Case study on the application of low-temperature plasma integration technology for the treatment mercury-containing waste gas from the crushing process of waste fluorescent lamps

Feng Qinzhong1,2, Chen Yang1,2*, Liu Liyuan1,2, Wei Shihao1,2, Wang Junfeng1,2, Li Yue1,2, Shen Ying3, Feng Xu4

1. University of Chinese Academy of Sciences, College of Resources and Environment, Beijing China
2. State Environmental Protection Engineering Center for Mercury Pollution Prevention and Control, Beijing, China
3. Beijing Ecological Island Technology Co., Ltd. Beijing, China
4. University of Queensland, Brisbane, Australia

*The corresponding author’s e-mail address: chenyang@ucas.ac.cn

Abstract: Because mercury has the characteristics of volatility, toxicity and global migration, mercury pollution has become a hot, difficult and focus issue of global concern. Based on China’s environmental technology verification method, the case study for low-temperature plasma integrated technology for the treatment mercury-containing exhaust gas in the treatment process of waste fluorescent lamps was carried out. The total gaseous mercury in the exhaust gas after treatment was less than 0.01mg/m³, which met the emission limit requirements in the Emission Standard (GB16297-1996). The pulse voltage of the plasma power supply is 10-35kV, the pulse current is 8-160A, and the pulse frequency is 100-1000Hz. Case study showed that low temperature plasma integrated treatment technology is the available technology for advanced treatment of mercury-containing waste gas.

1. Introduction
Mercury is volatile, persistent, toxic, and bio-enriched, improper management and disposal of mercury can cause environmental safety issues1,2. The Minamata Convention on Mercury officially entered into force on August 16, 20173,4, and its management and control measures run through the entire life cycle of mercury. Waste fluorescent lamp is one of the main sources of mercury pollution in the environment in China. The discarded mercury-containing lighting appliances in China are equivalent to 1 billion standard fluorescent lamps of 40 watts. At present, the main waste lamp treatment processes used in China are divided into landfill, incineration and dry recycling processes. The dry process includes two methods: end-purge separation and direct crushing and separation, which are useful for the recycling of mercury and rare earth materials. The mercury-containing waste gas generated during dry process treatment mostly adopts silver-loaded activated carbon adsorption technology, which has a high processing cost. The saturated activated carbon becomes a hazardous mercury-containing waste, and subsequent disposal is still required.
Since the mid-1990s, EPA in the United States, Canada, Japan, and South Korea have successively established and implemented environmental technology verification (abbreviation: ETV) systems. ETV is a relatively objective evaluation method. The verification object is usually various types of environmental innovation technologies that have just been commercialized or have commercial potential. The core of ETV is to comprehensively evaluate the environmental performance of the technology within a certain test period, that is, test technology performance parameters under actual operating conditions. In China, the Ministry of Ecology and Environment has also carried out active exploration and research for ETV, the "Environmental Technology Verification-General Specification for Testing (Trial)(T/CSES 2-2015)" and "Environmental Technology Verification-General Specification (Trial)(T/CSES 1-2015)" were implemented in 2015. At present, more than 30 environmental protection technologies in China have passed the verification using this method.

Compared with activated carbon adsorption technology and other removal technologies, low-temperature plasma technology has the characteristics of high mercury removal efficiency, deep purification, and less secondary pollution. It has become a research hotspot in the control of mercury pollution in exhaust gas. The case study was implemented in a Beijing technology limited liability company.

The case study results showed that the mercury removal efficiency is stable to more than 95%, and the total gaseous mercury in the exhaust gas after treatment is less than 0.01mg/m³. Other pollutants in the exhaust gas also meet the emission limit requirements in the Emission Standard "Comprehensive Emission Standards for Air Pollutants" (GB16297-1996). The pulse voltage of the plasma power supply is 10-35kV, the pulse current is 8-160A, and the pulse frequency is 100-1000Hz. Case study showed that low temperature plasma integrated treatment technology is the available technology for advanced treatment of mercury-containing waste gas.

2. Principle of mercury removal by low-temperature plasma integrated technology

Low-temperature plasma integration technology is an emerging treatment technology that integrates new environmentally friendly adsorption materials with plasma super oxidation as the core to achieve high-efficiency removal of mercury in flue gas. The mechanism is that the electrons continuously accelerate in the electric field to obtain energy and then form high-energy electrons, and inelastic collisions with N₂, O₂ and other gas molecules, which excite, ionize, and dissociate N₂, O₂ and other ground-state molecules (atoms) to generate free radicals and active particles such as O, OH, O₃, so that the pollutant molecules will oxidize in a very short time, and convert Hg⁰ into Hg²⁺, Hg⁺, and the targeted adsorption material realizes the process of Hg²⁺ and Hg⁺ capture and adsorption to achieve the purpose of purifying gas. The process flow is shown in Figure 1.
3. Application Case Location
The case study was in a mercury light source workshop of a Beijing company. The mercury-containing
exhaust gas with a flue gas volume of 1000m³/h was produced in crushing waste fluorescent lamp tube
process. At present, the company adopts the MRT treatment method and uses the silver-loaded activated
carbon to adsorb mercury-containing waste gas. Due to the high price of silver-loaded activated carbon,
the company urgently needs advanced technology to reduce operating costs.

The evaluation device is installed at the end of the company’s MRT production facility to implement
the purification treatment of the existing mercury-containing waste gas. The site layout of plasma
integrated equipment is shown in Figure 2.

![Figure 2 Field processing equipment diagram](image)

4. Case study process

4.1. Test parameter setting
The test parameters are divided into three categories: environmental effect parameters, operating process
parameters, and maintenance management parameters. In the case study, the appropriate parameters
were selected according to the characteristics of low-temperature plasma integrated processing
technology and the verification objectives, as shown in Table 1.

| Parameter category         | Specific parameters                                  |
|---------------------------|------------------------------------------------------|
| Environmental effect      | import and export flue gas                           |
| effect parameters pollutant emissions | temperature, pressure, gas flow                  |
|                           | atmospheric pollutant content of mercury, NOx, SO2 and particulate matter |
|                           | solid waste pollutants mercury salt             |
| Operating process         | low temperature plasma equipment equipment stable running time |
| parameters                | pulse frequency                                    |
|                           | pulse voltage                                      |
|                           | pulse current                                      |
|                           | processing gas scale amount of flue gas processed per unit time |
| Maintenance management    | power systems power consumption                      |
| parameters                | adsorption materials consumption                    |

4.2. Sampling and analysis of gas samples
(1) Collection of gas samples
According to the standard "Determination of Particulate Matter in Exhaust Gas from Fixed Pollution
Sources and Sampling Methods of Gaseous Pollutants" (GB/T 16157-1996), gas samples are sampled at the entrance of the system and the exit of the targeted adsorption device.

(2) Analysis method of gas samples
The test parameters of the sample are mercury and its compounds, NOx, SO2, particulates, exhaust gas temperature. The analysis methods are shown in Table 2.

| Analysis parameters | Analytical method                          | Method source                                                      |
|---------------------|--------------------------------------------|-------------------------------------------------------------------|
| Total mercury       | Cold atomic absorption spectrophotometry   | HJ 543-2009 Stationary source emission-Determination of mercury- Cold atomic absorption spectrophotometry |
| SO2                 | Iodometry                                  | GB 13271-2014 Boiler air pollutant emission standards             |
| NOx                 | UV spectrophotometry                       | GB 13271-2014 Boiler air pollutant emission standards             |
| Particulates        | Dust measurement method                    | GB/T 5468-1991 Boiler smoke test method                          |

5. Case study results and analysis
The case study started on March 15, 2017 and ended on March 30, 2017. The time span was 16 days.

5.1. Environmental effect parameters

5.1.1. Test data of gaseous total mercury
The change trend of total mercury in the exhaust gas at the system outlet is shown in Figure 3. The test results of the total mercury concentration are lower than the emission limit of 0.01mg/m³.

![Fig. 3 Change trend of total mercury concentration in the exhaust gas from the system](image)

5.1.2. Test data of NOx, SO2, particulate matter
The nitrogen oxide and sulfur dioxide test results were below the detection limit, and the particulate matter concentration was below the emission standard. The particulate matter concentration are shown in Figure 4.
5.1.3. Ambient air test data

(1) The change trend of the total mercury concentration in the working environment air is lower than the emission standard as shown in Figure 5.

(2) The detection results of nitrogen oxides and sulfur dioxide were below the detection limit, and the particulate matter concentration was lower than the emission standards of the Comprehensive Emission Standard for Air Pollutants (GB16297-1996). The particulate matter concentration are shown in Figure 6.
5.1.4. Analysis of test results
The exhaust gas sample test results are summarized in Table 3.

| Test items                     | Test Results(mg/m³) | Emission limits(mg/m³) |
|-------------------------------|--------------------|------------------------|
| Total mercury content in exhaust gas | 0.0057-0.0091      | 0.012                  |
| NOx content in exhaust gas    | N.D                | 240                    |
| SO2 content in exhaust gas    | N.D                | 260                    |
| Particulates content in exhaust gas | 0.5-5.9         | 120                    |
| Total mercury content in ambient air | 0.0022-0.0039    | 0.01                   |
| NOx content in ambient air    | N.D                | 5                      |
| SO2 content in ambient air    | N.D                | 15                     |
| Particulates content in ambient air | 0.5-1.3          | 10                     |

It can be seen from Table 3, treatment effect compliance rates of total mercury, nitrogen oxides, sulfur dioxide, and particulate matter in the exhaust gas and the ambient air of the operation during the case study are all 100%. The specific analysis is as follows:

1) The total mercury concentration in the exhaust gas of the system outlet is 0.0057-0.0091 mg/m³, which is lower than the emission limit requirements of mercury and its compounds (calculated as Hg, 0.012 mg/m³) in the "Comprehensive Air Pollutant Emission Standard" (GB16297-1996). The total mercury concentration in the working environment is 0.0022-0.0039 mg/m³, which is far lower than the maximum allowable concentration of mercury (0.01 mg/m³) in the "Design Standards for Industrial Enterprises" (GBZ1-2010).

2) The concentration of nitrogen oxides in the system outlet and operating environment is lower than the detection limit, far lower than the emission limit (240 mg/m³) of "Comprehensive Emission Standard of Air Pollutants" (GB16297-1996) and the emission limit (5 mg/m³) in the "Design Hygiene Standard for Industrial Enterprises" (GBZ1-2010).

3) The particle concentration in the system outlet and operating environment is stable between 0.5-5.9 mg/m³ and 0.5-1.3 mg/m³, which is far lower than the emission (120 mg/m³) in the "Comprehensive Emission Standards for Air Pollutants" (GB16297-1996) and the limits and the maximum allowable concentration (10 mg/m³) in the "Design Hygiene Standard for Industrial Enterprises" (GBZ1-2010).

4) The concentration of sulfur dioxide in the system outlet and operating environment is lower than the detection limit, far lower than the emission limit (7550 mg/m³) of "Comprehensive Emission Standards for Air Pollutants" (GB16297-1996) and the maximum allowable concentration (15 mg/m³) in the "Design Sanitation Standards for Industrial Enterprises" (GBZ1-2010).

5) No mercury-containing particulate matter was collected in the reactor. The total mercury concentration test result after the reactor was similar to the inlet gas concentration. The total mercury reduced by the system was adsorbed in the ceramic adsorption nanomaterial in the form of oxidized mercury. The total mercury mass is too small to measure the mass.

5.2. Operating process parameters
The operating process parameters and maintenance management parameters are measured and recorded, which are recorded in Table 4.

The low-temperature plasma integrated processing system continuously operated for 72 hours from March 15 to March 17. The mercury concentration at the inlet was stable at about 0.21 mg/m³ and was less than 0.012 mg/m³ at the outlet. The mercury removal amount is 0.2 mg/m³, the gas flow is between 600-1000 m³/h, the system internal pressure is stable at about -6500 Pa, and the power consumption is stable at about 0.5 kW·h. No water used in the treatment system.
Table 4 Record table of operating process parameters and maintenance management parameters

| Batch  | Waste disposal | Energy consumption | Process parameters |
|--------|----------------|--------------------|--------------------|
|        | Mercury concentration at the inlet (mg/m³) | Mercury concentration at outlet (mg/m³) | Power consumption (kW·h) | Pulse peak voltage (kV) | Pulse frequency (Hz) | Gas pressure (Pa) | Gas flow (m³/h) |
| Maximum value | 0.2371 | 0.0091 | 0.6 | 30 | 1000 | - | 6800.00 | 1000 |
| Minimum value | 0.1384 | 0.0057 | 0.4 | 21 | 100 | - | 6100.00 | 600 |
| Average value | 0.1992 | 0.0074 | 0.5 | - | - | - | 6500.00 | - |

5.3. Maintenance and management parameters

Maintenance management parameters mainly include the power consumption and the amount of absorbent materials in the process of low-temperature plasma device operation.

1) Direct cost
   The direct cost mainly includes three items: the pulse power supply, the power consumption of the system fan, and the consumption of the adsorption material. The direct cost is not higher than 20.67 yuan/1000m³ (exhaust gas mercury).

2) Indirect costs
   The indirect cost is 20.00 yuan/1000m³ (exhaust mercury).

3) Total cost
   The total cost is not higher than 40.67 yuan/1000m³ (exhaust gas mercury).

Compared with the silver-loaded activated carbon adsorption process, the low-temperature plasma integrated system reduces the disposal cost while achieving mercury emission standards.

6. Case study conclusion

According to case study results, low temperature plasma integrated treatment technology is the available technology for advanced treatment of mercury-containing waste gas.

1) The mercury removal efficiency is stable to more than 95%, and the total gaseous mercury at the outlet is less than 0.01mg/m³; other pollutants at the outlet have also reached the emission standard. All meet the emission limit requirements in the "Comprehensive Air Pollutant Emission Standard" (GB16297-1996).

2) The concentration of total mercury, NOx, SO2 and particulate matter in the ambient air meet the emission standards of "Design Standards for Industrial Enterprises" (GBZ1-2010).

3) The exhaust gas volume is 1000m³/h (limited by the field experiment conditions), which can be adjusted automatically.

4) The system power consumption is 15.24Wh/m³ (exhaust gas mercury), no water required for gas treatment process, the operating cost is not higher than 20.67 yuan/1000 m³ (exhaust gas mercury), and the total cost is not higher than 40.67 yuan/1000m³, it is lower than the operating cost of the currently used activated carbon adsorption technology.

5) The pulse voltage of the plasma power supply is 10-35kV, the pulse current is 8-160A, and the pulse frequency is 100-1000Hz. The operating parameters of the facility are normal, satisfying continuous and stable operation for 72 hours.

7. Application prospect analysis of low temperature plasma integration technology

In China, there are a wide range of sources of atmospheric mercury pollution, typical industries such as cement, coal, and waste incineration are key sources of mercury emissions. At the same time, to solving the problem of mercury pollution, it is also necessary to consider the emission of multiple pollutants such as dioxin, NOx, SO2, dust and so on.
The case study of low-temperature plasma deep purification technology and integrated equipment will help to promote its engineering applications in major mercury-related industries such as co-processing fly ash, waste incineration, and waste mercury catalyst disposal in cement kilns [18,19]. In this way, it can solve the technical bottleneck of mercury and dioxin and other pollutants in the key mercury-related industries [20] and comprehensively promote the implementation of the Minamata Convention on Mercury and improve mercury pollution control capabilities in China [21].

Acknowledgements

Financial support from National Key Technologies R&D Program of China 《Integration and industrialization of non-conventional pollutant air pollution prevention and control technology》 (2016YFC0209204) and Shanxi Province Key R&D Project 《Research on Waste Fluorescent Tube Treatment and Resource Recovery Technology》 (201903D321063).

References

[1] Yue, L., Yang, C., Feng, Q.Z., et al. (2019) Study of the adsorption mechanism on the surface of a ceramic nanomaterial for gaseous Hg(II) removal. Environ. Sci. Pollut. R., 26:28294-28308.
[2] Hou, M., Liu, R., Zhao, J., et al. (2020) Current situation and prospect of mercury removal technology from bituminous coal flue gas with adsorbent. Multipurpose. Util. Miner. R., 1(1):25-28.
[3] Ministry of Environmental Protection of the People's Republic of China, Ministry of Foreign Affairs of the People's Republic of China, National Development and Reform Commission of the People's Republic of China, etc. Announcement on the entry into force of the Minamata Convention on Mercury [No. 38, 2017]. [2017-08-20]. http://www.mee.gov.cn/gkml/hbb/bgg/201708/t20170816_419736.htm.
[4] Ye, J., Xu, J., Wang, Y. J., et al. (2018) Mercury-containing waste and suggestions on the conversion implementation in China. Environ. Pollut. Prevention., 40(5):616-619.
[5] Feng, Q. Z., Chen, Y., Liu, L. Y., et al. (2017) Application case study on high temperature dry heat technology for medical waste treatment. Environ. Eng., 35:438-443.
[6] Areyiguli., Chen, Y., Jia, B. J., et al. (2013) The mechanism of cooperative disposal of Hg\(^0\), NOx, SO\(_2\) by low temperature plasma. Environ. Eng., 31(5):67-70.
[7] Wei, S. H., Xu, D. D., Chen, Y., et al. (2017) Low-temperature plasma-ceramic nano materials intergerated system for flue gas demercuration research. Environ. Eng., 11:99-103+159.
[8] Sun, H., Zhang,Y., Zhang, A. C., et.al. (2020) Research progress of NO and Hg\(^0\) removal from waste gas by low temperature plasma technology. Energy Res. Manage., 1: 10-13.
[9] Fan, Y. X., Chen, Y., Yin, L. Q. (2017) Research on Hg\(^0\) oxidation effect by pulse corona induced plasma chemical process. Environ. Eng., 3:82-86.
[10] Environmental Protection Technology Verification and Evaluation Alliance, Chinese Society of Environmental Sciences. Evaluation report of low-temperature plasma integrated treatment technology for waste gas containing mercury (CNETV-2017-05), 2017.5.
[11] Zhen, L., Yang, C., Feng, Q. Z., et al. (2019) Industrial application of non-thermal plasma for mercury and dioxin removal in flue gas. IOP Conf. Series: Mater. Sci. Eng., 677:032022.
[12] Zhang, Y. S., Zhang, Y., Wang, T., et.al. (2019) Oxidation of elemental mercury with non-thermal plasma coupled with a wet process. Fuel, 197:320-325.
[13] Chen, Z. M., Liu, H. X., Cui, Y., et.al. (2019) Study on generation, treatment, testing and emission characteristics of Hg in flue gas of coal-fired power plants. Power Generation Technol., 40(4):355-361.
[14] Wang, Y. G., Li, X. (2019) Investigation of mercury emission from typical cement plants in some areas of China. Cem. Technol., 1:26-28.
[15] Wang, D. D., Lou, J., Zhang, S., et.al. (2019) Factor of oxidizing elemental mercury by surface discharge plasma. J. Shandong University Technol. (Nat. Sci. Edition), 33(1):1-5.
[16] Driscoll, C. T., Mason, R. P., Chan, H. M., et al. (2013) Mercury as a global pollutant: sources,
pathways, and effects. Environ. Sci. Technol., 47(10): 4967-4983.

[17] Wang, X. F., Wang, F., Wang, H. M., et al. (2018). Emission characteristics of pollutants from cement kilns with industrial wastes handling. Environ. Chem., 37(12):2784-2789.

[18] Jiang, Y. Y., Liang, M. S., Chen, Y., et al. (2019) Analysis of influencing factors on degradation of trichlorobenzene, a precursor of dioxin by pulse corona plasma. Environ. Eng., 37(7):124-129.

[19] Zhang, L. J. (2017) Research on simultaneous removal mercury and dioxins from flue gas with non-thermal plasma [D]. Beijing: Master Degree Thesis of North China Electric Power University (Beijing).

[20] Zhu, T., Zhang, X., Chen, Y., et al. (2019) Influence of gas atmosphere on synergistic control of mercury and dioxin by non-thermal plasma. High Voltage Eng., 45(6): 1907-1914.

[21] Hao, S. S., Chen, Y., Yin, L. Q., et al. (2016) Mechanism research of Hg⁰ oxidation by pulse corona induced plasma chemical process. Environ. Sci. Eng.: B, 1:1-10.