Industrial Application of Non-thermal Plasma (NTP) for Mercury and Dioxin Removal in Flue Gas

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Abstract. At present, there is an urgent demand for mercury and dioxin pollution control technology, internationally. It is necessary to find a solution other than the activated carbon adsorption process. In recent years, our self-developed low temperature plasma coupling system has been applied for mercury and dioxin removal in the flue gas, the system is composed of corona discharge plasma reactor and ceramic nano-material adsorption tank. The parameters of the plasma are 35-40kV, 400-450A, 1000Hz. The saturated adsorption capacity of ceramic nano-materials for Hg^{2+} is more than 5156 μg/(Hg^{2+})/g. Pilot plant tests have been conducted in several industries, including collaborative disposal of cement kiln, medical waste incineration, recovery of waste mercury catalyst, recycling of waste fluorescent tubes, and achieved ideal result (Hg removal efficiency > 95%). It is expected to be an economical and efficient technology for mercury and dioxin removal, with great promotion value and social significance.

1. Introduction
The current difficulty for mercury pollution control is Hg^0. Hg^{2+} and Hg^0 can be removed by conventional electrostatic dust removal device and bag filter, while Hg^{0} is water-insoluble and conventional dust removal equipment is inefficient [1]. At present, the main mercury removal technologies are activated carbon adsorption, wet / dry / semi-dry washing technology [2]. However, these synergistic mercury removal techniques are less efficient and will cause secondary pollution. Therefore, it is urgent to develop a special and efficient mercury removal technology.

The use of plasma technology to treat gas pollutants of flue gas is novel technologies that can accomplish many difficult things that ordinary gas gcan hardly achieve [3]. The type of gas discharge plasma includes glow discharge, corona discharge, dielectric-barrier, spark discharge, and microwave discharge etc [4]. It is considered as an attractive and promising method for flue gas deep purification. Plasma technique utilizes the energy generated in the non-equilibrium plasma microdischarge process to excite the dissociation of atoms and molecules in the gas, forming electrons, ions and free radicals, so that Hg is efficiently oxidized [5]. Meanwhile, high-energy particles generated by the NTP repeatedly bombard the dioxin gas in the exhaust gas at an extremely high speed, and the chemical
bond of the dioxins is twisted and broken [6]. Compared with conventional flue gas purification technology, plasma technique is a novel technology with high efficiency and low cost.

Recently, a kind of ceramic nanomaterial possessing higher Hg$^{2+}$ sorption capacity and satisfactory reproducibility were evaluated by our lab. The nanomaterial holds promise as an effective sorbent for the removal of Hg$^{2+}$ from flue gas from coal combustion and cement industry.

From the perspective of practical environmental treatment applications, the scheme of “plasma + ceramic nanomaterial” could solve the problem that flue gas treated by adsorption technology. As activated carbon based method is not economical to meet the Hg0 and dioxin emission standards and produce secondary pollution [7].

As reported in this paper, pilot tests for deep purification were set up, which determined the overall technical performance and effect. The applicability and effect of the equipment on mercury and dioxin containing tail gas are evaluated.

2. Methods

2.1. Non-thermal plasma

The power supply is based on the MARX generator circuit, which generates high voltage instantaneously (Figure 1.a). The technical parameters of 35KV power supply for plasma is listed as Table 1. Advanced switching devices and controlling effective energy storage circuits are adopted, which overcome the nanosecond emission challenge and successfully realized the pulse rising edge within 100ns, which achieves a higher duty cycle, greatly shortens the energy release time, and reducing instantaneous power (instantaneous power > 16MW). In addition, the product is designed to be adjustable from 0-1000Hz, which greatly improves the removal efficiency of pollutants and reducing operating costs.

![Figure 1. Circuit diagram of pulse power (a) and schematic of wire-cylinder reactor (b).](image-url)
The end of the discharge electrode of the wire-tube reactor has a large curvature, and its structure is shown in Figure 1.b. Generally, the distance between the two electrodes in reactor does not be adjusted, the discharge corona area is reasonable, the electron flow density in the corona space is average, the gas fluid characteristics are met, and the structure is favorable for separating the liquid, colloid or granular solid produced by the reaction.

2.2. Ceramic Nanomaterial
Ceramic nanomaterial with an adsorption capacity of ~5000μg/g has excellent capability and reproducibility to remove gaseous Hg\(_{2}^{+}\). The nanomaterial can be regenerated at least five times by thermal desorption.

| Item                        | Value | Unit | Notes                        |
|-----------------------------|-------|------|------------------------------|
| Waveform                    | Trapezoid | DC, high voltage, narrow pulse |
| Repetition rate (pulse frequency) | 0-1000 | Times/second  |
| Rising edge                 | <50-100 | Nanoseconds/time |
| Wave width                  | <200   | Nanoseconds/time |
| Pulse current               | 8-160  | A    |
| Input voltage               | 220    | V    | AC                           |
| Output voltage              | 35     | kV   | Peak                         |
| Output power                | 2      | kW   | Output power 2kW             |
| Instantaneous power         | 5.6    | MW   |

2.3. Pilot test of fly ash
The 50m\(^3\)/h plasma integrated system (Figure 2) is applied for flue gas demercuration, which composed of plasma reactor and ceramic nanomaterial adsorption device. Fly ash containing high concentration of mercury is discharged from the ash silo, and transported to the silo of the thermal desorption rotary kiln by spiral. After entering the rotary kiln, the fly ash slowly moves toward the kiln tail, and the temperature rises slowly. After sintering at an effective heating section of 150°C for 20 min, the mercury in the fly ash enters into flue gas. The flue gas containing mercury is taken out from the thermal desorption furnace, then pass through a condensing line (2°C, φ 47mm, 10m) and a bag filter.

High-voltage pulse power supply (21KV) is employed for the four stainless steel tubes NTP reactor. Nanomaterial adsorption device is installed after plasma reactor, which containing about 10kg ceramic nanomaterial. At the end of the system, a 2350Pa inverter fan (20-50Hz) was placed. Atmospheric sampling devices are used separately for total mercury and particulate mercury at the sampling rate of 0.5-1.5L/min. Finally, the mercury concentration is measured by ICP-OES.

![Figure 2. Pilot system for mercury removal from fly ash.](image)
2.4. Verification test of cement kiln

The 1000m³/h plasma system (Figure 3) is applied for flue gas demercuration at the tail of cement kiln. A tubular plasma reactor is applied, which composed of nine stainless steel tubes and titanium discharge electrodes wires, as listed in Table 2. Plasma can be generated by high-voltage pulse power (35KV), and then used for the treatment of mercury-containing flue gas. Two 300kg nanomaterial adsorption devices are placed behind plasma reactor. DN350 stainless steel tube is used as the inlet and outlet ducts. Hg0 is real-time detected by VM-3000 mercury vapor monitor.

| Item                  | Unit | Parameter |
|-----------------------|------|-----------|
| Tube length (l)       | cm   | 80        |
| Tube diameter (d)     | mm   | 85        |
| Number of tube (n)    |      | 10        |
| Effective volume (1 tube) | dm³ | 4         |
| Dwell time            | S    | 0.33      |

In the verification system, the non-thermal plasma integrated equipment is connected to the side line of the cement kiln in Beijing Jinyu Liushui Cement Plant. Kiln tail flue gas enters non-thermal plasma integrated system through the pipeline, a draft fan is set at the end of the pipeline.

2.5. Pilot plant testes of medical waste incineration

Pilot plant testes are conducted in Shanxi Runhe Environmental Protection Engineering Equipment Co., Ltd, whose designed incineration scale is 50tons/day, and the actual processing capacity is 20tons/day. In the process of incineration, the flue gas treatment adopts high temperature incineration (temperature above 1100°C) + flue gas quenching (temperature is reduced from 950°C to 299°C) + PBF (activated carbon injection + bag dedusting system) process to remove heavy metals and dioxins in flue gas. The exhaust emissions meet the requirements of the Hazardous Waste Incineration Pollution Control Standard (dioxin emission concentration 0.5ngTEQ/m³). In fact, due to the large changes in the composition of medical waste, the concentration of pollutants in the incineration flue gas of medical waste fluctuates greatly, and it is difficult to achieve stable discharge standards. It is urgent to improve the process and improve the efficiency of dioxin treatment. As shown in Figure 4 the project uses a combination of non-thermal plasma and nano-adsorption technology.
3. Results and discussion

3.1. Pilot test of fly ash
The results of the pilot test are shown in Figure 4. In each trial, 500g fly ash is thermal desorption at 500°C. The effective pyrolysis (>99%) time is 15min, and the flue gas outlet concentration is about 10mg/m³ Then, pyrolysis gas passes through the condensation line (2°C), the concentration of mercury in the gas reduced about 88%. 21kV 79A 420Hz is the optimal parameter of the power supply; under the optimal parameters, the oxidation rate of mercury in the pyrolysis gas by the non-thermal plasma is about 97%. No Hg⁰ was detected after passing through ceramic nanomaterials, Hgp was only detected at the end of the thermal desorption furnace, which was about 0.4mg/m³.

3.2. Verification test of cement kiln
The verification test results are shown in Table 3. The output performance of the non-thermal plasma system can reach a high level. Under the air volume of 150-450m³/h, without the interference of liquid
water, the non-thermal plasma system works well, and the system can stably achieve the mercury removal rate of about 95% for the flue gas of cement kiln.

### Table 3. List of mercury removal from flue gas of cement kiln.

| Volume (m³/h) | Voltage (kV) | Current (A) | Frequency (Hz) | Inlet (ug/m³) | Outlet (ug/m³) | Removal rate (%) |
|---------------|--------------|-------------|----------------|---------------|----------------|------------------|
| 150           | 38           | 100         | 800            | 230           | 8              | 96.4             |
| 250           | 38           | 100         | 800            | 220           | 6              | 97.2             |
| 350           | 38           | 100         | 800            | 213           | 9              | 95.7             |
| 450           | 38           | 100         | 800            | 256           | 15             | 94.1             |

3.3. **Adsorption effect of ceramic nanomaterials**

According to previous research experience, the residence time of flue gas in ceramic nanomaterials can be controlled by the amount of ceramic nanomaterials. The effect of adsorption time on the adsorption of Hg²⁺ on ceramic nanomaterials is shown in Figure 5. Then, the replacement time of ceramic nanomaterials at a certain amount can be inferred.

![Figure 5. Effect of residence time on adsorption rate of Hg²⁺.](image)

When the concentration of Hg²⁺ is 0.20-0.40mg/m³, the residence time of flue gas in ceramic nanomaterials is not less than 2s. The amount of ceramic nanomaterial is 300kg. The disposal volume is 1000m³/h and the treatment time is 8h/day. The average concentration of Hg²⁺ adsorbed by the material is calculated as 0.2mg/m³, and the mass of Hg²⁺ adsorbed by the material for 60 days is 120g.

3.4. **Pilot plant tests of medical waste incineration**

Intake conditions: particulate matter ≤ 50 mg/m³, water ≤ 15%, imported dioxins < 2 TEQ ng/Nm3. Plasma parameters: 33kV, 220A, 750Hz. Treatment effect: dioxins <0.1 TEQ ng/Nm³, mercury ≤0.01mg/m³. Dioxin removal efficiency is high: ≥ 95%; mercury removal efficiency is high: ≥95%.

4. **Conclusion**

As stated above, synergistic control of mercury and dioxins could be achieved in flue gas by NTP. NTP has the characteristics of small footprint and high degree of automation, no personnel operation is required on site during normal operation, environmentally friendly, does not consume water, and the
adsorbent material can be regenerated. For 10,000 m$^3$/h scale, operating cost of NTP system is as low as 125,600 yuan/a. Therefore, NTP system is potential to be an economical and efficient technology for mercury and dioxin removal, with great value and social significance.

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