, 기술적인 한계점을 가지고 있다. 최근에 이러한 혼합 시스템을 대체하기 위한 NO_x, SO_2 동시 저감 기술이 연구되고 있으며, 제안된 기술들은 흡수, 고도 산화(AOPs), 저온 플라즈마(NTP), 전자 빔(EB) 등이 있다. 이러한 기술들은 강한 수용성 산화제 및 산화력을 가진 화학활성종에 의한 NO_x, SO_2를 HNO_3, H_2SO_4 형태로의 산화 반응, 기-액 계면에서 HNO_3와 H_2SO_4 흡수 반응, 화학 첨가제에 의한 중화 반응을 기본으로 하고 있다. 본 논문에서는 각각의 동시 저감 공정에 대한 기술적인 특징과 대용량 처리 공정 응용을 위한 향후 전망을 정리하였다.

Abstract

Harmful air pollutants are exhausted from the various industrial facilities including the coal-fired thermal power plants and these substances affects on the human health as well as the nature environment. In particular, nitrogen oxides (NO_x) and sulfur dioxide (SO_2) are known to be causative substances to form fine particles ($PM_{2.5}$), which are also deleterious to human health. The integrated system composed of selective catalytic reduction (SCR) and wet flue gas desulfurization (WFGD) have been widely applied in order to control NO_x and SO_2 emissions, resulting in high investment and operational costs, maintenance problems, and technical limitations. Recently, new technologies for the simultaneous removal of NO_x and SO_2 from the flue gas, such as absorption, advanced oxidation processes (AOPs), non-thermal plasma (NTP), and electron beam (EB), are investigated in order to replace current integrated systems. The proposed technologies are based on the oxidation of NO_x and SO_2 to HNO_3 and H_2SO_4 by using strong aqueous oxidants or oxidative radicals, the absorption of HNO_3 and H_2SO_4 into water at the gas-liquid interface, and the neutralization with additive reagents. In this paper, we summarize the technical improvements of each simultaneous abatement processes and the future prospect of technologies for demonstrating large-scaled applications.

Keywords: DeNOx, DeSOx, oxidation, absorption, process design

1. Introduction

In the combustion of fossil fuels by incinerators, marine vessels, vehicles, and thermal power plants, the various air pollutants, such as carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x), particulate matters (PM_{10}), and volatile organic compounds (VOCs), are released into the atmosphere. The consumption of fossil fuels in the worldwide has been increasing continuously since 2000, regardless of many efforts to reducing fossil fuel consumption. The consumption of fossil fuels in 2011 (7,653 Mton) was raised by approximately 31% compared to the consumption in 2000 (5,821 Mton)[1].

NO_x and SO_2 are the most serious pollutants because of their great global emission and a long range of transport in the atmosphere, making the emission no more a local air pollution problem. These pollutants are a major causative substance to acid rain, greenhouse effect, photochemical smog, and harmful effects on the nature environment as well as human health[2,3]. Furthermore, the fine particulate matter

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**Table 1. Oxidation and Absorption Reactions in Different Oxidant Absorbents**

Reagents/Ref.	Chemical reactions	No.
NaClO$_2$/[4]	$4NO + 3ClO_2^- + 2H_2O \rightarrow 4NO_3^- + 4H^+ + 3Cl^-$	(4)
	$2SO_2 + ClO_2^- + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ + Cl^-$	(5)
KMnO$_4$/[7]	$3NO + 2MnO_4^- + 2H_2O \rightarrow 3NO_3^- + 4H^+ + 2MnO_2$	(6)
	$3SO_2 + 2MnO_4^- + 2H_2O \rightarrow 3SO_4^{2-} + 4H^+ + 2MnO_2$	(7)
NaClO/[21]	$NO + ClO^- + H_2O \rightarrow NO_3^- + 2H^+ + Cl^-$	(8)
	$SO_2 + ClO^- + H_2O \rightarrow SO_4^{2-} + 2H^+ + Cl^-$	(9)
ClO$_2$/[22]	$5NO + 3ClO_2 + 4H_2O \rightarrow 5NO_3^- + 8H^+ + 3Cl^-$	(10)
	$5SO_2 + 2ClO_2 + 6H_2O \rightarrow 5SO_4^{2-} + 12H^+ + 2Cl^-$	(11)
Fenton reagents/[24,25]	$NO + 3HFeO_4^- + 4H_2O \rightarrow NO_3^- + 2OH^- + 1.5O_2 + 3Fe(OH)_3$	(12)
	$SO_2 + 3HFeO_4^- + 3.5H_2O \rightarrow SO_4^{2-} + OH^- + 1.75O_2 + 3Fe(OH)_3$	(13)

(PM$_{2.5}$), that are also deleterious air pollutants to human health, are formed via the photochemical transformations of NO$_x$ and SO$_2$ in the atmosphere[4].

The selective catalytic reduction (SCR) and wet flue gas desulfurization (WFGD) are well known as the commercialized processes for cleaning NO$_x$ and SO$_2$ from the flue gas. WFGD is a widely utilized in the most thermal power plant to control of SO$_2$ emission by the absorption processing with a calcium carbonate (CaCO$_3$). In WFGD process, over 95% of SO$_2$ gas can be treated as a following reaction step[5].

$$SO_2 + CaCO_3 + 2H_2O + 0.5O_2 \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \qquad (1)$$
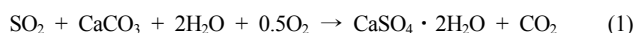
Typically, NO$_x$ gas, which is formed to N$_2$O, NO, N$_2$O$_3$, NO$_2$, N$_2$O$_4$, NO$_3$, and N$_2$O$_5$, represents two major formations (NO and NO$_2$), existing in the flue gas. NO gas is usually accounted for more than 90% of NO$_x$ in a typical flue gas[6]. In order to control NO$_x$ emission, the SCR technologies are generally employed in the thermal power plants, vehicles, and various industrial plants[7,8]. In the SCR process, ammonia (NH$_3$) are commonly used as a reductant to convert NO$_x$ into nitrogen (N$_2$). SCR is one of the effective technique for NO$_x$ emission control and it is able to cleaning more than 90% of NO$_x$ in the off-gas from the thermal power plant[9,10]. The reaction pathways for NO$_x$ reduction in the SCR process were summarized as below[11].

$$2NH_3 + 2NO + 0.5O_2 \rightarrow 2N_2 + 3H_2O \qquad (2)$$

$$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O \qquad (3)$$
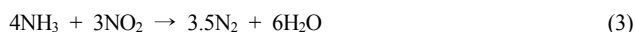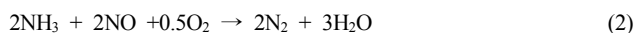
NO$_x$ and SO$_2$ gases are individually controlled step by step with the high removal efficiencies by an integrated system composed of SCR and WFGD. However, such system has drawbacks that includes requiring a large installation area, it being a complex system, and necessitating a huge investment[12,13]. In addition, 0.2-2.0% of SO$_2$ gas could be oxidized to SO$_3$, which reacts with CaO and NH$_3$ to form undesired

solid products, such as a calcium sulfate (CaSO$_4$) and an ammonium sulfate ((NH$_4$)$_2$SO$_4$), in the SCR process. Produced substances can easily form a scale film that accumulates in the interior of heat exchangers, pipes, and other equipment. Besides, solid by-products cover the active surface of noble catalysts in the SCR, that is leading to deactivation, clogging, and corrosion of catalysts[14]. For these reason, the NO$_x$ removal efficiency should be declined constantly during a continuous operation of integrated system.

Many studies have focused on the simultaneous denitrification (DeNO$_x$) and desulfurization (DeSO$_x$) in a single or hybrid compact system based on the technologies of absorption, non-thermal plasma (NTP), advanced oxidation processes (AOPs), and electron beam (EB) to apply the off-gas cleaning. The purpose of this article is to summarize the abatement technologies for simultaneous DeNO$_x$ and DeSO$_x$ from the flue gas and to provide the knowledge and technological pros and cons of each method.

2. Abatement Technologies for Simultaneous DeNOx and DeSOx

2.1. Absorption wet process

In the absorption wet process for the simultaneous DeNO$_x$ and DeSO$_x$, the solubility of gaseous pollutants in the water should be carefully considered to realize the great performance with a reasonable gas-liquid contact time and liquid-gas ratio (L/G ratio) for the industrial application. There are several types of absorbents, such as urea ((NH$_2$)$_2$CO)[15,16] and sodium hydroxide (NaOH)[17], were used in the conventional wet scrubbing process. The absorption using a common absorbent is quite help for reducing SO$_2$ emission, although it does not effective to removing NO$_x$ due to a low solubility of NO gas in water.

In order to improving the efficiency of NO$_x$ control, the strong aqueous oxidants including sodium chlorite (NaClO$_2$)[4,18-20], sodium hypochlorite (NaClO)[21], chlorine dioxide (ClO$_2$)[22], Fenton reagents [23,24], sodium persulfate (Na$_2$S$_2$O$_8$)[25], calcium hypochlorite (Ca(OCl)$_2$)

Table 2. Overview of Experimental Results in the Absorption Process

Ref.	Reactor type	Absorbents	Gas flow rate	Inlet concentrations	Removal efficiencies	Operating condition
[4]	Wet electrostatic precipitator	NaClO$_2$ (50 mmol/min)	1,000 L/min	NO (500 ppm) SO$_2$ (500 ppm)	NO (94%) SO$_2$ (100%)	Gas-liquid contact time : 1 s Liquid-gas ratio : 0.1 L/m^3 Initial solution pH : 6 Reaction temp : 25 ℃
[7]	Bubbling reactor	KMnO$_4$ (7 mM) Urea (5 wt%)	1 L/min	NO (650) SO$_2$ (2,900)	NO (53%) SO$_2$ (99%)	Gas-liquid contact time : 118 s Initial solution pH : 5.5 Reaction temp : 55 ℃
[16]	Wet scrubbing	NaClO$_2$ (1 wt%) Urea (5 wt%)	1 L/min	NO$_x$ (1,250 ppm) SO$_2$ (2,000 ppm)	NO$_x$ (93%) SO$_2$ (100%)	Gas-liquid contact time : 140 s Initial solution pH : 7 Reaction temp : 60 ℃
[17]	Wet scrubbing	NaOH (2 wt%)	3,300 L/min	NO (212 ppm) NO$_2$ (59 ppm) SO$_2$ (340 ppm)	NO (77%) NO$_2$ (88%) SO$_2$ (100%)	Gas-liquid contact time : 4 s Liquid-gas ratio : 1.2 L/m^3 Reaction temp : 35 ℃
[19]	Wetted wall column	NaClO$_2$ (0.1 M)	45 L/min	NO (850 ppm) SO$_2$ (640 ppm)	NO$_x$ (67%) SO$_2$ (100%)	Gas-liquid contact time : 5 s Liquid-gas ratio : 7.7 L/m^3 Initial solution pH : 4.5 Reaction temp : 30 ℃
[20]	Wet scrubbing	NaClO$_2$ (0.2 M)	5,000 L/min	NO (250 ppm) SO$_2$ (100 ppm)	NO$_x$ (81%) SO$_2$ (100%)	Gas-liquid contact time : 5 s Liquid-gas ratio : 6.5 L/m^3 Initial solution pH : 6 Reaction temp : 35 ℃
[24]	Bubbling reactor	K$_2$FeO$_4$ (0.25 mM)	1 L/min	NO (700 ppm) SO$_2$ (2,000 ppm)	NO (65%) SO$_2$ (100%)	Gas-liquid contact time : 15 s Initial solution pH : 8 Reaction temp : 47 ℃
[25]	Bubbling reactor	Na$_2$S$_2$O$_8$ (0.1 M)	5 L/min	NO (1,000 ppm) SO$_2$ (1,550 ppm)	NO (83%) SO$_2$ (100%)	Gas-liquid contact time : 12 s Initial solution pH : 7 Reaction temp : 50 ℃
[27]	Bubbling reactor	HA-Na (50 mM)	3 L/min	NO (200 ppm) NO$_2$ (300 ppm) SO$_2$ (2,000 ppm)	NO (68%) NO$_2$ (98%) SO$_2$ (100%)	Gas-liquid contact time : 11 s Initial solution pH : 12 Reaction temp : 50 ℃
[29]	Wet scrubbing	NaClO$_2$ (8 mM) CaCO$_3$ (10 wt%)	2 L/min	NO (200 ppm) SO$_2$ (1,500 ppm)	NOx (50%) SO$_2$ (100%)	Gas-liquid contact time : 2736 s Liquid-gas ratio : 4.2 L/m^3 Reaction temp : 55 ℃
[30]	Bubbling reactor	NaClO$_2$ (0.7 wt%) HA-Na (4 wt%)	2.6 L/min	NO (300 ppm) SO$_2$ (2,000 ppm)	NO (98%) SO$_2$ (100%)	Gas-liquid contact time : 13 s Initial solution pH : 8 Reaction temp : 60 ℃
[31]	Bubbling reactor	NaClO$_2$ (1.5 M) NaBr (0.05 M)	3 L/min	NO (550 ppm) SO$_2$ (3,000 ppm)	NO (91%) SO$_2$ (100%)	Gas-liquid contact time : 5 s Initial solution pH : 7 Reaction temp : 140 ℃
[32]	Bubbling reactor	NaClO$_2$ (0.1 mM) NaClO (0.4 mM)	3 L/min	NO (500 ppm) SO$_2$ (2,000 ppm)	NO (85%) SO$_2$ (100%)	Gas-liquid contact time : 20 s Initial solution pH : 5.5 Reaction temp : 50 ℃
[33]	Bubbling reactor	NaClO$_2$ (0.1 M) H$_2$O$_2$ (4 M)	3 L/min	NO (500 ppm) SO$_2$ (4,000 ppm)	NO (87%) SO$_2$ (100%)	Gas-liquid contact time : 6 s Initial solution pH : 4.5 Reaction temp : 150 ℃
[34]	Bubbling reactor	NaClO (32 mM) NH$_4$OH (32 mM)	2 L/min	NO (1,020 ppm) SO$_2$ (1,807 ppm)	NO (93%) SO$_2$ (99%)	Initial solution pH : 5-6 Reaction temp : 40-50 ℃
[35]	Bubbling reactor	Fe$_2$SO$_4$ (2.8 mM) H$_2$O$_2$ (11 wt%)	0.3 L/min	NO (420 ppm) SO$_2$ (2,400 ppm)	NO (90%) SO$_2$ (100%)	Gas-liquid contact time : 200 s Initial solution pH : 3 Reaction temp : 55 ℃
[36]	Wet scrubbing	Fe(Ⅱ)EDTA (50 mM) (NH$_4$)$_2$SO$_4$ (2.5 M)	833 L/min	NO (400 ppm) SO$_2$ (1,200 ppm)	NO (52%) SO$_2$ (100%)	Gas-liquid contact time : 8 s Liquid-gas ratio : 12 L/m^3 Initial solution pH : 5.5 Reaction temp : 80-160 ℃
[37]	Bubbling reactor	Fe$_2$SO$_4$ (0.3 M) NaClO (0.3 M) H$_2$O$_2$ (8 M)	2 L/min	NO (500 ppm) SO$_2$ (2,000 ppm)	NO (81%) SO$_2$ (100%)	Gas-liquid contact time : 7 s Initial solution pH : 2 Reaction temp : 130 ℃

Absorption process

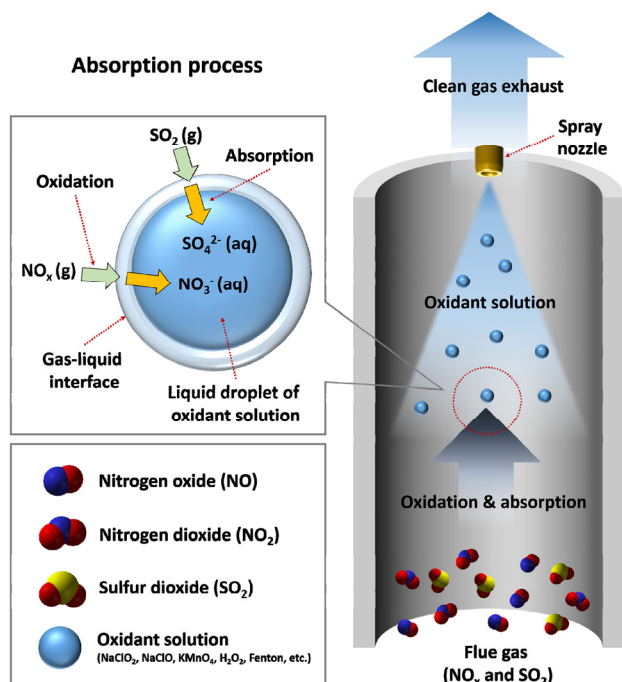**Figure 1. Schematic diagram of the absorption process.**

[26], sodium humate (HA-Na)[27], hydrogen peroxide (H_2O_2)[28], and their complex absorbents[29-38] have been used in the previous researches. Table 1 shows the global reaction pathways for the oxidation and absorption of NO and SO_2 by the representative oxidant absorbents[4,7,21,22,24,25]. NO gas is oxidized to the high-ordered nitrogen species (NO_2, NO_3, HNO_3, and N_2O_5) via the spontaneous oxidation by aqueous oxidants at the gas-liquid interface. Converted high-ordered N species, which characterizes a higher solubility compared to NO, could be favorably absorbed into water to form nitrite (NO_2^-) or nitrate (NO_3^-). SO_2 gas is also converted to form sulfate (SO_4^{2-}) with a higher reaction rate than that of NO_x. Figure 1 exhibits a typical absorption process for simultaneous $DeNO_x$ and $DeSO_x$ in the wet scrubbing towers.

The gas-liquid interfacial area and absorbent compositions play the most important role to reach high removal efficiencies of flue gas. Current researches for absorption technique have focus on the proposing a new complex absorbent in the conventional wet process or demonstrating a novel type wet process to increasing gas-liquid interfacial area.

The experiment results in the different previous approaches are summarized in Table 2. $NaClO_2$ that is the demonstrative oxidant, and mostly applied due to its good solubility in water, easy to use, and high oxidation efficiency. Lee et al.[19] have carried out the simultaneous $DeNO_x$ and $DeSO_x$ in the wetted-wall column using only $NaClO_2$ solution. The efficiencies of NO_x and SO_2 were identified to be 67% and 100%, respectively, with the gas-liquid contact time of 5 s and L/G ratio of 7.7 L/m^3. Additional absorbents such as urea[16], HA-Na[30], NaBr[31], $NaClO$[32], and H_2O_2[33] mixed with $NaClO_2$ solution contributes to improving NO_x removal efficiency. Fang et al.[16] confirmed 93% of NO_x removal in a countercurrent packed column using $NaClO_2$

(1 wt%) solution mixed with urea (5 wt%). Moreover, Hao et al.[30] observed 98% of NO_x removal by utilizing a complex absorbent composed of $NaClO_2$ (0.7 wt%) and HA-Na (4 wt%).

A novel absorption processes in the pilot scale have been facilitated to enhancing removal efficiencies through the high gas-liquid interfacial area. Park et al.[4] proposed a wet electrostatic precipitator installed an ultrasonic humidifier. In this system, there is two process steps including flue gas absorption by a $NaClO_2$ solution mist supplied from the ultrasonic humidifier and the electrostatic precipitation of solution mist. Ultrasonic humidifier can make a smaller liquid droplet (liquid droplet size: 1-5 μm) than that of a general spraying nozzle (liquid droplet size: 428-1085 μm)[18,39]. Thus, the gas-liquid interfacial area could be maximized using the ultrasonic humidifier that leads to reducing the gas-liquid contact time (1 s) and L/G ratio (0.1 L/m^3) with high efficiencies compared to the conventional wet scrubbing. Pourmohammadbagher et al.[20] demonstrated the large scale swirl wet system (gas flow rate : 300 Nm^3/h) for reducing the liquid droplet size through an interior axial plate and high speed electric motor (rotation speed: 1,800 rpm). $NaClO_2$ solution sprays to internal fan, where the rotor plate shears the sprayed solution into smaller liquid droplets. The turbulence flow from internal fan also donates to form small liquid droplets. Such wet scrubbing design can be applied to realize industrial application with the high efficiencies.

2.2. UV advanced oxidation processes (UV-AOPs)

Recently, there are feasibility studies for the simultaneous $DeNO_x$ and $DeSO_x$ by using ultraviolet advanced oxidation processes (UV-AOPs)[2,40-42]. This method is well known as one of the advanced oxidation processes (AOPs) that is able to produce strong oxidative radicals (O·, OH·, and HO_2·) from H_2O_2 via UV decomposition as follows.

$$H_2O_2 + hv \rightarrow 2OH \cdot \tag{14}$$

Generally, AOPs including UV/H_2O_2 process have been widely applied in the field of wastewater purification due to their strong oxidation ability and environmental friendly[42].

Figure 2 shows the UV-AOPs for the simultaneous $DeNO_x$ and $DeSO_x$. An UV lamp is installed at the center of bubbling reactor filled H_2O_2 solution and OH radicals are produced from H_2O_2 via UV light irradiation. Introduced flue gas are oxidized and absorbed systemically by reactions with produced OH radicals.

The experimental results using UV-AOPs for the simultaneous $DeNO_x$ and $DeSO_x$ are summarized in Table 3. Liu et al.[42] applied the UV lamp of 254 nm wavelength in a bubbling reactor using H_2O_2 solution to conduct feasibility study for the flue gas treatment. The efficiencies of NO and SO_2 were identified to be 73% and 100%, respectively, in a laboratory bench scale. Liu et al.[40] proposed H_2O_2/NaOH complex solution utilized from the UV-AOPs and they confirmed that NO removal was considerably improved when 10 mM of NaOH added into H_2O_2 solution. Hao et al.[41] proposed a new type of UV/H_2O_2 AOPs catalyzing vaporized H_2O_2 solution. In this process,

Table 3. Overview of Experimental Results in the UV Advanced Oxidation Process

Ref.	Reactor type	Absorbents	Energy density of UV light	Gas flow rate	Inlet concentrations	Removal efficiencies	Operating condition
[2]	Vacuum UV irradiation reactor	-	0.036 W/mL	0.5 L/min	NO_x (350 ppm) SO_2 (800 ppm)	NO_x (95%) SO_2 (90%)	Gas residence time : 241 s $O_2/CO_2/H_2O$ contents : 8%/10%/8% Reaction temp : 60 ℃ UV wavelength : 185/254 nm
[40]	Bubbling reactor combined with UV	NaOH (10 mM) H_2O_2 (1.5 M)	0.012 W/mL	1.2 L/min	NO (400 ppm) SO_2 (1,000 ppm)	NO (90%) SO_2 (100%)	Gas-liquid contact time : < 30 s Solution temp : 25 ℃ UV wavelength : 254 nm
[41]	Bubbling reactor combined with UV	H_2O_2 (15 wt%)	0.064 W/mL	4 L/min	NO (500 ppm) SO_2 (2,500 ppm)	NO (88%) SO_2 (100%)	Gas-liquid contact time : 4.2 s Initial solution pH : 6 Reaction temp : 90 ℃ UV wavelength : 254 nm
[42]	Bubbling reactor combined with UV	H_2O_2 (2.5 M)	0.06 W/mL	0.5 L/min	NO (414 ppm) SO_2 (1,013 ppm)	NO (73%) SO_2 (100%)	Gas-liquid contact time : < 72 s Initial solution pH : 3.2 Reaction temp : 25 ℃ UV wavelength : 254 nm
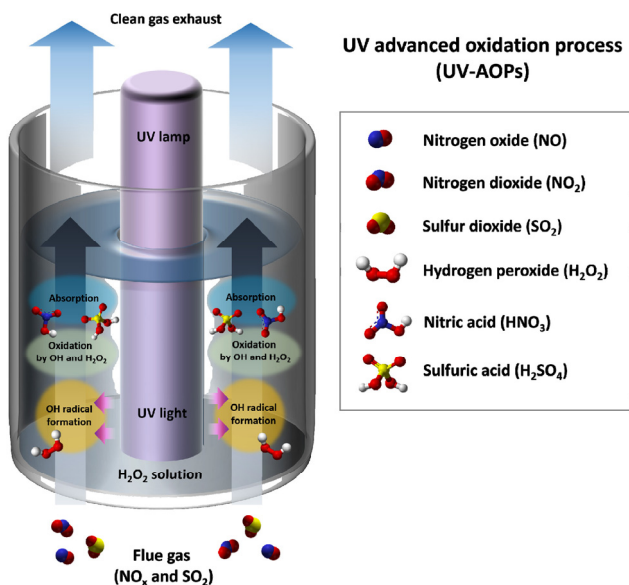
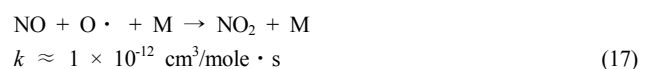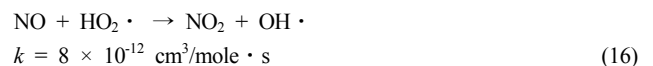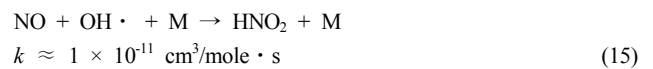**Figure 2. Schematic diagram of the UV advanced oxidation process.**

vaporized H_2O_2 solution was introduced into the UV irradiation reactor with the gaseous pollutants. It shows that the gas residence time in the UV irradiation reactor (4.2 s) was remarkably reduced with a suitable efficiencies compared with other UV-AOPs. However, this kind of UV/H_2O_2 removal process has been demonstrated only in a small laboratory scale and it is still not developed so far.

2.3. Non-thermal plasma process (NTP)

Technology based on non-thermal plasma (NTP) is one of the promising methods for air pollution control. Electrical discharges, which known as dielectric barrier discharge (DBD), corona discharge (CD), and pulsed corona discharge (PCD), are developing as a successful process to converting gaseous pollutants into inert or treatable substances.

NTP is a partially ionized gas composed of ions, atoms, and chemically active molecules, as well as a highly energetic electron (electron energy: 5-10 eV)[43]. Energetic electrons in the plasma region can generate free radicals (O ·, OH ·, HO$_2$ ·) through the direct electron impact on O_2 or H_2O molecules. Produced radicals act as a reactive source to oxidize NO_x and SO_2 into HNO_3 and H_2SO_4 at atmospheric pressure and ambient temperature. Oxidation reactions involving radicals is terminated in a very short time (usually less than 10^{-3} s)[43]. Therefore, NTP process have great advantage to realize a compact system for the simultaneous DeNO$_x$ and DeSO$_x$ compared to the conventional ones.

The process of NO_x removal in NTP system that is divided into two steps including the oxidation of NO to NO_2 or HNO_3, and absorption and neutralization of oxidized species. The oxidation reactions of NO in the plasma region are considered as below[44].

$$NO + OH \cdot + M \rightarrow HNO_2 + M$$
$$k \approx 1 \times 10^{-11} \text{ cm}^3/\text{mole} \cdot \text{s} \tag{15}$$

$$NO + HO_2 \cdot \rightarrow NO_2 + OH \cdot$$
$$k = 8 \times 10^{-12} \text{ cm}^3/\text{mole} \cdot \text{s} \tag{16}$$

$$NO + O \cdot + M \rightarrow NO_2 + M$$
$$k \approx 1 \times 10^{-12} \text{ cm}^3/\text{mole} \cdot \text{s} \tag{17}$$

Furthermore, NO_2 is converted to form of HNO_3 via the oxidation reactions by OH radicals as follows.

$$NO_2 + OH \cdot \rightarrow HNO_3$$
$$k = 1.2 \times 10^{-11} \text{ cm}^3/\text{mole} \cdot \text{s} \tag{18}$$

The oxidations by O ·, OH ·, and HO$_2$ · play the most important role for NO_x removal in NTP process due to their fast reaction rates. The reaction pathways of SO_2 oxidation by free radicals are listed below.

Table 4. Overview of Experimental Results in the Non-thermal Plasma Process

Ref.	Reactor type	Gas flow rate	Gas residence time	Additives	Energy density	Inlet concentrations	Removal efficiencies
[8]	Pulsed corona discharge	-	6 s	H_2O (1%) N_2 balance	53 kV 300 Hz	NO (479 ppm) SO_2 (1,040 ppm)	NO (80%) SO_2 (43%)
[45]	Pulsed corona discharge	150 L/min	4 s	H_2O (4%) Fly ash (2.58 g/m^3) Air balance	65 J/L	NO (330 ppm) SO_2 (333 ppm)	NO (55.8%) SO_2 (91.8%)
[46]	Pulsed corona discharge	4 L/min	1.2 s	H_2O Air balance	39 J/L	NO (200 ppm) NO_2 (33 ppm) SO_2 (200 ppm)	NO_x (64%) SO_2 (>95%)
[47]	Microwave discharge + electron beam	10 L/min	-	H_2O (12-18%) CO_2 (5,000 ppm) Air balance	7,176 J/L	NO_x (900 ppm) SO_2 (1,350 ppm)	NO_x (81%) SO_2 (91%)
[48]	Pulsed corona discharge + wet scrubbing	72 L/min	4.4 s	$Ca(OH)_2$ solution Air balance	45.8 J/L	NO (180 ppm) SO_2 (1,013 ppm)	NO (40%) SO_2 (75%)
[49]	Corona discharge + wet scrubbing	6 L/min	5 s	$(NH_4)_2SO_4$ with $S_2O_3^{2-}$ O_2 (6%) CO_2 (12%) H_2O (3%) N_2 balance	80 J/L	NO (120 ppm) SO_2 (525 ppm)	NO_x (71%) SO_2 (100%)
[50]	Dielectric barrier discharge + catalysts	5 L/min	1 s	TiO_2 catalyst Air balance	11 kV 300 Hz	NO (570 ppm) SO_2 (420 ppm)	NO (65%) SO_2 (75%)
[51]	Dielectric barrier discharge + catalysts	5 L/min	1 s	TiO_2 catalyst Air balance	12 kV 600 Hz	NO (300 ppm) SO_2 (260 ppm)	NO (85%) SO_2 (100%)
[52]	Dielectric barrier discharge + catalysts	5 L/min	2 s	TiO_2 catalyst Air balance	15 kV 900 Hz	NO (400 ppm) SO_2 (400 ppm)	NO (73%) SO_2 (100%)

$$SO_2 + OH \cdot\ + M \rightarrow OHSO_2 + M$$
$$k = 8 \times 10^{-12}\ cm^3/mole \cdot s \tag{19}$$

$$SO_2 + O \cdot\ + M \rightarrow SO_3 + M$$
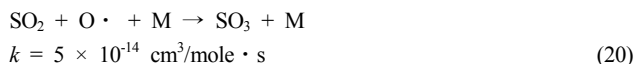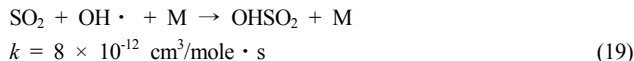$$k = 5 \times 10^{-14}\ cm^3/mole \cdot s \tag{20}$$

Table 4 tabulates the overview of experiment results of NTP only and NTP combined with wet scrubbing or catalysts[45-52]. In the previous works, PCD and DBD are usually utilized because the electron energy can be increased by the dielectric materials or pulse waveform compared to CD. Typically, H_2O and air are used as a plasma forming gas to producing O and OH radicals. In the case of NTP only, the removal of NO_x and SO_2 were insufficient, while the gas residence time was very short (1-4 s). However, the removal efficiencies could be enhanced through the integrated system of NTP and wet scrubbing or catalysts. High energy consumption is necessary to reach high removal efficiencies in NTP only. In order to reducing energy consumption, the hybrid system based on NTP technology could be an advanced process to demonstrating industrial application. The ozone oxidation process was suggested to approach a feasible method for the simultaneous DeNO$_x$ and DeSO$_x$ with a low energy consumption.

Figure 3 shows the typical ozone oxidation process composed of DBD ozonizer and wet scrubbing. DBD offers a high electron temperature ranging 10^4 to 10^5 K and it is the effective method for the ozone generation from O_2[53]. In the DBD ozonizer, O_2 gas is excited to O radicals and these are converted to O_3, known to be the main reactions
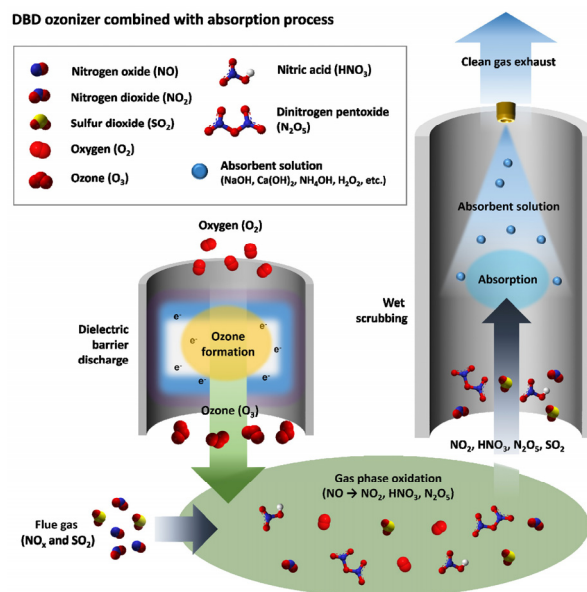
Figure 3. Schematic diagram of the DBD ozonizer combined with absorption process.

of ozone formation. "e*" and "e" represent high and low energy electrons, respectively[54].

$$e^* + O_2 \rightarrow 2O \cdot\ + e \tag{21}$$

$$O \cdot\ + O_2 + M \rightarrow O_3^* + M \rightarrow O_3 + M \tag{22}$$
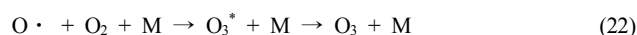
Table 5. Overview of Experimental Results in the DBD Ozonizer Combined with Absorption Process

Ref.	Reactor type	Reagents	Gas flow rate	Inlet concentrations	Removal efficiencies	Operating condition
[3]	DBD ozonizer/ Bubbling reactor	Ozone (900 ppm) Pyrolusite slurry (40 g/L)	15 L/min	NO (750 ppm) SO_2 (2,000 ppm)	NO_x (82%) SO_2 (90%)	Gas residence time : 20 s Reaction temp : 25 ℃ O_3/NO molar ratio : 1.2 Composition of pyrolusite : MnO_2/Fe/Ca/K/Mg/Pb/Ni/Co (27.2%/3.4%/3.5%/1.7%/0.6%/0.1%/0.03%/0.02%)
[5]	DBD ozonizer/ Bubbling reactor	Ozone (200 ppm) NaOH (40 mM)	17 L/min	NO (200 ppm) SO_2 (2000 ppm)	NO_x (90%) SO_2 (100%)	Gas residence time : 7 s Reaction temp : 150 ℃ Initial solution pH : < 11 O_3/NO molar ratio : 1
[9]	DBD ozonizer/ Wet scrubbing	Ozone (350 ppm) $Ca(OH)_2$ (1 wt%)	1 L/min	NO (215 ppm) SO_2 (220 ppm)	NO_x (97%) SO_2 (100%)	Gas residence time in gas phase reactor : 0.1 s Gas-liquid contact time : 9.7 s Liquid-gas ratio : 500 L/m³ Reaction temp : 150 ℃ O_3/NO molar ratio : 1.6
[54]	DBD ozonizer/ Wet atomizing reactor	Ozone (630 ppm) H_2O_2 (35 mmol/min)	150 L/min	NO (350 ppm) SO_2 (800 ppm)	NO_x (89%) SO_2 (100%)	Gas residence time in gas phase reactor : 0.1 s Gas-liquid contact time : 3 s Liquid-gas ratio : 0.33 L/m³ Reaction temp : 25 ℃ Initial solution pH : 7 O_3/NO molar ratio : 1.8
[55]	DBD ozonizer/ Bubbling reactor	Ozone (200 ppm) NH_4OH (0.3 vol%)	16 L/min	NO (200 ppm) SO_2 (2000 ppm)	NO_x (90%) SO_2 (99%)	Gas residence time : 7 s Reaction temp : 150 ℃ Initial solution pH : 10 O_3/NO molar ratio : 1
[56]	DBD ozonizer/ Wet scrubbing	Ozone (200 ppm) MgO slurry (25 mM)	8 L/min	NO (200 ppm) SO_2 (700 ppm)	NO_x (76%) SO_2 (98%)	Gas residence time : 26 s Liquid-gas ratio : 4,375 L/m³ Reaction temp : 95 ℃ Initial solution pH : > 4 O_3/NO molar ratio : 1

Gaseous NO are oxidized to NO_2 and NO_3 through the gas phase oxidation by O_3 with an extremely high reaction rate[44,54].

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$k = 5.3 \times 10^{-14} \text{ cm}^3/\text{mole} \cdot \text{s} \qquad (23)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$k = 1.5 \times 10^{-16} \text{ cm}^3/\text{mole} \cdot \text{s} \qquad (24)$$

When the O_3/NO molar ratio is higher than 1, oxidized NO_2 and NO_3 could be further oxidized into HNO_3 and N_2O_5, which solubility in water is higher than that of NO and NO_2.

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (25)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (26)$$

In contrast, the reaction rate of SO_2 oxidation is lower than NO oxidation due to the high energy barrier of reaction (27).

$$SO_2 + O_3 \rightarrow SO_3 + O_2$$
$$k = 1.8 \times 10^{-24} \text{ cm}^3/\text{mole} \cdot \text{s} \qquad (27)$$

It means that SO_2 removal in the O_3 oxidation process does not effective, whereas SO_2 emission can be easily controlled by the conventional wet scrubbing method. In the typical O_3 oxidation process, DBD ozonizer is usually combined with the wet scrubbing or bubbling reactor.

The experimental results of O_3 oxidation process are summarized in Table 5[3,5,9,54-56]. The high efficiencies of NO_x and SO_2 were achieved at the reaction time shorter than 10 s and the O_3/NO molar ratio over than 1[5,9,54,55]. The treatment of NO_x and SO_2 were confirmed to be 97% and 100%, respectively, using $Ca(OH)_2$ wet scrubbing tower, at the gas phase oxidation time of 0.1 s, the gas-liquid contact time of 9.7 s, and the O_3/NO molar ratio of 1.6[9]. Especially, Yoon et al.[54] demonstrated the DBD ozonizer combined with wet atomizing system and they recognized that the high efficiencies were reached at a relatively short reaction time (3.1 s) and low liquid-gas ratio (0.33 L/m³) compared to other ones.

The gaseous NO_x and SO_2 are directly decomposed in the NTP reactor that has technological limitations of an extremely high power consumption (70-780 eV/mole) when the chemical bonds of air pollutants are directly broken[54]. Therefore, NTP combined with wet scrubbing system such as DBD ozonizer/wet scrubbing is more acceptable to facilitating industrial scale application than NTP only. Though, the technological upgrades for DBD ozonizer including durability of

Table 6. Overview of Experimental Results in the Electron Beam Flue Gas Treatment Process

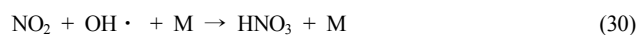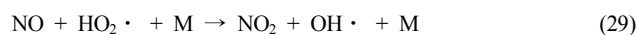| Location/Year/Ref.	System	Gas flow rate /Power consumption	Initial concentrations	Additives	Gas composition	By-products	Removal efficiencies
Coal-fired power plant, Shin-Nagoya EPS, Japan/1995/[59]	EB + ESP + Bag filter	12,000 Nm³/h /9 Wh/Nm³	NO$_x$ (160-240 ppm) SO$_2$ (650-950 ppm)	NH$_3$	N$_2$ (73%) O$_2$ (10.5%) CO$_2$ (12.5%) H$_2$O (5.5%) Dust (30 mg/m³)	NH$_4$NO$_3$ (7%) (NH$_4$)$_2$SO$_4$ (91%) Fly ash (2%)	NO$_x$ (80-95%) SO$_2$ (94-99%)
Coal-fired power plant, Kaweczyn EPS, Poland /1995/[60-62]	EB + Bag filter	20,000 Nm³/h /5 Wh/Nm³	NO$_x$ (135 ppm) SO$_2$ (1,000 ppm)	NH$_3$ (1,495-2,670 ppm)	N$_2$ (70-80%) O$_2$ (8-10%) CO$_2$ (10-12%) H$_2$O (30-50 g/m³) Dust (20-250 mg/m³)	NH$_4$NO$_3$ (15%) (NH$_4$)$_2$SO$_4$ (76%) Fly ash (9%)	NO$_x$ (70-88%) SO$_2$ (75-95%)
Heavy oil-fired boiler, Fujisawa EPS, Japan /1996/[63]	CD + EB + ESP + Bag filter	1,200 Nm³/h /12.6 Wh/Nm³	NO$_x$ (60 ppm) SO$_2$ (230 ppm)	NH$_3$ (300 ppm)	-	-	NO$_x$ (65-85%) SO$_2$ (92-98%)
Coal-fired power plant, Chendu EPS, China /2000/[64]	EB + ESP	300,000 Nm³/h /2.1 Wh/Nm³	NO$_x$ (400 ppm) SO$_2$ (1,800 ppm)	NH$_3$	Dust (200 mg/m³)	NH$_4$NO$_3$ (0.8%) (NH$_4$)$_2$SO$_4$ (91.9%) Fly ash (7.3%)	NO$_x$ (18%) SO$_2$ (80%)
Coal-fired power plant, Sviloza EPS, Bulgaria /2011/[65]	EB + ESP	600,000 Nm³/h /2.3 Wh/Nm³	NO$_x$ (731 ppm) SO$_2$ (1,575 ppm)	NH$_3$ (2,822 ppm)	N$_2$ (70.6%) O$_2$ (7.8%) CO$_2$ (9.7%) H$_2$O (11.6%) Dust (375 mg/m³)	NH$_4$NO$_3$ (10.7%) (NH$_4$)$_2$SO$_4$ (85.1%) Fly ash (4.2%)	NO$_x$ (40%) SO$_2$ (90%)
Heavy oil-fired boiler, Saudi Aramco's refinery plant, Saudi Arabia/2016/[66]	EB + bag filter + cyclone	620-920 Nm³/h /10 Wh/Nm³	NO$_x$ (124-136 ppm) SO$_2$ (1,320-1,420 ppm)	NH$_3$ (2,488-2,678 ppm)	N$_2$ (73.3%) O$_2$ (6.6%) CO$_2$ (9.2%) H$_2$O (10%) C$_x$H$_y$ (0.8%) CO (10 ppm)	NH$_4$NO$_3$ (< 1%) (NH$_4$)$_2$SO$_4$ (99%)	NO$_x$ (80%) SO$_2$ (99%)
Heavy oil-fired boiler, TUPRAS's Refinery plant, Turkey/2016/[67]	EB	1,300 Nm³/h /7.7 Wh/Nm³	NO$_x$ (420 ppm) SO$_2$ (4,600 ppm)	NH$_3$ (9,139 ppm)	-	NH$_4$NO$_3$ (< 1%) (NH$_4$)$_2$SO$_4$ (45-73%) (NH$_4$)$_3$PO$_4$ (9-31%)	NO$_x$ (81%) SO$_2$ (99%)
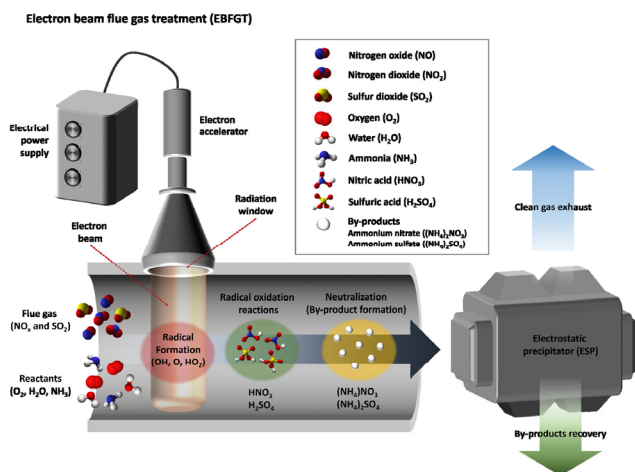
Figure 4. Schematic diagram of the electron beam flue gas treatment process.

dielectric material, steady production of O$_3$, design of efficient power supply, and configuration for low power dissipation, are still required to demonstrating large-scaled O$_3$ oxidation process.

2.4. Electron beam flue gas treatment processes (EBFGT)

The electron beam flue gas treatment (EBFGT) is a great promising technology that is consistently developing within the field of simultaneous DeNO$_x$ and DeSO$_x$ in the industrial application. Figure 4 presents the EBFGT process that commonly comprises the water cooling system to decreasing exhaust gas temperature, electron accelerators, electron beam (EB) irradiation chamber, and electrostatic precipitator (ESP) or bag filter. Flue gas containing air and water vapor is irradiated with the EB and the oxidative radicals of OH·, HO$_2$·, and O(^{3}P) are generating from the radiolysis of O$_2$ and H$_2$O molecules. NO$_x$ and SO$_2$ are oxidized to HNO$_3$ and H$_2$SO$_4$ via radical oxidation reactions as below[57,58].

$$NO + O(^3P) + M \rightarrow NO_2 + M \tag{28}$$

$$NO + HO_2\cdot + M \rightarrow NO_2 + OH\cdot + M \tag{29}$$

$$NO_2 + OH\cdot + M \rightarrow HNO_3 + M \tag{30}$$

$$SO_2 + OH\cdot + M \rightarrow HSO_3 + M \tag{31}$$

Table 7. Contents of Heavy Metals in the By-products in Comparison to Fertilizer Limits

Heavy metal	Content in byproduct (mg/kg)		Fertilizer content limits (mg/kg)		
	Bag filter	ESP	US EPA CFR40 Part. 503	Canadian fertilizer act	Polish standard
As	< 0.02	0.24	41	75	50
Cd	< 0.01	0.09	39	20	50
Cr	0.43	1.61	-	-	-
Co	0.03	0.03	-	150	-
Pb	1.01	0.54	300	500	140
Hg	< 0.03	1.41	17	5	2
Ni	63.5	22.80	420	180	-
Zn	18.3	1476	2,800	1,350	-

Table 8. Costs of flue gas treatment processes for retrofit 120 MW power plant

Emission control method	Investment cost (USD/kW (e))	Annual operational cost (USD/MW (e))
Wet flue gas desulfurization (WFGD)	120	3,000
Selective catalytic reduction (SCR)	110	4,600
WFGD + SCR	230	7,600
EBFGT	160	7,350

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{32}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{33}$$

NH_3 gas or NH_4OH is also injected together with flue gas before EB irradiation chamber and reacts with produced HNO_3 and H_2SO_4 under EB irradiation to form the final solid phase by-products of ammonium nitrate (NH_4NO_3) and ammonium sulfate (($NH_4)_2SO_4$).

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{34}$$

$$SO_2 + 2NH_3 \rightarrow (NH_3)_2SO_2 \tag{35}$$

$$(NH_3)_2SO_2 + 0.5O_2 + H_2O \rightarrow (NH_4)_2SO_4 \tag{36}$$
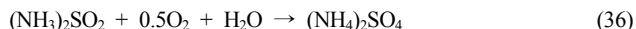
By-products, which can be used as a good quality of fertilizer, is finally collected in the ESP or bag filter after EB irradiation chamber.

Table 6 summarizes the pilot and large scale demonstration of EBFGT for the simultaneous DeNO$_x$ and DeSO$_x$[59-67]. The EBFGT process was first investigated by joint research of the Japan Atomic Energy Research Institute (JAERI, Japan) and Ebara Co., Japan in the early 1980s. The technology has been developed from the laboratory scale to large scale through innovative R&D projects in Japan, United States, Germany, Bulgaria, China, Poland, and South Korea. The JAERI, the Institute of Nuclear Chemistry and Technology (ICHTJ, Poland), and the Institute of Atomic Energy (IAE, Poland) cooperated with Ebara Co., Japan and EB Tech Co. Ltd., South Korea have demonstrated the final engineering technology for industrial applications in Nagoya, Japan[59], Kaweczyn, Poland[60-62], and Siloza, Bulgaria [65]. Through the pilot system testing, the new idea for engineering

solutions were examined: double-longitudinal gas irradiation, NH$_3$ injection system (steam or ammonia water injection), and others. The highest elimination of NO$_x$ and SO$_2$ were reached to be 80-99% and the by-products of (NH$_4$)$_2$SO$_4$ (76-92%), NH$_4$NO$_3$ (0.8-15%), and fly ash (2-9%) were obtained from the by-products collected in the ESP.

Recently, the pilot scaled demonstration was conducted in the cooperation of ICHTJ (Poland), Saudi Aramco (Saudi Arabia), and EB Tech Co. Ltd. (South Korea) at the Saudi Aramco's Jeddah Refinery Plant, Saudi Arabia[66]. The unique mobile EB system manufactured by EB Tech Co. Ltd was installed at the heavy oil fired boiler of the Jeddah Refinery. The schematic diagram and picture of the mobile EBFGT process installed in Jeddah, Saudi Arabia is presented in Fig. 5. The efficiencies achieved 99% for SO$_2$ and 80% for NO$_x$ under the optimal conditions (NH$_3$ stoichiometry of 0.9, gas humidity of 10.3 vol%, and absorbed energy dose of 12 kGy). Specially, the by-products were acquired as a high quality grade of fertilizer, which can be used as a substrate for NPK fertilizer blend. Table 7 shows the comparison of heavy metal contents in the produced by-products with the standard in the United States, Canada, and Poland. The new type of EBFGT called to VGS® (VIVIRAD gas scrubber) is introduced that allows simultaneous treatment of flue gas and recovery of solid by-products without ESP or bag filter[67]. This distinctive EBFGT was implemented in 2011 at the Saraykoy Nuclear Research and Training Center (SANAEM, Turkey) collaborated with the Turkish Petroleum Refinery Co. (TUPRAS, Turkey). The VGS® EBFGT comprises three parts that includes the upper part for flue gas injection and EB irradiation, the center of reactor for chemical reactions by NH$_3$ and water fog, and the lower part for separation of liquid and gas phase by gravity. High efficiencies of NO$_x$ and SO$_2$ were 81% and 99%, respectively, under the optimal conditions (EB voltage of 500 keV, EB current of 8 mA, NH$_3$

(a)

(b)
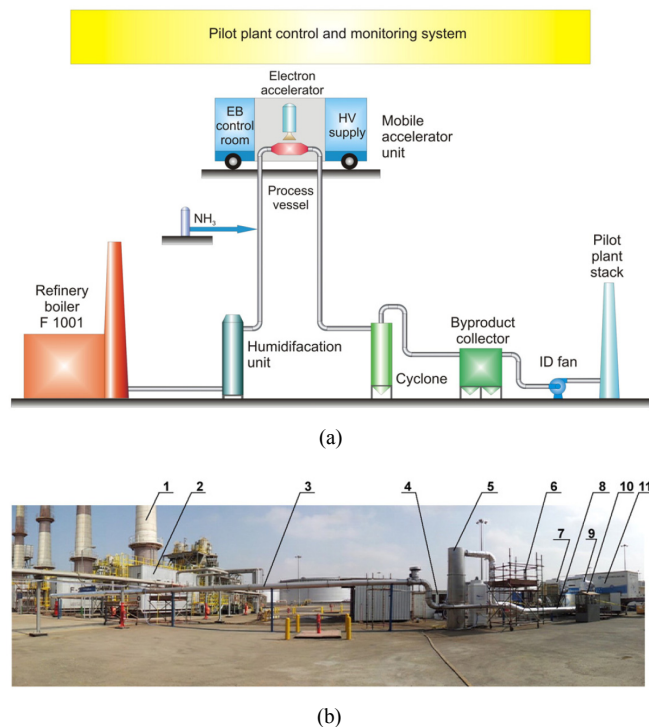
Figure 5. Layout (a) and picture (b) of the EBFGT pilot system demonstrated in Saudi Arabia. (1) stack of F 1001 boiler, (2) boiler F 1001, (3) flue gas duct, (4) pilot plant control room, (5) gas conditioning column, (6) pilot plant stack, (7) cartridge bag filter, (8) thermal insulated duct, (9) cyclone, (10) ammonia dosing unit, (11) mobile accelerator unit[66].

stoichiometry of 0.94, and water inlet flow of 260 L/h). The main compositions of by-products were obtained to be $(NH_4)_2SO_4$ of 45-73% and $(NH_4)_3PO_4$ of 9-31% in dry basis.

EBFGT is a very competitive in comparison with the other process to commercialize the industrial scale for the simultaneous cleaning of flue gas. EBFGT allows the effective treatment of flue gas and the production of high quality by-products as a fertilizer. In addition, EBFGT offers economic and technical point of view compared with conventional ones. The comparison of investment and operating costs between EBFGT and current integrated system for 120 MW power plant is listed in Table 8[68].

3. Summary

The proposed technology was focused on the optimizing and developing new and current processes that simultaneously remove NO_x and SO_2 exhausted from coal-fired power plant, fossil fuel combustor and diesel engine. There are two approaches to obtain a successful demonstration for the simultaneous cleaning of flue gas. One is to improving a typical absorption process by utilizing new complex absorbents including strong aqueous oxidants. The other is to developing an entirely new method based on non-thermal plasma, electron beam, ozone oxidation, UV irradiation, and their hybrid system. The hybrid systems such

as DBD ozonizer/wet scrubbing, wet scrubbing/ESP, and electron beam/ESP have been found to be attractive to applying industrial applications. In addition, proposed complex absorbents are great possibilities for the further improvement of current wet flue gas desulfurization process for the simultaneous DeNO$_x$ and DeSO$_x$.

However, further development and optimization of the hybrid system is still necessary to be done from the economic and technical point of view. Together with the investment cost, a system volume (reaction time and pressure drop), low consumption of reagents and energy (cost effective reagents, low liquid-gas ratio, and high efficient power technique), and environmental impacts (no secondary pollutants) have to be dealt with simultaneously to commercialize more effective flue gas cleaning processes.

Acknowledgment

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