Non-thermal Plasma Technology
for Pollution Control

Jae-Ou Chae[*], Yuriy Dessiaterik[**]

[*] : Inha University, Inchon, S.O. Korea

[**] : Institute for High Temperature, Russian Academy of Sciences, Izhorskaya 13/19, 127412 Moscow, Russia

Contents of Report

1. Basic processes in non-thermal plasma devices for pollution control.

The essence of non-thermal plasma techniques is the efficient use of electrical energy through selective decomposition of the pollutant molecules. Non-thermal plasmas, as a name implies, are plasmas in which the electron temperature (i. e. mean energy) is considerably higher than those of the components of the ambient gas. Non-thermal plasma techniques are particularly efficient when the pollutant molecules are present in small concentrations, as it is the case for flue gas emission. The purpose of the plasma is to create radicals through electron-impact dissociation and ionization of the molecules in the effluent gas.

There are many types of non-thermal plasma devises that have been developed for environment application. These devices operate on the same basic principle: produce plasma in which a majority of the electrical energy goes into the production of energetic electrons. Even though the electrons are shot living under atmospheric pressure conditions and rarely collide with a pollutant molecules, they undergo many collisions with the dominant background gas molecules, thus producing radicals that, in turn, lead to the decomposition of the toxic molecules. The efficiency of the approach arises from the fact that the radicals have long lifetimes and react selectively with the pollutant molecules.

Table 1-1. shows an evaluation of efficiency of production of radicals and ions by e-beam given by Penetrante and by Willis and Boyd. As it can be seen from the table, there are large discrepancies for H_2O, but as we will see late it has small influence on the production of OH radicals, because main sources of OH radicals are ions reactions.

Table 1-1. efficiency of production of radicals and ions by e-beam

PROCESS		Initial Yield (per 100 eV)	
		Penetrante 1992	Willis&Boyd 1976
Pure N_2			
$e+N_2 \rightarrow e+N+N$	Dissociation	2.06	2.36
$e+N_2 \rightarrow 2e+N+N^+$	Dissociative Ionization	0.61	0.69
$e+N_2 \rightarrow 2e+N_2^+$	Molecular Ionization	2.01	2.27
$e+N_2 \rightarrow e+N_2(A^3_u{}^+)$	Excitation	0.27	0.29
$e+N_2 \rightarrow e+N_2(B^3_g)$	Excitation	0.45	-
Pure O_2			
$e+O_2 \rightarrow e+O(^3P)+O(^3P)$	Dissociation	1.04	-
$e+O_2 \rightarrow e+O(^3P)+O(^1D)$	Dissociation	3.88	-
$e+O_2 \rightarrow e+2O$ (total)	Dissociation	4.92	5.05
$e+O_2 \rightarrow 2e+O+O^+$	Dissociative Ionization	1.4	1.23
$e+O_2 \rightarrow 2e+O_2^+$	Molecular Ionization	2.2	2.07
Pure H_2O			
$e+H_2O \rightarrow e+H+OH$	Dissociation	1.42	3.58
$e+H_2O \rightarrow 2e+H+OH^+$	Dissociative Ionization	0.95	0.67
$e+H_2O \rightarrow 2e+H^++OH$	Dissociative Ionization	0.95	0.57
$e+H_2O \rightarrow 2e+H_2O^+$	Molecular Ionization	2.90	1.99
Pure CO_2			
$e+CO_2 \rightarrow e+CO+O$	Dissociation	4.90	4.51
$e+CO_2 \rightarrow 2e+CO^++O$	Dissociative Ionization	0.48	0.51
$e+CO_2 \rightarrow 2e+CO+O^+$	Dissociative Ionization	0.17	0.21
$e+CO_2 \rightarrow 2e+CO_2^+$	Molecular Ionization	2.36	2.24

In case of electron beam, yield of active particles can be evaluated from this data for given gas composition. For some gas composition the evaluation has been done by Penetrante.

Table 1-2. Active particles production by electron beam

PROCESS	Energy Dissipation (% of Input Energy)		
	Mixture 1	Mixture 2	Mixture 3
N_2 Vibrational	5.3	3.1	3.3
$N_2(A^3_u{}^+)$	1.1	1.0	1.1
$N_2(B^3_g)$	1.8	1.7	1.9
N_2 Dissociation	24.0	19.1	21.3
N_2 Dissociative Ionization	13.9	10.8	12.1
N_2 Molecular Ionization	28.3	22.3	24.8
O_2 Vibrational	0.6	0.09	0.3
$O_2(a^1_g)$	0.7	0.07	0.2
O_2 Dissociation	8.3	2.0	4.2
O_2 Dissociative Ionization	2.9	0.7	1.3
O_2 Molecular Ionization	2.8	0.6	1.2
H_2O Vibrational		1.8	0.7
H_2O Dissociation		2.5	0.5
H_2O Dissociative Ionization		0.8	0.2
H_2O Molecular Ionization		0.8	0.2
CO_2 Vibrational		2.6	2.8
CO_2 Dissociation		10.4	6.9
CO_2 Dissociative Ionization		0.8	1.9
CO_2 Molecular Ionization		0.8	4.5
Others	10.3	10.0	10.6
Mixture 1: 80% N_2 + 20% O_2			
Mixture 2: 70% N_2 + 5% O_2 + 10% H_2O +15% CO_2			
Mixture 3: 78% N_2 + 10% O_2 + 2% H_2O +10 % CO_2			

It gives follow yield of active particles for gas composition Mixture 2 for e-beam: per 100 eV energy 3 OH radicals, 0.4 O atoms and 4 N atoms produced. If we now injected in to gas energy, we can calculate the concentration of active particles.

For corona discharge Penetrante gives follow number of active particles per 100 eV of energy: 1.2 OH radicals, 0.8 O atoms and 0.4 N atoms.

He assumed that strength of electric field in the streamer is about 40 kV/cm. In this calculations he did not take in to account electronically

exited state of nitrogen molecules, that could also lead to dissociation of H_2O. A number of simulation for streamer propagation that have bean done until now shows that electric field in the streamer head can be in range of 150 ~ 200 kV/cm. This fact can increase a number of active particles, because of rates of ionization and dissociation strongly depend upon electric field. It can be seen from the fig. 1-1
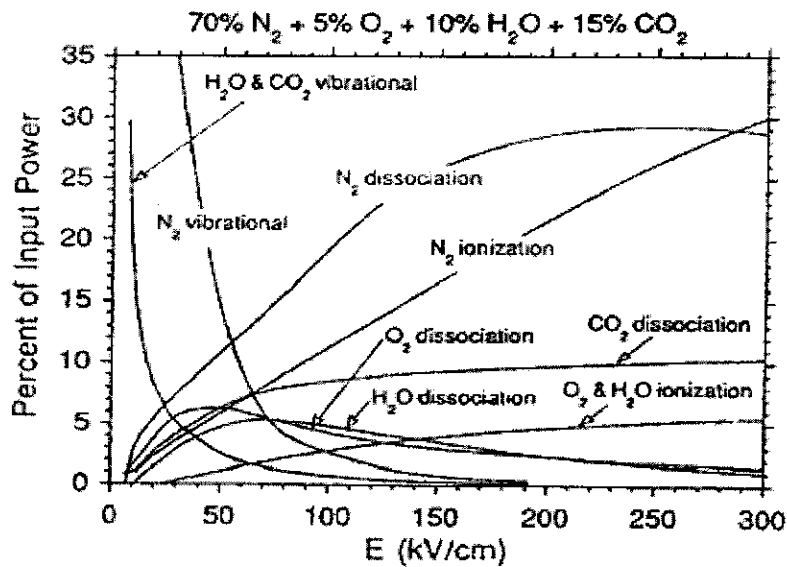

Fig. 1-1 Energy fissipation in a discharge consisting of a gas mixture of 70% N_2+5%O_2 +10%H_2O+15%CO_2 showing the percent of input power consumed in the electron impact processes leading to vibrational excitation, dissociation and ionization of N_2, O_2, H_2O

Mainly process of ionization and dissociation goes in the streamer head, were the strength of electric field is maximum. Simulation made by Biturin give the concentration of active particles inside streamer:

Table 1-3. Initial concentration of active particles inside streamer

Particle	Concentration (1/cm^3)	Particle	Concentration (1/cm^3)
e	$8*10^{14}$	OH$^-$	$7*10^{13}$
O$_2^+$	$4*10^{13}$	H	$4*10^{13}$
N$_2^+$	$6*10^{14}$	N$_2^*$	$3*10^{13}$
H$_2$O$^+$	$1*10^{14}$	N	$3*10^{14}$
O$_2^-$	$5*10^{13}$	O$_2^*$	$4*10^{14}$
O$^-$	$6*10^{12}$	O	$7*10^{14}$
O(^{1}D)	$2*10^{14}$	OH$^+$	$3*10^{13}$
H$^+$	$3*10^{13}$		

For gas composition 71% N2, 16% H$_2$O, 5% O$_2$, 8% CO$_2$ 400ppm NO, 1000 ppm SO$_2$, average energy input in streamer channel in this calculation was 0.1 J/cm^3, streamer radius was chosen 1 micrometer.

Primary active particles are:

Positive ions: N$_2^+$, O$_2^+$, H$_2$O$^+$, OH$^+$, H$^+$,

Negative ions: O$_2^-$, O$^-$,

Exited molecules and atoms: O$_2^*$, N$_2^*$, O(^{1}D)

Radicals: O, OH, N, O.

Positive ions react within around 1 ns in charge transfer reactions. In this reactions positive ions are converted to N$_4^+$, O$_2^+$(H$_2$O), H$_3$O$^+$. Follow by production of ions: N$_4^+$ and H$_3$O$^+$(H$_2$O)$_2$ and finally recombination reactions with electrons and negative ions.

Most important result of these reactions is production of OH and H radicals that gives around 85 % of OH radical production.

It can be see from table that big part of energy goes to exiting on exited molecules and atoms. Around 20   30 % of this molecules consumed in reaction that produce OH radicals:

N$_2^*$ + H$_2$O → OH + H + N$_2$,   k=4.2*10^{-11} s/cm^3;
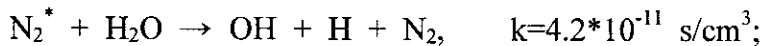
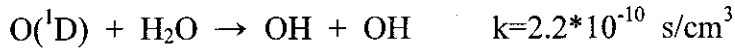Other part is lost in reaction:

$$N_2 + N_2^* \rightarrow N_2 + N_2 \qquad k=2.7*10^{-11} \text{ s/cm}^3$$

For $O(^1D)$:

$$O(^1D) + H_2O \rightarrow OH + OH \qquad k=2.2*10^{-10} \text{ s/cm}^3$$

Role of radicals for removing SO_2 and NO_x is summarized in the table 1-4

Talbe 1-4. Role of radicals for removing SO_2 and NO_x

Radical	NO cleaning	NO restoring	SO_2 cleaning	SO_2 restoring	Radical recombination	Radical conversion
N	80 %	20 %	0	0	0	100% to O,H
O	15 %	5 %	5 %	Low	65 %	15 % to O_3
H	Low	low	low	Low	low	95 % to HO_2
O_3	95 %	low	low	Low	low	Low
OH	25 %	low	15 %	Low	60 %	Low
HO_2	49 %	low	low	Low	60 %	40 %

Numbers show which part of radicals consumed in the process.

That gives basic data to evaluate efficiency of streamer corona discharge for NO_x and SO_2 removal. Unfortunately, in case when ammonia is added to the flue gas, calculations give less removal efficiency than it has been demonstrated by experiment. It was suggested that heterogeneous reactions play an important role.

The main conclusion that can be drawn from this consideration is that processes in the corona discharge are more complicate than that for e-beam and in spite of big progress achieved until now more fundumental study is needed to make possible reliable prediction of experimental result by simulation.

2. Electron beam plasma for pollution control

History of electron beam processing for environmental pollution control.

Effort to use radiation to prevent pollution was initiated by Ebara Corporation in Japan in 1970 and 1971. Table shows the various testes that have been conducted around the world, from the beginning until 1993, were many plants are operational. The first batch test study defined the radiation chemical reaction of SO_2 and NO_x, resulting from the irradiation of flue gas. The success of these initial batch tests indicated a future potential use for the electron beam process.

Subsequent development of the process continued with join effort by Ebara and Japan Atomic Energy Research Institute (JAERI) in 1972. This was 60 Nm3/h test facility which tested heavy oil combustion gase with concentrations of 900 ppm SO_2 and 80 ppm of NO. Indication were that Nox removals of almost 100 % could be obtained with total dose of 2 megarads (~ 7.2 Wh/m3). The SO_2 removals were in the range of 80 % but the total dose was about 4 megarads (14.4 Wh/m3) at the high temperatures.

After joint effort, Ebara was encouraged to build a 1,000 Nm^3/h heavy oil combustion gas pilot plant at their central research facilities in 1974 for further study and to demonstrate the scale-up principles.

Some of the highlights of this pilot-plant test:

It was confirmed that the simultaneous removal of SO_2 and NOx is possible in the range 80-90 % with dry process.This was the first rest of the process using ammonia injection. The reacted products can be continuously collected as a dry powder by an electrostatic precipitator.

Stoichiometric data was obtained during ammonia-addition test for the removal of SO2 and Nox decrease with increase of reaction temperature.

Table 1-2 The experiments for NOx, SOx removal

Institution (year)	Volume flowrate	Accelerator	Input SO_2/Nox ppm	NH_3 ppm	Temp, °C
EBARA, 70-71	20 L	1.2 kW 2-12 MeV	1000/-	-	100
JAERI, 72-74	60 m³/h	15 kW	900/80	-	90-120
EBARA, 74-77	1000 m³/h oil fired	30 kW 300-750 kV	200/240	700	
Univ. Tokyo, 74-78	36-84 m³/h	90-120 W 1 MeV	900/-		70-120
Univ. Tokyo, 74-78	120 l/h	100 W 1.1 MeV	-/1000		115
EBARA, 77-78	3000-10000 m³/h iron industry	2*(10-45kW) 600-750 kV	200/180	1-1.2 st.	70-90
JAERI, 72-74	900 l/h	1.5 MeV 20 mA	1000/ 5000		80-150
Research Cottrell, 84-85	5300 m³/h coal fired	80 kW 2*800 kV	400-2500/30 0	Lime St	60-150
EBARA Indianopolis, 84-88	8000-24000 m³/h coal fired	160 kW 2*800 kV 1000/400	St	65-150	65-150
Univ. Ka. 1984	100-1000 m³/h gas fired	22 kW 190-220 kV	0-1000 / 50-400	St	75-170
KFK KA Agate, 1984	60-1000 m³/h crude oil	36 kW 150-300 kV	400-1000 300-1000	St	60-120
Badenwerk Karlsruhe, 1985	10000-20000 m³/h coal fired	180 kW 260-300 kV	50 500/ 300-500	St	70-100
ICHJT Warsaw, 1989	400 m³/h oil-fired	5.4 kW 775 kV	0-1200 0-400		60-150
KFK KA Agate II, 1989	1000 m³/h crude oil	50 kW 500 kV	400-1000 300-1000	St	60-120
EBARA FUJISAWA, 1991	1500 m³/h, oil fired and incineration gas	15 kW 500 kV	0-1000 0-200	St	65

ICHT-KWECZYN 1992	20000 m3/h coal fired	20-50 kW 500-700 kV	200-600 250	St	60-120
NKK-JAERI Matsudo city 1992	1000 m3/h incineration gas	15 kW 900 kV	100/100 HCl 1000	St	150
EBARA-JAERI Chubu, 1992	12000 m3/h coal fired	3*36 kW 800 kV	800-1000 150-300	St	65
EBARA-TOKYO-EPA, 1992	50000 m3/h auto-tunnel exhaust gas	2*12.5 kW 500 kV	0/0-5	St	Ambient 20
JAERI, Chubu Electr. Powere Co. 1998 (project)	620,000 m3/h	N/A	N/A	N/A	N/A
China, 1997	300,000m3/h	320 kW / unit 800 kV	1800/400	N/A	150
IAEA, JAERI Poland, 1998 (project)	270,000 m3/h	N/A	385/520	N/A	140
IAEA, JAERI Bulgaria, 1998 (project)	10,000 m3/h	N/A	5500/390	N/A	140

It was found than determined that temperatures below 90 °C are advantageous for the reaction.

The by-products were a mixture of ammonium sulfate and ammonium nitrate, and were easier to capture than the aerosol without ammonia.

The results of plant growing test with various vegetables indicated that the by-product had the same degree of fertilizing effect as ammonium sulfate and ammonium nitrate.

Based of the good result of pilot plant test in 1977, Ebara in a joint effort with Nippon Steel, the Nox Association and others built and tested a 10,000 Nm3/h flue gas treatment plant at Wakamatsu, Japan to remove SO2 and Nox from the exhaust of steel sintering plant. Some of

highlights of this test are:

Many experiments were carried out on treated gas volumes ranging between 3,000-10,000 Nm^3/h.

An optimal condition was found to be in the range of an inlet gas temperature of 60 °C and a total dose 1.5 megarad (5.4 Wh/m^3), with ammonia injection at about a 1.0 stoichiometric ratio.

During the one-month continuous operation, the Nox removal was over 90 % and the SO_2 removal was over 95 %.

During the period of 1974 to 1978, basic research was conducted on the electron beam flue gas process at Tokyo University. The first stage was to establish basic scientific and technological background information, which would help to realize the industrial use of the process and to show The capability of the electron-beam, flue-gas process which would turn SO_2 and NO_x in the flue gases into solid aerosol which could be collected by an electrostatic precipitator.

The work was conducted by to group, comprised of electrical technology and chemical technology. The chemical group was staffed with three different types of expertise, namely the high-speed reaction group, the inorganic analytical chemistry group and the radiation chemistry group. The collaboration and efforts of the various work helped to get a better understanding of the process. Some of the result of this work are as folow:

It was found that the produced aerosol can be directly collected on electrodes by charging the space electrically with the electrodes, installed directly in the electron beam radiation chamber. Therefore, it was conceivable that an electrostatic precipitator would not be required downstream of the process.

It was also found that the reaction speed of the $DeSO_2$ and $DeNO_x$,

induced by radiation chemistry, enhanced by the above-described electrical charging phenomena. This gave an indication that possibly the capacity of accelerator could be reduced, along with their operation costs.

They found that OH radicals play an important role at the initial stage of the electron-beam reaction and that the formation of aerosol depends on the process temperature.

They found that an equilibrium between the reduction of NO and the formation of NO_2 and the conversion from NO to NO_2 increases with the presence of water vapor, and also HNO_3 is produced. It was also confirmed that ammonium sulfate and ammonium nitrate salts are formed with the presence of ammonia.

Test indicate that the by-product is approximately a 1-3 mixture of ammonium sulfate/nitrate salts and ammonium plays a role of preventing reverse reactions by solidifying the mixture of acid mist.

Early DOE-sponsored research was done by Research Cottrell in 1979-1980, and continued through 1985. They utilized bench-scale tests to evaluate the technical and economical feasibility of the Electron beam Process to remove SO_2 and Nox from typical electrical utility flue gases. In 1984, Research Cottrell built a pilot plant, at TVA Shawnee Stream Plant and conducted tests under a contract from the DOE (Department of Energy) to study the effects on an alternate reagent on the Electron Beam Process. An alkali-slurry spray of hydrated lime in a spray dryer was used for acids neutralization. The products formed were calcium sulfate and calcium nitrate. SO_2 removals greater than 90 % and NOx removals grater than 80 % were achieved.

In 1983 Ebara International Corporation, under a cost-sharing agreement with DOE, embarked upon program to build and operate an Electron Beam FGT plant at the Indianapolis. Flow rate up to 24,000 m^3/h was

treated and total power of the accelerators was 160 kW. As the result of the testing and operation in 1984-1988, it was demonstrated that the Electron Beam FGT process was suitable to scale up to a full-sized commercial application. Major conclusions are as follows:

More than 95 % SO_2 and 90 % NOx were simultaneously removed from the flue gas under optimum operation conditions. SO_2 removal depends strongly on the flue-gas temperature and ammonia stoichiometry at radiation doses greater than 1 megarad (3.6 Wh/m^3). NOx removal, however, depends primary on electron-beam radiation. Gas temperature and ammonia stoichiometry are secondary order effects. High SO_2 concentrations in the flue gas improved NOx removal efficiency, indicating the process is most efficient on high-sulfur coal. The by-product particulate can be efficiently collected by an electrostatic precipitator. The baghouse-only operation caused high system pressure drops, due to amount of by-product on the bags that would not release, under normal process operating conditions and required special cleaning treatment. More detail about last conclusion, because it is important issue for pulse corona discharge technology also. A baghouse was initially selected as the by-product collector. Prior to the initial start up process, the bags were pre-coated with flyash from the utility's stack gas. The purpose of this procedure was to protect the bag's surface from direct contact with the by-product and provide a stable, porous surface to pass the gas. When a predetermined amount of by-product collected on this flyash, the baghouse pressure drop would increase. This increase would initiate a pulse jet of air within each bag which would theoretically shock the collected by-product from the bag, but retain the flyash pre-coat. However this was not the case, the collected by-product could not be fully removed from the bags by this method and tended to cause

excessive baghouse pressure drops. Off-line cleaning methods were required to remove the by-product from the bags. Eleven types of bag materials were tried, but the results of each trial were similar. Diatomic earth was finally used as a pre-cat material for the bags, replacing flyash. This result in lower initial pressure drops and permitted longer test runs before large baghouse pressure drops were experienced. Despite of all efforts, a reliable method of controlling baghouse pressure drop was not found.

A mobile electrostatic precipitator was installed upstream, in series with the baghouse. It was able to remove a high percentage of the by-product from the gas stream and successfully dispose of it to the by-product storage vessel.

In 1984, the Nuclear Research Center in Karlsruhe, Germany and the University of Karlsruhe both built pilot-scale plants to study the reaction mechanism of the process and perform other tests to improve the process.

In 1989, the Nuclear Research Center in Karlsruhe added a second pilot plant to continue work on mechanism, aerosol formation and filtration.

Also in 1989, the Institute of Nuclear Chemistry and Technology in Warsaw, Poland built a small laboratory test unit to obtain information to build a 20,000 m3/h demonstration facility and the Electric Power Station Kaweczyn. Both facilities are operational.

In 1992 pilot plant of 1,000 m3/h for treating incinerator gases from the Mutsudo City, Japan Incinerator. The plant treats SO2, Nox and HCl.

In 1992 a 12,000 m3/h coal burning facility was completed in Nagoya, Japan at Chubu Electric Company.

EPRI completed their study over 70 processes for air pollution control. The study was performed by Radian Corporation. The Electron beam Process was rated very high and for combined SO2/Nox technologies, the

report stated for retrofit, the Electron Beam Process rated equivalent of preferable to FGD/SCR .

EBARA Corporation proceeded to build the first commercial plant in China in 1997 at the Chengdu Electrical Plant. The target removal efficiency of SO_2 and Nox was fully achieved and the resulting by-product has been utilized for agriculture use. In addition to China, a full-scale plant using e-beam is now under construction in Japan. At the same time two demonstration plants are under design in East Europe.

3. History of Pulse Corona Discharge for DeNOx DeSO2.

Masuda with his co-worker investigate a possibility of enhancing $DeNO_x$ and $DeSO_x$ in E-beam method from a thought that copious electrons, produced by ionizing collisions of primary high energy electrons and remaining with low energy after performing useful chemical reactions, could be regenerated in energy by applying an electric field. The results of experiments were very positive, but only under conditions that corona discharge took place. Further more, the use of DC voltage produced a comparatively large ionic current to cause quite a high electric loss. This suggested that a very narrow pulse high voltage or microwave high voltage must be used for exploitation of such effect in order to avoid energy loss due to acceleration of ions.

After completing the nanosecond pulse power supply Masuda and co-workers started $DeNO_x$ $DeSO_2$ test in laboratory and an incineration plant, tests of mercury vapor control at incineration plant and ozone production test in laboratory. Laboratory investigation with artificial gas supported the possibility of removing NOx (Masuda and Nakao 1986) or SO_2 (Mizuno at al. 1986) by means of pulse corona discharge.

These observations were the starting steps for research on the possible application of pulse corona to flue gas treatment that is being pursued at a coal-burning power station of ENEL, Pisa, Italy (Civitano at al. 1986-1992)

The limits of this process are:

The NOx initial concentration must be equal to or less than 250 ppm if we need final concentration of 100 ppm, or 550 ppm if we can accept final concentration 325 ppm. Sulfur dioxide initial concentration must be less than 1500 ppm. These limits are due to economical reason in order to use acceptable energy consumption (5-6% of power plant produced energy) and in order to limit N_2O production to about 10 ppm.

The main features of this technology are:

The prospect of a simultaneous Nox and SO_2 removal with a single dry process;

The ability to base the process in existing electrostatic precipitators;

Low ground surface requirement;

By-product may be used as fertilizer;

Lower cost than tradition process.

The main steps of the process may be summarized as follow:

Production of free electrons having energy in the range 5-20 eV;

Production of radicals O, OH, HO_2, N necessary to partially convert SO_2 into H_2SO_4 and NO into HNO_3, NO_2 and N_2;

Injection of ammonia to convert acids into ammonia salts;

Collection of the produced salts by an electrostatic precipitator;

An additional structure (bag filter) to enable heterogeneous reactions among NO_2, H_2O, O_2 and NH_3 in order to increase removal efficiency of NO and NO_2.

It was found that by the heterogeneous reactions it is possible to remove about 50 % or Nox from flue gas that has been previously energized in order to convert NO into NO_2. Gas phase reactions alone allows to remove 15 % of Nox. The removal efficiency increases as the relative humidity on the surface of solid media increases. When a fabric filter is used, increasing the relative humidity, the salts produced become stickier and fabric filter clog rapidly. It is possible to increase the clog time by coating the fabric filter with particles having high specific surface. In this way problem is reduced but not solved.

ENEL has patented a technology that permit to obtain heterogeneous phase reactions without this inconvenience.

4. Modern status of corona discharge technologies

In order to increase removal efficiency further experimental investigation of pulse corona discharge were made.

In 1992, Mizuno used hydrocarbon additions to diesel engine exhaust gas. With initial concentration of NOx 630 ppm, and gas temperature 240 °C the removal efficiency was 15 % by pulse corona discharge only and 50 % when 500 ppm of C_2H_4 were added.

Penetrante and Vogtlin also did the experiments on Nox removal from air with hydrocarbon additives. They found that 400 ppm of NO were removed with energy consumption 24 Wh/m^3, when stoichiometric amount of n-octane was added.

Some study of NOx and SO_2 removal by pulse corona discharge was made by Zhou and van Veldhousen in the Netherlands in 1996. The experiments show that treatment time is important of NOx removal. Optimal gas residence time was about 16 s for the experimental

conditions. Energy price for NO removal was 27 eV/NO. For reaction time 6 s and 30 s energy of NO removal was increased up to 40 eV/NO.

Also they have found that injection of 300 ppm of SO_2 improves NO removal efficiency by factor 3, and injection of 600 ppm of ammonia improves NO removal efficiency by factor 2. When SO_2 and NH_3 were added to gas simultaneously, enhancement of NO removal rate was about 1,5. In order to use this so called synergetic effect it was suggested, that ammonia is injected after reactor.

During the SO_2 removal experiments with NH_3 injection it was observed that the SO_2 removal rate has a strong history effect. Removal efficiency increases during the operation, even when injected in to gas energy decreases. For example at the beginning of test SO_2 removal efficiency was 74 % of initial 300 ppm with energy consumption 7.7 Wh/m^3 and after 1 h operation energy consumption was decreased to 1.9 Wh/m^3, but removal efficiency increased op to 84 %. Ammonia leak was also reduced.

History effect was also reported by Li. Removal efficiency of SO_2 in his experiment increases from 30 % up to around 90% after 10 hours of continuous operation. It was noticed that this effect related to the ammonium sulfate powder that covers the reactor walls. Possible explanation of this phenomenon is that salt particles has a big surface area and may enhance the SO_2 removal rate by initialization of heterogeneous reactions.

Recently, the use of photocatalyst (TiO_2) and H_2O_2 injection was tested in order to increase NOx removal efficiency. Experiments made by Mizuno show that removal efficiency of 400 ppm of the initial NOx concentration increased at least 2 times when catalyst used in comparison with

conventional corona reactor.

5. Other type of discharges used for pollution control

5.1 Dielectric barrier discharge reactors.

Dielectric barrier discharge reactors, ac high voltage are applied between electrodes, one or both of which are covered with a thin dielectric layer, such as glass. Dielectric barrier discharge reactors are also referred to as silent discharge reactors. The geometry is commonly either planar (parallel plates) or cylindrical (coaxial tubes). Configurations like those used in corona discharges are also used in which one of the electrodes (e.g. a wire) is highly stressed, and the outer electrode is metal foil wrapped around a glass tube. Dielectric-barrier discharge processing is a very mature technology, first investigated by Siemens in the 1850's for production of ozone. It is routinely used to produce very large quantities of ozone for applications such as water purification, and the bleaching of textile and pulp.

Whereas in the pulsed corona method the transient behavior of the plasma is controlled by the applied voltage pulse, the plasma that takes place in a dielectric-barrier discharge self-extinguishes when charge build up on the dielectric layer reduces local electric field. For some applications, this feature presents an advantage for the dielectric barrier discharge approach since simpler electrical power supplies can be used.

Many papers presented application of this type of discharge for decomposition of various pollutants.

Paper by Fudji present the simultaneous removal of Nox, SO2 and soot from diesel engine exhaust gas.

In some cases, the efficiency of barrier discharge reactor can be improved significantly by applying high voltage pulses in manner similar to that in pulsed corona reactor. Paper by Abolentsev present the barrier discharge reactor used for H2S dissociation. The most interesting future of this experiment is the use of liquid water for prompting heterogeneous phase reactions and collecting by-product.

In paper by Rosocha VOC removal by barrier discharge is presented.

5.2 Surface Discharge Reactors

A Surface Discharge Reactors consist or a planar of cylindrical alumina ceramic having a series of strip-like electrodes attached to one of its surface and a film like electrodes counter electrodes embedded inside the ceramic. A high-frequency AC high-voltage is applied to generate the surface discharge, starting from the side edges of the strip electrodes and uniformly covering the ceramic surface.

The use of surface discharge processing for the removal of NOx and VOCs is presented in the paper by Masuda. This paper presents results on the removal of NOx in combustion gas from an oil-burning boiler. It is also shown that this reactor can achieve 100 % decomposition of CFC-113 with low power consumption, without producing poisonous products like pophosgene or fluorophosgene; a liquid or solid absorbent is used to remove the final decomposition products. It is interesting to note that Masuda's surface discharge reactor seems to be very effective in decomposing CFC-113, which is one of the most difficult VOCs to decompose. It can hardly be decomposed by advanced oxidation process like UV radiation in combination with ozone. CFC-113 also could not be completely decomposed by either the pulsed corona reactor of the

ferroelectric bed reactor, as reported in Yamamoto paper.

5.3 Ferroelectric Bed Reactors.

The Ferroelectric bed reactor employs a high-voltage AC power supply in conjunction with tubular reactor packed with ceramic pellets with high dielectric permeability. The pellets are held within the tube arrangement by two metal mesh electrodes. When external AC voltage is applied across the high dielectric layer, the pellets are polarized, and an intensive electric field is formed around each pellet contact point. Many pulsed discharges take place around each contact point of ferroelectric pellets, and the discharge energy can be controlled by changing the dielectric constant of the pellet, and by the voltage waveform.

The papers by Masuda et. al presents results on the decomposition of CH4 and CO2 using ferroelectric pellet bed reactor. This reactor can also destroy a variety of hazardous organic compounds, including toluene, methylene chloride and CFC-113 as reported in the paper by Yamamoto.

5.4 DC Discharge Reactor with Fast Flow Gas

A discharge can be established using a simple DC high voltage power supply. The construction of the reactor is simple, typically consisting of an anode plate and cathode containing a lot of sharp metallic pins. By pumping gas through the discharge volume to produce fast flow at atmospheric pressure (1-2 bar), a stationary discharge can be established without overheating the gas.

The use of fast gas flow for stabilization of a point-to-plane corona discharge is presented in the paper by Napartovich. They used flow speeds of 70 to 200 m/s across the discharge. It was used for ozone

production, SO2 removal from model gas and for Nox removal from a natural gas fired boiler flue gas.

A different kind of discharge presented in paper by Csernichowski. It is a tapered gaps, called a gliding discharge, in which the stationary glow discharge is replaced by a moving arc. This operates at much lower gas speed of around 10 m/s. The discharge were used for H2S removal.

6. Cost evaluation

Evaluation of capital cost of e-beam process made by Frank shows that it can be around 200 $/kW for 300 MW power plant fired 2.6% Sulfur coal. This number is extremely competitive with other desulfurization systems, wet scrubbers, dry scrubbers and sulfur recovery system. From another side, economical evaluation has been made after runs of pilot plant in Italy. It is presented is paper by Civitano. Based on this data, cost comparison of three technologies for DeNOx, DeSOx has been made in a committee in the Research Institute of Energy Engineering in Japan. Pulse Plasma DeNOx, $DeSO_2$ process was compared with E-beam process and conventional Calcium-Gypsum for $DeSO_2$ and Ammonia Catalyst Process for DeNOx processes.

This evaluation show that first year total cost for Pulse plasma Process can be 25 % less than Calcium Gypsum and Ammonia catalyst process and 19 % less than e-beam process.

7. Conclusions

Main conclusion that can be made is that electron beam process is in more developed state than pulse corona discharge nowadays. Mainly, because of generators with bigger power per module are available.

Anyway e-beam process has more than 10 years longer history of research and development effort.

The processes in the pulse corona discharge are not so clear as in e-beam.

In spite of this based on the Masuda calculation it seems that corona discharge can be competitive with e-beam, because of lower investment cost.

8. References

1. Norman W. F. and S. Hirano History of electron beam processing for environmental pollution control and work performed in the United States. NATO asi SERIES, v. G34 Part B, edited by B.M. Penetrante and S.E. Schultheis, Berlin 1993. Pp 1-26.