Recent development of plasma pollution control technology: 
a critical review

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Received 15 December 2000; accepted 28 February 2001

Abstract

Gaseous pollution control, solid and liquid waste treatments have been commercialized based on incineration, catalysis, adsorption, disposal with landfill, etc. More recently technology based on plasmas has become significant due to the advantages such as lower costs, higher treatment and energy efficiencies, smaller space volume, etc. In order to commercialize this new technology, the treatment rate, energy efficiency of treatment, pressure drop of reactor, reusable by-products production rate, must be improved, based on the identifications of major fundamental mechanism of processes, optimizations of reactor, and power supply for an integrated system. In this work, recent development of plasma pollution control technology was critically reviewed and the principle of processes and reactor technologies were outlined. Special attention will be focused on material processing generated pollutants. © 2001 Published by Elsevier Science Ltd.

Keywords: Material processing flue gas; Thermal plasma; Pollution control; Waste treatments; Non-thermal plasma; PFCs; VOCs; Greenhouse gas; ODS; Water contamination

1. Introduction

In a pollution control technology, normally three approaches are proposed as follows:

1. Collecting solid wastes for landfill and discharge liquid and gaseous wastes to water streams or open air with dilutions to accepted levels;
2. Conversion of wastes to harmless products such as water, N₂, CO₂, O₂ etc. and discharge to open air, water streams or landfills;
3. Conversion of wastes to a reusable product such as construction materials, agricultural fertilizers, syngases etc.

The aims of plasma gaseous pollution control solid and liquid waste treatment technologies are basically combining approach 2 for low concentration pollutants and approach 3 for high concentration pollutants. In other words, it is a near zero-emission technique.

In a conventional metal processing industry such as iron making, light metal processing, etc., the major gaseous pollutants are combustion generated pollutants such as greenhouse and acid gases. However, in a high technology industry such as semiconductor devices, glass fibres, ceramics, etc., the pollution gas becomes more complex and toxic. Hence, more advanced pollution control technologies such as plasma, catalytic, etc. are required. These problems are also true for water contamination liquid and solid wastes generated in high technology industries. In this paper, the recent development of plasma pollution control technology is critically reviewed and special attention also given to the advanced material processing generated pollutants.

2. Air and gaseous pollution control techniques

Air and gaseous pollutants can be categorized as follows: (1) particulate matter (PM); (2) acid gases (SO₂, NOₓ, HCl, etc.); (3) greenhouse gases (CO₂, NOₓ, PFCs — perfluoro-carbons, etc.); (4) ozone depletion substances (ODS — freons, halon, etc.); (5) volatile organic compounds (VOC — TCE, TCA, toluene, etc.); (6) toxic gases (Hg, dioxines, etc.); (7) radioactive gases (isotopes of C, Rn, I, Cs etc.); and (8) biological cells and bacteria.

2.1. Plasma pollution control devices

These pollutants are normally mixed and requires integrated pollution control systems to remove all pollutants. One advantage of plasma technology is to simplify these integrated systems. For example, an advanced indoor air
cleaning system requires PM control-devices (filters or electrostatic precipitator ESP), bacteria control devices (UV lamps or injecting chemicals), doors and VOC control devices (UV photocatalysts — normally needs different wave length UV lamps, catalysts, and adsorbents for each chemical species). However, non-thermal plasma method based on pulsed corona can act as the combined ESP, UV source and chemical decomposition reactor to reduce the volume of, or even removing in some cases, catalysts, adsorbents or injection chemicals for the treatment of mixed VOCs and odors.

Schematics of plasma devices used in a gas cleaning is shown in Fig. 1. Since details of the principle and nature of each device can be found in many recent reviews [1–4] only characteristics of plasma method and their plasma parameters are summarized in Table 1 [1]. Table 1 shows that the near atmospheric plasmas can be generated by [1,4]: (1) electron beam through vacuum shield window; (2) barrier discharges — silent, surface, barrier discharge radical injection, ferroelectric packed bed discharges; (3) pulsed corona and power discharges; (4) capillary tube spark discharges; (5) flow stabilized corona — corona radical shower, corona radical injection, corona torch systems; (6) DC, AC and grinding arc discharges and plasma torches; (7) RF discharge — inductive coupling and capacitive coupling discharge; and (8) microwave discharges. Plasma sources (1)–(3) and (5) are non-thermal plasmas and (4) and (6)–(8) are thermal plasmas, where non-thermal plasma sources are categorized based on the methods to stabilize streamer corona without transition to spark discharges [1]. These tables and various experimental results [1,2] show that depending on pollutants different plasma devices should be used for gas cleaning.

Plasma conversion of pollutants to harmless gases (approach 2) is normally using corona radial injection techniques based on reduction chemistry, where radical injection techniques using ammonia type reductants or hydrocarbons have also had the potential advantage of not activating unwanted flue gas components, CO2, O2 etc. to enhance energy efficiency. However, more recently plasma oxidation—catalyst reduction is also well developed for automobile exhaust cleaning applications [4]. Plasma conversion of pollutants to reusable by-products (approach 3) is normally oxidation chemistry and requires additives such as ammonia, hydrocarbons, Ca-based compounds, etc., but for gas to solid by-products conversion, an electrostatic precipitator is used for particle collection.

| Process | Gas | Process by-products in flue gases |
|---------|-----|----------------------------------|
| Ashing  | Toxic gas—ozone | Ozone, PM, etc. |
| Etching | PFCs, toxic gas | HF, fluorides, chlorides, etc. |
| Deposition | Toxic gas | SiO2, GeO2, metals, fluorides, PM, chlorides, etc. |
| Cleaning | PFCs | HF, fluorides, etc. |
| Nitrifying | Acid gas | NOx, NH3, PM, etc. |
| Substrate cleaning | VOCs, ODS | Fluorides, chlorides, hydrocarbons, PM, etc. |

a Waste gas destructions.
products as shown in Table 2. Since a major target gas (in terms of amounts) is a process equipment cleaning gas, PFCs such as NF₃, C₂F₆, CF₄, SF₆, etc., non-thermal plasma-adsorbent hybrid system could be the most promising, in terms of cost and effectiveness [9,10]. A typical mixed PFCs treatment by ferroelectric packed bed reactor-adsorbent hybrid system is shown in Figs. 2 and 3 for C₂F₆/CF₄ and NF₃/SiF₄ mixed PFCs, respectively [11].

Fig. 2 shows that C₂F₆ and CF₄ removal efficiencies increase with increasing applied AC peak-to-peak voltage with and without artificial zeolite adsorbent reactor at the downstream of reactor, where C₂F₆ removal efficiency is much higher than that of CF₄ due to the larger direct electron impact dissociation reaction rates [10]. Fig. 2 also shows that the hybrid system can prolong the life of zeolite adsorbent reactor (the major cost of the commercial zeolite
adsorbent reactor currently used in the semiconductor industry lies in the zeolite replacement and disposal-related costs). Fig. 3 also shows results similar to Fig. 2, but the plasma decomposition efficiency of NF3 is much higher than that of SiF4, CF4 and C2F6 due to the radical electronic and ionic processes [9].

3. Water and liquid treatments

Three types of plasma water and liquid treatment methods [3] have been used. They are as follows:

1. Remote plasma methods. Ozone and various hydroxyls were generated by a high-pressure discharge plasma reactor and injected into liquids. Glow discharge falling liquid film treatments are also in this category.
2. Indirect plasma/radiation methods. High and low pressure gas discharge lamps were used to generate UV with and without photocatalysts for treatments of waste. Electron beam and high-energy gamma irradiation of liquids are also in this category.
3. Direct plasma methods. Pulsed arc and/or pulsed corona discharges were generated in polluted liquid and treating liquid directly by electron, ion and radical chemical processes, as well as by pressure waves and supercritical formations.

![Image 1](https://example.com/image1.png)

**Fig. 2.** Removal efficiency of mixed PFCs as a function of applied voltage for simulated process flue gases (C2F6 = 1950 ppm, CF4 = 800 ppm, dry air = 1%, N2O = 1000 ppm and bal. N2) by ferroelectric packed bed-adsorbent hybrid reactor at $Q_F = 1$ l/min [11].

![Image 2](https://example.com/image2.png)

**Fig. 3.** Removal efficiency of mixed PFCs as a function of applied voltage for simulated process flue gases (NF3 = 1900 ppm, SiF4 = 900 ppm, N2O = 200 ppm, dry air = 1% and bal. N2) by ferroelectric packed bed-adsorbent hybrid reactor at $Q_F = 1$ l/min and dielectric constant of pellets = 106 [11].

Capabilities of these plasma methods for water treatment are compared in Table 4. Compared with conventional Cl injections with sand/gravel filters, ozone injections to replace Cl or adding UV–C lamps are the commercialized plasma techniques and pulsed arc, electron beam and UV-photocatalyst pilot scale tests are the on-going plasma processes. However, based on bench scale tests, a combination of more than two methods, hybrid or superimposed, may have more potential advantage compared with single stand-alone techniques.

Destruction of liquid waste oils, old-ODS, and solvents are mainly conducted by thermal plasma techniques [5] (discussed in Section 4), where all the toxic compounds based on Cl, F, Br etc. will be fixed to Ca-compounds for recycling, i.e. road construction materials.

4. Solid waste treatments

Solid waste plasma treatments mainly use thermal plasmas [6] and are divided into three types as follows:

1. Plasma oxidation/incineration methods. Non-combustible solid wastes were melted and oxidized in thermal plasmas for detoxification.
2. Plasma pyrolysis. Combustible solid wastes were melted

| Table 3 | Pollution control methods for advanced material processing |
|---------|----------------------------------------------------------|
| Methods | Operating pressure side | Treatment gases | Final products |
| Adsorbent/absorbent | High | PFCs, acid gas | Solid wastes |
| Catalytic incineration | High | PFCs | HF in water |
| Incineration/combustion | High | PFCs | HF in water |
| Non-thermal plasma | High | PFCs, VOCs, ODS | Ca compounds |
| RF plasma | Low | Deposition gas, acid gas | PM |
| Microwave plasma | Low | PFCs | Ca Compounds |
Table 4
Comparison of plasma and conventional water purification processes (▲ Good; O Adequate; △ Partial; X None)

| Target pollutants       | UV–C | UV photo-catalyst | Ozone | Electron beam | γ-Ray | Glow discharge | Barrier discharge | Pulsed corona | Pulsed arc | Sound gravel | Cl(ClO₂) |
|-------------------------|------|------------------|-------|---------------|-------|----------------|-------------------|---------------|------------|-------------|----------|
| Micro-organisms         | ▲    | △                | O     | △             | X     | X              | △                 | △            | △          | O          | △        |
| Oxidation power         | X    | △                | O     | △             | O     | O              | △                 | △            | △          | X          | X        |
| Algae destruction       | O    | △                | X     | △             | X     | X              | △                 | △            | △          | O          | △        |
| Urine components        | X    | O                | △     | △             | △     | △              | △                 | △            | △          | O          | △        |
| VOCs destruction        | X    | △                | △     | △             | △     | △              | △                 | △            | △          | O          | △        |
| Removal of inorganics   | X    | △                | △     | △             | △     | △              | △                 | △            | △          | O          | △        |

Table 5
Applications of thermal plasma solid waste treatments (OO good; △△ partially applicable; XX not applicable)

| Plasma processes                     | Municipal waste | Construction waste | Municipal sludge | Incineration ashes | Waste electronics | Polymer waste | Medical waste |
|--------------------------------------|-----------------|--------------------|------------------|-------------------|-------------------|---------------|---------------|
| Plasma oxidation/incineration        | △               | O                  | O                | △                 | △                | △             | O             |
| Plasma pyrolysis                      | O               | O                  | X                | X                 | △                | O             | O             |
| Plasma shock wave                     | X               | O                  | △                | X                 | O                | X             | △             |

in reductive gas environments to gasified and converted to reforming gases.

3. Pulsed arc generated shock wave. Pulsed arc or pulse power generated pressure waves were used to decompose solid wastes and separate them into metals, plastics, inorganics etc. for recycling.

Applications for the above mentioned three methods are summarized in Table 5. The majority of reusable by-products by plasma oxidation/melts are construction materials and oxidized metals for recycling, the plasma pyrolysis normally produces syngases (the mixture of CO, CO₂, H₂, HC, etc.) for combustion, iron ore reductions, driving gas for fuel cell, etc. One significant problem which applies to thermal plasmas is the formation of thermal NOₓ (10⁻¹⁻¹⁰⁷ ppm) in plasma flue gases. Hence the non-thermal plasma gas cleaning system is required as an integrated process.

5. Concluding remarks

Plasma pollution control technology for gaseous pollutants, liquid and solid wastes were critically reviewed. It is recommended that each pollution control technology must be evaluated based on: (1) the removal or treatment efficiency (%) and rates (kg/h); (2) the energy efficiency of removal or treatments (g/kWh or J/m³); (3) the pressure drop of devices (KPa/m); (4) the integrated system compositions; (5) the reusable material production rate (Kg/h); and (6) unwanted by-products concentration (ppm) as well as economic annual cost estimations. Depending on target pollutants and concentration of pollutants, different types of plasma processes and integrated pollution control systems should be used.

Acknowledgements

The author wishes to express his appreciation to T. Sato, K. Urashima, M. Inutake, T. Okhubo, T. Oda, G. Touchard, N. Karpel, Vel Leitner, A. Mizuno, J. Mizracyk, B. Locke, M. Sato for various discussions and comments. This work is supported by NSERC of Canada.

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