



Using Non-Thermal Plasma to Control Air Pollutants

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FOREWORD

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INTRODUCTION

This paper is about using a non-thermal plasma process to remove pollutants from emissions. It is probably a good idea to begin with the definition of non-thermal plasma. As we learned in grade school, matter exists in three phases: solid, liquid, and gas (for example; ice, liquid, and vapor are the three phases of water). What Miss Bromley didn't tell you is that there is a fourth phase in which matter can exist. This phase is called plasma, and it exists when molecules are heated to extremely high temperatures. At high temperature, electrons in molecules become excited and increase velocity to a point they leave their orbits and fly out of the molecule's influence. As the non-thermal plasma name implies, plasma also can occur at room temperature if the molecules are exposed to a strong electrical field. More on this later.

Non-thermal plasma has been around a long time. It was observed in a laboratory over a hundred and fifty years ago. It enjoyed original success for many years by making ozone from air and water. It was researched to death, but commercially, it remained mainly a laboratory curiosity. It appears that everyone that has studied the non-thermal plasma process has felt obligated to change the name of the process. It is called dielectric barrier discharge, dielectric barrier corona discharge, silent discharge plasma, high energy corona, electron beam plasma, corona destruction, electro-catalytic oxidation, capillary discharge, and God knows what else. This is not an exhaustive list.

Well, if non thermal plasma has been around since forever, and everybody and his brother have worked it to death, why is there suddenly renewed interest? A couple of events have occurred to cause researchers to re-open the books on non-thermal plasma. The first was a fact sheet on mercury issued by U.S. EPA on December 14, 2000. Along with identifying sources of mercury and health effects of mercury, it contained this statement: "EPA must propose regulations to control mercury emissions - and any other air toxic the Agency deems necessary - from coal- and oil-fired power plants by December 15, 2003."¹ At the time the fact sheet was issued, there was not a reliable, consistent and affordable control for mercury. However, it has since been shown that non-thermal plasma will convert elemental mercury to mercury oxide, which is a solid and can be removed using a fabric filter or an electrostatic precipitator (ESP).²

The second event that occurred was that the Partnership for a New Generation of Vehicles (US DOE)³ began a project that would develop the technology to build a family automobile-type engine that could achieve a fuel efficiency of 80 miles per gallon. The good news is that they found an engine that would accomplish this. The bad news is that emissions from this engine are worse than current regulations allow. They call this "new" engine the CIDI engine for Compression-Ignition, Direct-Injection Engine. Non-scientific-types call it a diesel engine. The Partnership supports the use of a non-thermal plasma type reactor to clean-up the CIDI's emissions and this has spurred a number of groups to begin research to develop a non-thermal

plasma control device for automobiles. Although this is important work, it falls under the area of mobile sources and will not be explored in this paper.

Other areas being investigated for possible non-thermal plasma use include:

- Liquid food (fruit juices, bottled water, milk, etc.) pasteurization.⁴
- Livestock operations odor abatement.⁵
- Disposal/conversion of Halon (branded electrical fire suppressant) stockpile.⁶
- Destruction of 1,1,1-Trichloromethane.⁷

As with the mobile emission source, the above research is above and beyond the scope of this paper and will not be discussed here.

THE PROCESS

What Is Non-Thermal Plasma?

Everyone is familiar with static electricity that occurs when reaching for a metal door handle after walking across a carpet. In technical terms, static electricity is the discharge of electricity that occurs when the potential (that is, voltage) exceeds the insulating effect of the air gap between your finger and the door handle. Non-thermal plasma uses a reactor that utilizes a similar effect. The reactor consists of two electrodes (one electrode is in the form of a metal pipe, and the other electrode is a metal wire that runs down the middle of the pipe) separated by a void space that is lined with a dielectric material and is filled with glass beads. This type of reactor is called Dielectric-Barrier Discharge (DBD). See Figure 1.

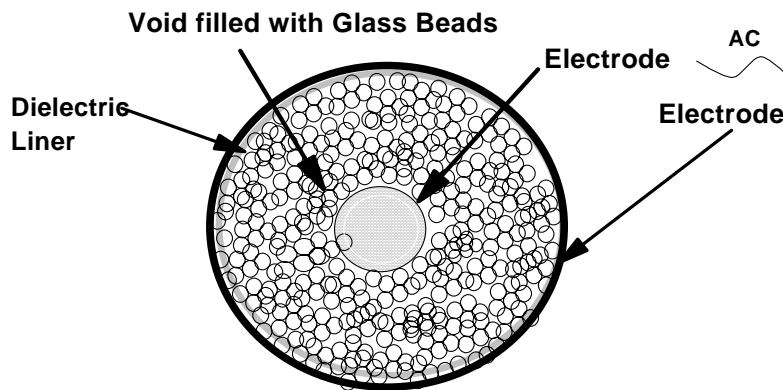


Figure 1. DBD Type Non-Thermal Plasma Reactor

Emissions flow inside of the pipe. A phenomenon occurs when the voltage through the beads exceeds the insulating effect of the beads and millions of micro-discharges occur. The duration of these discharges is measured in nano-seconds.⁸ The individual discharges cannot be seen with the human eye, but the overall effect produces a silent glow. This effect will only occur when the power source is alternating current (AC). DBD cannot be induced with direct current (DC) power because the capacitive coupling of the dielectric necessitates an AC field.

In this environment, in addition to electrons flying about, atoms are being separated from their molecules to become free radicals. Since free radicals are highly reactive, they quickly recombine with other atoms and/or molecules to form new compounds. Using oxygen as an example, the normal state of oxygen is a molecule containing two oxygen atoms. Thus, it is written as O_2 . In a DBD field, the oxygen molecules splits into two atoms of oxygen, O^+ and O^+ . The elemental oxygen radical, being very reactive, will form ozone, O_3 , when the radical oxygen

atom reacts with a normal molecule of oxygen (O₂).

The oxygen radicals also react with other compounds. For example, oxygen radicals react with carbon monoxide (CO) to form carbon dioxide (CO₂), sulfur dioxide (SO₂) to form sulfur trioxide (SO₃), and nitrogen oxide (NO_x) to form nitric acid (HNO₃) in the presence of moisture. Ozone will also react with small (2.5 micron) carbon particles (soot) to form carbon dioxide, and reacts with elemental mercury (Hg) to form mercury oxide (HgO). Oxidizing elemental mercury changes it from a vapor to a solid phase. Sulfur trioxide hydrolyzes into sulfuric acid, when exposed to moisture. Depending on the concentrations of nitrogen and sulfur compounds, this process is capable of producing significant amounts of mineral acids.

What Is the Status of Non-Thermal Plasma Research and Development?

As mentioned above, there is much activity (and hype) about non-thermal plasma processes, but what is really going on with this technology? A search of the Internet reveals two companies that have developed their processes to commercial scale. The following is a brief description of their efforts to date.

Powerspan Corporation⁹ has been one of the leaders in developing non-thermal plasma technology for multi-pollutant control in coal-fired powerhouse emissions. In 1998, Powerspan signed an agreement with FirstEnergy Corporation¹⁰ to design, construct, and operate a \$2.8 million pilot plant containing a non-thermal plasma reactor, along with a wet electrostatic precipitator (WESP), for collecting particulate and neutralizing acids in the emissions. They located the plant at FirstEnergy's R.E. Burger facility near Shadyside, Ohio. This plant generates electricity by burning only coal. The pilot plant was designed to treat a one percent slipstream, or about 4,000 CFM¹¹. (In powerhouse terms, this is equivalent to the emissions from a 2 megawatt facility.) After two years of operations, the pilot plant showed promise, but it was unable to obtain the levels of pollutant removal efficiency desired. Additionally, the presence of acids in the WESP caused significant corrosion and other operating problems, to the point the WESP became a high-maintenance item.

In June 2001, Powerspan received a two million dollar grant from the Department of Energy to study the capacity of its pilot plant to remove mercury emissions. With this additional funding, they installed an ammonia scrubber to the process line, upstream of the WESP. As a result of this change, they were able to achieve the independently verified¹² DRE's indicated in Table 1.

Based on these results, Powerspan was given a \$4.5 million grant by the Ohio Coal Development Office, which is within the Ohio Department of Development, to aid in the construction a \$16.9 million, 50 megawatt slipstream demonstration unit at FirstEnergy's Shadyside plant in June 2001.¹³

POLLUTANT	DRE
Sulfur Dioxide, SO ₂	98 %
Nitrogen Oxides, NO _x	90 %
Total Particulate, TPM	99.9 %
Fine Particulate, PM _{2.5}	95 %
Mercury, Hg	80 -90 %

Table 1. Typical DRE's From Modified Pilot Plant.¹⁴

On October 10, 2002, Powerspan announced plans to construct a full-scale, 510 MW Electro-Catalytic Oxidation (ECO) unit at AmerenUE's¹⁵ Sioux Plant located in St. Charles County, Missouri.¹⁶ Powerspan proposes a three-stage process including a Dielectric Barrier Discharge (DBD) reactor, followed by a combination ammonia scrubber and absorber unit to neutralize and absorb the acids formed; and finally, a wet electrostatic precipitator to remove the mists and aerosols from in the emissions. See Figure 2.

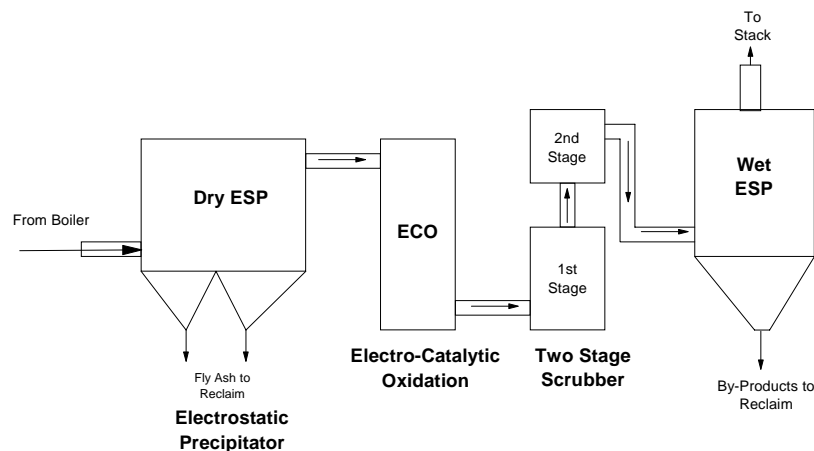


Figure 2. Revised Powerspan Process

The plan was to install the ECO unit on Sioux Plant Number Two Unit. This plant burns Power River Basin (PRB) coal and uses Illinois bituminous coal as a backup. Sulfur content of PRB coal is relatively low, ranging from 0.06 to 2.4 percent. Mean sulfur content is 0.48 percent.¹⁷ The plans called for starting with a pilot plant to collect design data for the full-scale plant. Construction on the full-scale plant was scheduled to begin in the winter of 2003. Plant startup was scheduled for spring of 2006. Plans were to conduct performance testing for a full

year after startup. The cost of the entire project was estimated at \$146 million. The primary partners requested co-funding under DOE's Clean Coal Power Initiative program.

Further contact with Powerspan¹⁸ indicated that they were unsuccessful in their bid for funding from DOE. They cannot proceed without the funding and the project is dead until they can find alternative funding for it. Through the conversation, it was learned that work continues on the commercial scale (50 MW) unit at FirstEnergy's East Lake facility. This plant was expected to be online by the late fall, 2003.

BOC Gases¹⁹ has licensed²⁰ a process that uses ozone to reduce pollutants in a reaction chamber. After the pollutants have been converted to the higher-oxidized state they are hydrolyzed and removed with a caustic scrubber. BOC calls their process LoTOx process. See Figure 3.

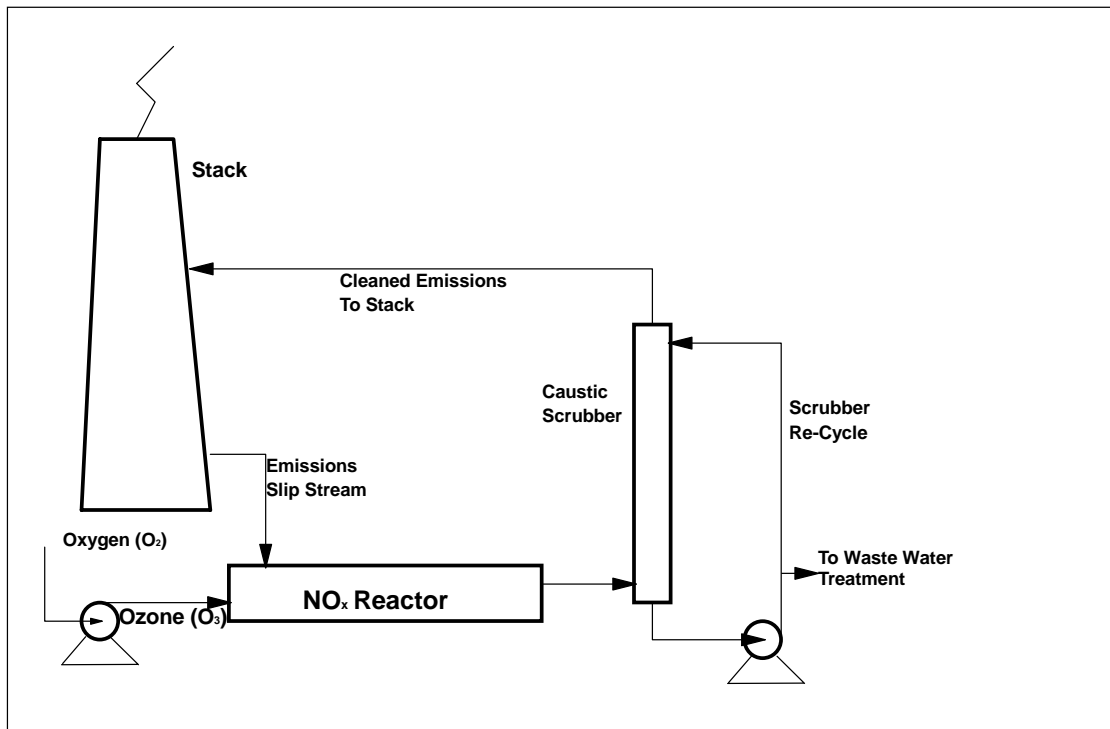


Figure 3. BOC's LoTOx Ozone Process

The process used by BOC has some differences with the Powerspan and other non-thermal plasma processes. First, it uses industrial-grade oxygen instead of the oxygen in the emissions stream. The ozone reactor is described as a "corona discharge" reactor. Corona Discharge is another name for non-thermal plasma. The ozone reactor is free-standing and is located outside of the duct transporting the emissions. Another difference is that they operate continuous NO_x monitors and the readings are used to match the oxygen/ozone flow rates to the concentration of NO_x in the emissions. BOC is marketing this process as a primary NO_x control technology.

Some of their literature mentions “multi-pollutant control”, but gives no specifics.

The California Air Resources Board (CARB) partially funded a demonstration project of the LoTOx process at a secondary lead reverberatory furnace operated by Quemetco, a subsidiary of RST Corporation, located in City of Industry, CA. The demonstration was completed toward the end of 2001. BOC has issued a status report on the demonstration project and CARB published the report on their web site.²¹

Quemetco’s Pilot Test Conditions:

Emissions Flow Rate	Up to 3,000 cfm
Inlet Temperature	150 to 250 degrees F
Inlet NOx	Up to 500 ppmvd
Inlet SO2	Up to 5,000 ppmvd
Inlet O2	20 to 25 %
Inlet CO	0 to 100 ppmvd

Quemetco’s Pilot Test Results:

Optimum Operation Temperature	175 degree F
Optimum Residence Time	4 seconds
NOx Removal	80 to 95 % DRE

Quemetco’s Pilot Test Report Conclusions

- BOC’s LoTOx process effectively removes 80 to 95 % of the NOx.
- Using LoTOx process allows the facility operator to optimize the combustion process to achieve the most cost efficient burner conditions without regard to the generation of NOx.

As the result of the demonstration project, BOC was awarded a contract to install a full-size LoTOx process Unit at Quemetco’s City of Industry, CA plant.²² Size, capital costs and operating costs were not disclosed.

In another situation, Ohio Coal Development Office (OCDO) provided 65 percent of the capital to install a \$6.3 million LoTOx unit at the Medical College of Ohio.²³ The project includes two processes: LoNOx for NOx and particulate material control and Rapid Absorption Process (RAP, another BOC licensed process) for sulfur dioxide control. The controls are for 25

megawatt capacity boilers burning Ohio coal containing 3 percent sulfur.

According to the BOC Company literature, the unit is designed to remove about 90 percent of the NO_x in emission gases. The RAP process uses a slurry of lime injected into the flue gas to capture SO₂ and a fabric filter (baghouse) to remove the calcium sulfate particles. According to the company, it is also designed for 90 percent DRE.²⁴ Cost effectiveness has been estimated to be in the range of \$1,700 to \$1,950 per ton NO_x removed.²⁵

In June 2001, BOC announced that they had installed, started up and commissioned a LoTOx unit at J & L Specialty Steel's Midland, PA plant. Details of the installation are sketchy. However, Robert Ferrell, BOC Vice President of Business Development, said, "We were able to modify the system to achieve a higher level of control than was originally anticipated. We have been able to reduce NO_x emissions by more than 95 percent."²⁶ No costs or capacity numbers were available.

A subsequent search of EPA's RBLC²⁷ Database indicate that at least two other plants in the U.S. are using (or are planning to use) BOC's LoTOx process in their facilities. These plants are Lion Oil Company in El Dorado, AR and Marathon-Ashland Oil in Texas City, TX. Both plants use (or will use) the LoTOx on their Fluidized-Bed Catalytic Cracking Units (FCCU) for NO_x control. Operating conditions and performance results are not available.

COST OF NON-THERMAL PLASMA

The problem with determining the cost of a new control technology is the lack of public information. So it is with non-thermal plasma.

One reference to cost was found in an article in the “FGD & DeNOx Newsletter²⁸ that describes the BOC’s LoTOx technology installed at the Medical College of Ohio. The exact statement that concerned cost effectiveness was, “Cost effectiveness of NOx removal using LoTOx on a 200 MW coal-fired electric generating unit with existing FGD was estimated to be in the range of \$1,700 to \$1950 per ton of NOx removed.” Unfortunately, the source of the estimate, the percent DRE, the furnace type, and a number of other variables were not identified.

Another article, written by a BOC employee²⁹, stated, “The capital (recovery) and operating costs for the (LoTOx) system have been evaluated for various system sizes and (they) fall well within the costs per ton of NOx removed typical for post-combustion treatment technologies in non-utility applications.” Unfortunately, this information is not very helpful since a paper published by NESCAUM³⁰ gives the cost effectiveness range for NOx removal from \$390 to \$5,450 per ton NOx. Cost effectiveness is heavily dependent on each individual facility’s situation. This includes their existing control equipment, extent of modifications necessary to install new control equipment, and the degree of DRE required to achieve the desired results.

Apparently, the LoTOx technology is not effective in removing multi-pollutants. In fact, at the facility cited above (the Medical College of Ohio), it was necessary for BOC to install another one of their licensed processes to remove sulfur dioxides (SOx) from the same emission stream that the LoTOx process was used on. The SOx process is called Rapid Absorption Process (RAP) and uses a lime slurry injected in the hot flue-gas prior to the fabric filter. Heat from the flue-gas dries the lime while SOx is absorbed on the lime. The contaminated lime is removed from the gas stream using a fabric filter.

No cost effectiveness numbers were found in the public records for the Powerspan process.

CONCLUSIONS

The following conclusions were made based on the data gathered during the research on non-thermal plasma.

1. It appears that non-thermal plasma technology works to reduce certain pollutants from emissions. However the technology is still in the early developmental stage. The control cost and control efficiencies need to be documented and published by an independent third party.
2. Multi-pollutant control appears to be possible using the Powerspan process.
3. Capital and operating costs for a turn-key installation are probably not available and can only be determined by the installation and operation of a pilot plant at the individual facility.
4. Until more information is published, BOC's LoTOx should be considered a single pollutant (NOx) control technology.

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