

Multi-pollutants Simultaneous Removals from Flue Gas

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Abstract: With the stricter emission standards, more pollutants in the air need to be controlled. If the traditional mean of using a technology to treat a pollutant is adopted, there are high investment running cost and complex operation system. So the multi-pollutants simultaneous removal technology from flue gas is paid more and more attention in the recent ten years. The plasma technology and semi-dry flue gas cleaning technology are two very promising multi-pollutants simultaneous removal technologies. In our researches, a plasma technology of corona radical shower and a semi-dry flue gas cleaning technology using circulating suspension and multistage humidification were selected. A series of fundament and industry application works were done. In the paper, some current results are opened out to provide some reference.

Keywords: Multi-pollutants, simultaneous removal, plasma, semi-dry

1 INTRODUCTION

China is the largest exploiter and consumer of coal in the world. Since the 1980s, coal consumption has continuously grown by 4%-9% every year, which produced various atmosphere pollutants including dust, SO₂, NO_x, heavy metal, etc. The annual economic loss only caused by acid rain exceeds 100 billion RMB. Coal is mainly used for power plant boilers, industrial boilers and industrial furnaces in China. So these boilers and furnaces become the emphases treatment objects. According to the statistic, 25.49 million tons of SO₂ was emitted in 2005. What's more serious, the emission of SO₂ reached 25.888 million tons in 2006. NO_x emission is increasing year by year. The total amount of NO_x emission has been more than 18 million tons currently. If some effective measures don't taken, NO_x emission will reach 30 million tons after ten years. Some reports show that the average NO₃⁻ concentration of the precipitation in the 1990s is 2.1 mg/L. However, it is 2.8 mg/L from 2000 to 2003. Equivalent concentration ratio of NO₃⁻ and SO₄²⁻ of the precipitation also presented an upward trend since 1999. It is 0.17 in 2003, the highest value in the last 14 years [1,2].

To prevent air pollution from becoming worse, many law, statute, policy and standard have been established. "The Outline of the Eleventh Five-year Plan for National Economic & Social Development of the PR China" (hereinafter referred to as 'the outline') claims that energy consumption per-unit GDP must descend 20% and major pollutants descend 10% during the 11th Five-Year Plan in Mar, 2006. To achieve the SO₂ control target, the work of energy saving and emission reduction has been emphasized strongly since 2006. In Jun., 2007, a special work group led by the Premier, Wen Jiabao, was come into existence to respond to climate change, energy saving and emission reduction. From these actions, it can be appeared that pollutant emission reduction has

obtained unprecedented attention in China. The future energy structure of China will be no significant change. Coal is still the main energy source. China certainly faces the terrible flue gas multi-pollutants control problem.

Through the long-term investigation and engineering practice, the developed countries have basically solved dust, SO₂ and NO_x emission problem under the existing emission standards. The corresponding control equipment has been widely used. In China, dust collector and DeSO₂ from flue gas have already had a good application. The research and industrial application of flue gas DeNO_x have been underway on the support of overseas technology. However, for multi-pollutants reductions from flue gas, the commonly adopted pathway is that these pollutants are treated respectively using different processes, e.g., SO₂ reduction by wet flue gas DeSO₂ (WFGD) and NO_x reduction by selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR). Subsequently, high investment cost, large installation space and complex system will appear. This is a headachy problem for some developing like China. Fig. 1 shows the traditional pollution control combination system from flue gas.

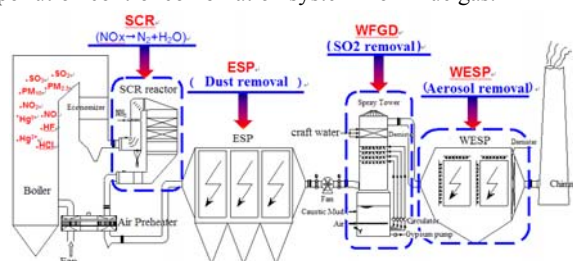


Fig. 1 The traditional combination techniques for flue gas multi-pollutants control

To overcome the shortcomings of the existing flue gas pollution control technology, simultaneously controlling two or more pollutants has become a research hotspot at home and

abroad. Some developed countries such as USA, Germany and Japan have carried out very active investigation on the simultaneous removals for multi-pollutants in the recent ten years. Through the long-term effort, some technologies have already been in the early commercialization stage. Currently, the simultaneous removal technologies focus SO_2 and NO_x mainly. The concrete technologies are as follows: active carbon [3], SNO_x [4], SNRB [5], NO_xSO_x [6], electron beam (EB) [7]. But most technologies are in the demonstration stage due to unripe craft. For example, the EB devices installed in the Chengdu Thermoelectric Plant and Hangzhou Xielian Thermoelectric Plant have been stopped operating because of serious erosion, high energy consumption, ammonia pollution and low running reliability.

In a word, developing a high-efficiency, stable operation and inexpensive multi-pollutants simultaneous control technology is very pressing and necessary. The fundamental theory research needs to be strengthened. We always go on the research on the flue gas multi-pollutants simultaneous removal technology using plasma and semi-dry flue gas cleaning methods since 1998. In the paper, some researching results will be provided to discuss.

2 PLASMA MULTI-POLLUTANTS FLUE GAS CLEANING TECHNOLOGY

Plasma has an important role in treating the complex and toxic pollution gases. It expresses a special ability of non-selectivity for multi-pollutants, high reduction efficiencies and rapid chemical reaction, so using plasma to treat various gaseous pollutants at one time is being paid more and more attention recently.

2.1 Plasma Devices

The core of plasma pollution control technology is how to generate high-activity plasma. Many plasma generation methods have been developed. Some schematics of plasma devices commonly used in a flue gas cleaning system are shown in Fig. 2. The details of principle and nature of each device can be found in many recent reviews [8-12]. From Fig. 2, the plasma can be generated through the following methods: (1) EB; (2) dielectric barrier discharge; (3) corona radical shower; (4) pulsed corona; (5) arc discharge; (6) RF discharge; (7) microwave discharge.

EB and pulse corona are two non-thermal plasma technologies that are earlier and more broadly used for flue gas treatment. However, overmuch energy consumption is always a puzzled problem that restricts their large-scale industry applications. High-energetic electrons from EB or pulse corona are directly injected into the reactor and collided with the main components of flue gas (N_2 and CO_2), which will lead to much energy waste [13].

In order to improve energy efficiency of plasma technology, Chang et al [14-17] brought forward a corona radical shower (CRS) system. A nozzle electrode was used as a discharge electrode instead of corona wire. Under strong electric field, the stable and intensive corona can be formed

near the nozzle. What's better, the high-energetic electrons mainly collided with additional gas from nozzle, which makes the energy loss obviously decrease. So the CRS technology was chose for flue gas multi-pollutants simultaneous removal in our research.

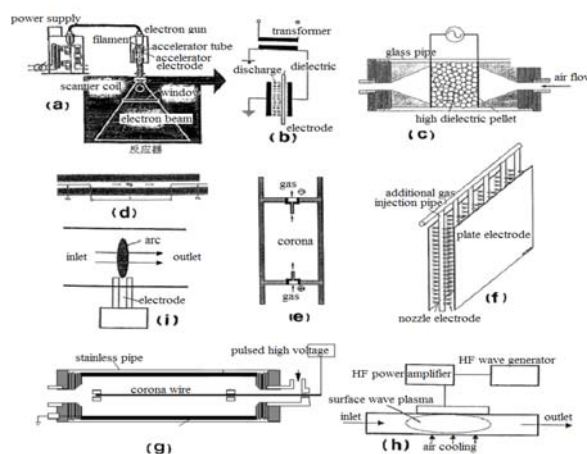


Fig. 2 Some plasma devices [12]

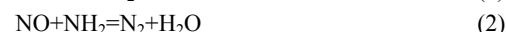
2.2 The CRS Multi-pollutants Simultaneous Removal

In the CRS technology, a pipe electrode with nozzles was used as a discharge electrode. Positive DC high voltage was applied to the nozzle electrode where active radicals were produced. Additional gases (O_2 , H_2O , NH_3 , etc.) were introduced into the pipe and injected into the reactor through the nozzle. Because of intensive electric field at the tip of nozzle, the additional gases from nozzles were dissociated into various active species (such as OH^* , O^* , O_3 , etc.). Therefore, more electrons were collided with the additional gas molecules but not N_2 and CO_2 in the flue gas. As a result, the energy waste will decrease much.

In our research, the simultaneous removals of SO_2 and NO_x using CRS system can be achieved through two processes according to the different additional gases.

(1) NH_3 as the additional gas. In this process, SO_2 removal mainly depends on the thermal chemical reactions between SO_2 and NH_3 [18]. But NO_x removal depends on the radical reactions during corona discharge SO_2 removal mechanism isn't given unnecessary details. NO_x may be removed through the following approaches:

(a) The direct reduction processes with NH and NH_2 produced by NH_3 dissociation could take place when NH_3 was injected from nozzle electrode. The corresponding reactions are as follows [19]. Comparing with NO , no significant NO_2 direct reduction reactions take place with the addition of NH_3 [20].

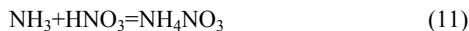
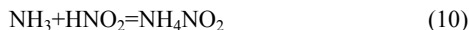


(b) Since air is used as the balance gas of NH_3 in the additional gas, N_2 and O_2 will be dissociated or ionized to assist direct reduction and oxidation under strong streamer corona. The possible reactions are as follows [19]:





(c) Because there is little H_2O , the following reaction could be generated [19]:



(d) In addition, $(\text{NH}_4)_2\text{SO}_3$ and NH_4HSO_3 generated by the thermal chemical reactions of SO_2 and NH_3 can also reduce NO_2 into N_2 .



In the CRS system of NH_3 as the additional gas, the final byproducts are dry $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , which can be collected through a ESP or FF. The applicative schematic diagram is shown in Fig. 3.

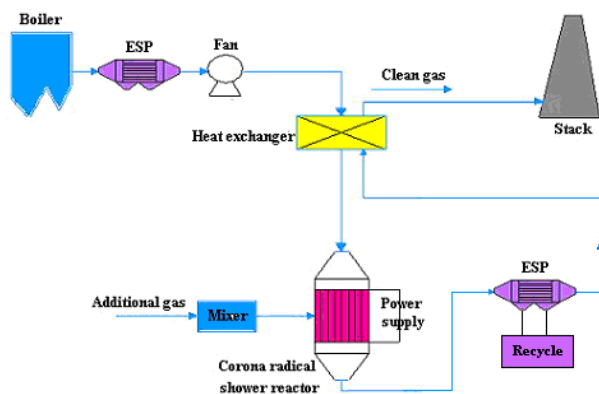


Fig. 3 The applicative schematic diagram using the CRS system of ammonia as additional gas

(2) O_2 as additional gas. In this process, NO is oxidized into NO_2 firstly in the CRS system. And then NO_2 can be absorbed by $\text{Ca}(\text{OH})_2$ or NaOH . The NO oxidization process can be express as follows [19]:



However, SO_2 is oxidized very little in the CRS system of O_2 as additional gas [21]. How to absorb SO_2 and these NO oxidized byproducts becomes a hot potato. In fact, many WFGD systems have been operated in China. Considering that NO_2 can be absorbed well by alkali solution, if the CRS system of O_2 as additional gas is set up before the former WFGD, SO_2 and NO_x can be removed simultaneously. Furthermore, the whole system can be applied in the reconstruction of the former WFGD, which will decrease investment cost greatly. For developing countries like of China, it is a certainly good idea. The applicative schematic diagram is shown in Fig. 4.

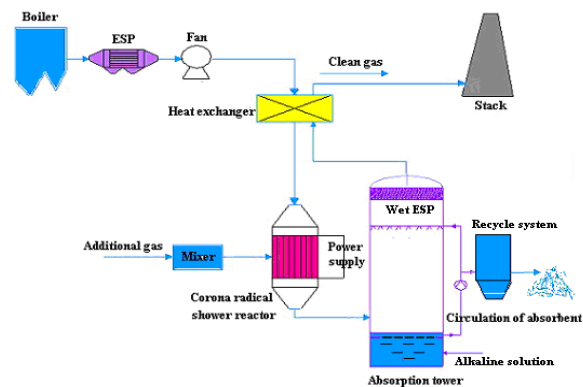


Fig. 4 The applicative schematic diagram using the CRS system of oxygen as additional gas

2.3 The CRS System of Ammonia as the Additional Gas

Some experimental results were given about the simultaneous removals of SO_2 and NO_x . SO_2 and NO initial concentrations are 205 ppm and 160 ppm respectively. $[\text{NH}_3]/([\text{NO}]+[\text{SO}_2])$ MR value was 0.5, 0.76, 1 and 1.2 respectively. Fig. 5 shows SO_2 removal rate under different MR. It is clear that SO_2 removal rate improves obviously without corona discharge with the increasing MR. Under 0.76 MR, SO_2 removal rate reaches 76% without corona discharge. After discharge, SO_2 removal rate can improve 20%.

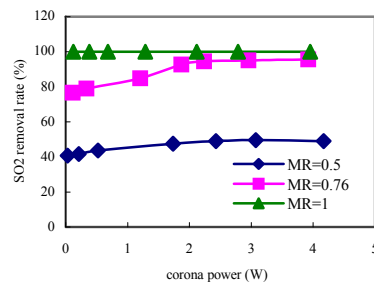


Fig. 5 SO_2 removal using a CRS of ammonia

In addition, NO and NO_x removal rates under different MR are also analyzed in Figs. 6 and 7 respectively. With the increasing MR, NO removal rate has not obvious change. For NO_x removal, when the MR increases from 0.5 to 0.76, the NO_x removal rate increases quicker. With the further increasing MR, the increasing rate becomes slow. The NO_x removal rate is 27.5%, 31%, 31% and 31.5% respectively under 3 W power. From the two figures, NO and NO_x removal rates depend on the input power. With the increasing power, NO and NO_x removal rates improve obviously.

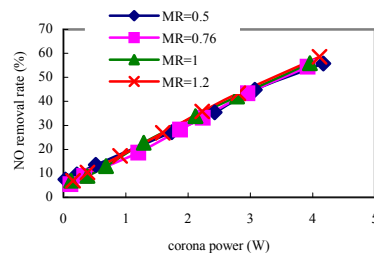


Fig. 6 NO removal using a CRS of ammonia

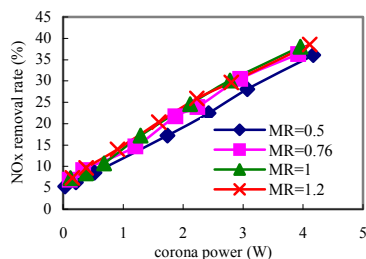


Fig. 7 NO_x removal using a CRS of ammonia

In a word, the increasing MR can promote the SO₂ removal but have not big effect on NO and NO_x removal. The corona discharge has some promotion for SO₂ removal but NO_x removal is dependent on the corona power.

2.4 The CRS System of Oxygen as Additional Gas

In the experiment, the flue gas coming from the reactor is conducted to the NaOH solution (26%), where the NO, NO₂ and HNO_x contained in the flue gas are absorbed. The gaseous HNO_x cannot be measured due to the unavailability of a measuring instrument. Only the NO_x in the flue gas needs to be measured on the assumption that gaseous HNO_x can be completely absorbed by the NaOH solution.

Figs. 8 and 9 show the change of the NO_x concentration after the reactor and the absorption bottle (the curve signed with AB-NO_x) with the discharge voltage. The NO_x concentration drops after the flue gas passes through the absorption bottle because NO and NO₂ are absorbed by the NaOH solution. The transition curve of NO_x concentration is analogous with that of NO concentration, this proves that the NaOH solution absorbs NO₂ completely and dissolves NO in small quantities.

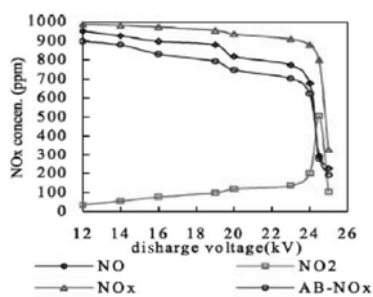


Fig. 8 NO_x reduction in the CSR combined NaOH absorption under 42% RH

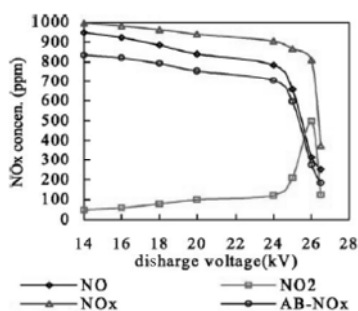


Fig. 9 NO_x reduction in the CSR combined NaOH absorption under 68% RH

Due to being absorbed by the NaOH solution, the NO_x decreases to some extent. The overall NO_x reduction rate is calculated and shown in Fig. 10. Apparently, the overall NO_x reduction rate increases as the discharge power increases. With a corona power of 11W, 81.7% of the NO_x is reduced corresponding to a relative humidity of 42%. Only 8W is needed to reduce the same NO_x corresponding to a RH of 68%.

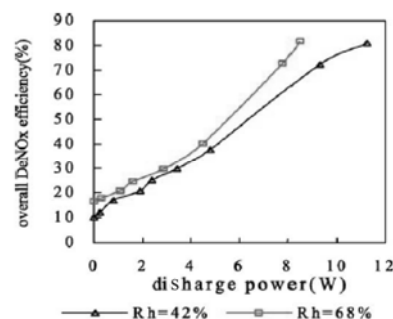


Fig. 10 DeNO_x efficiency under different power

3 SEMI-DRY MULTI-POLLUTANTS FLUE GAS CLEANING TECHNOLOGY

In semi-dry flue gas cleaning technology for multi-pollutants simultaneous removal, acidity substances such as SO₂, HCl, HF are removed by Ca(OH)₂-based absorbent from flue-gas and converted into saline material. Due to the active surface of the absorbent in absorber, NO_x, heavy metal and other pollutants are absorbed through physic and chemical reactions.

Composite additives with multi-components and high activity in absorbent can oxidize NO to NO₂, and prolong the time of liquid phase ionic reaction. At the meantime, due to the developed stoma configuration and huge inner surface area of absorbent and assistant active carbon, heavy metal and organic compounds are absorbed and removed. Eventually, most pollutants deposit in outcome ash collected by dust precipitator. Fig. 11 is the process schematics of semi-dry flue gas cleaning technology for multi-pollutants simultaneous removals.

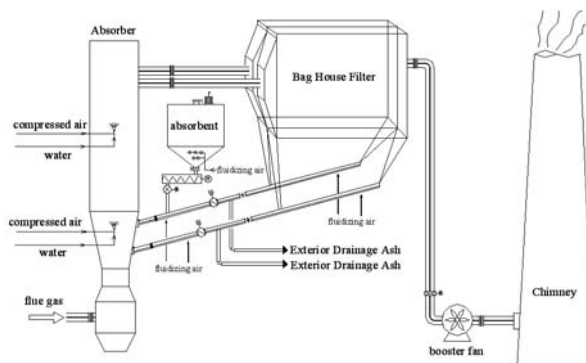


Fig. 11 Process schematic diagram of semi-dry flue gas cleaning technology

3.1 Multi-stage Humidifier

Chemical reactions in absorber can be divided into two stages: constant and deceleration reactions. In constant reaction stage, absorption rate of SO₂ is high and fall slowly

with time. Therefore, when other parameters (inlet temperature, inlet SO₂ concentration, Ca/S and circulation rate) are the same, multi-stages humidifier (see in Fig. 12) are used to distribute water reasonably to avoid over-humid absorbent locally and prolong constant reaction stage and promote DeSO₂ performance.

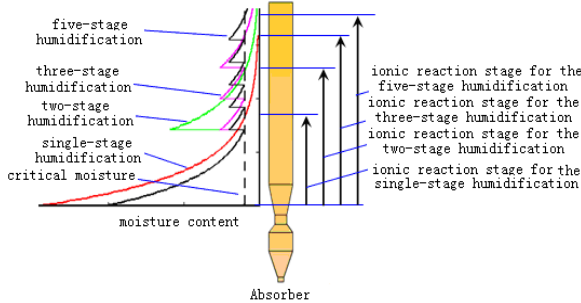


Fig. 12 Schematics of multistage humidifier

The effect of humidifier stages on DeSO₂ performance is shown in Fig. 13. The results indicated that adding humidifier stages can improve DeSO₂ efficiency. Considering the factors of drop collision and system complexity, two or three-stages humidifier is recommended in engineering (see Fig. 14).

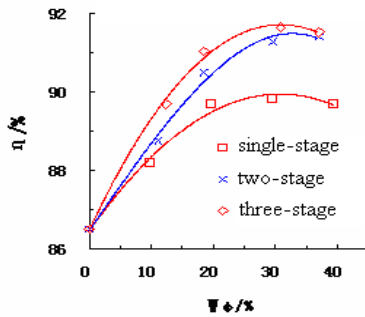
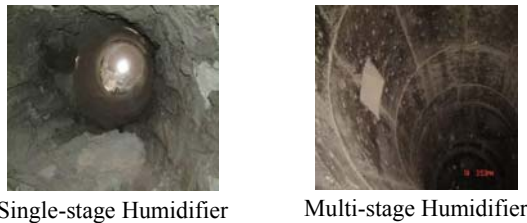


Fig. 13 Stages of humidifier effect on DeSO₂



Single-stage Humidifier Multi-stage Humidifier

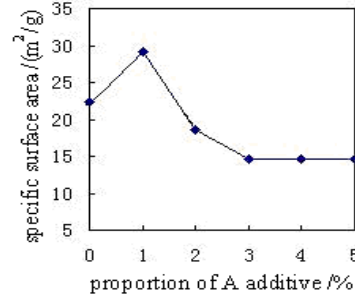
Fig. 14 Status inside the absorber

3.2 Additive with Multi-components and High Activity

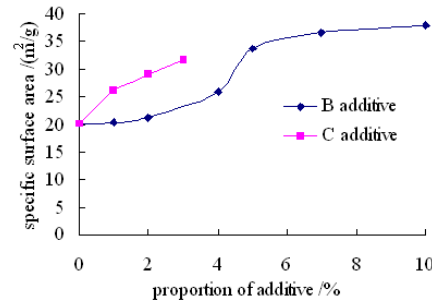
The microcosmic characteristics and absorptive capability of absorbent can be promoted by increasing its specific surface area and porosity through hygroscopic and oxidative additive. Hygroscopic additive prolongs the time of liquid drop evaporation and accelerates pollutants absorption. In addition, oxidative additive oxidizes NO to NO₂ that can be neutralized by alkali matter. The modified absorbent can improve removal efficiency of mercury effectively.

Fig. 15 shows that specific surface area and porosity of absorbent increases from 22 m²/g to 29 m²/g and 53□ to 63□ respectively while hygroscopic additive ratio is 1%. They also

increase with the increasing additive. The microcosmic characteristic of improving absorbent is good for its capability of purification.



(a) The Effect of Hygroscopic Additive on Specific Surface Area of Absorbent



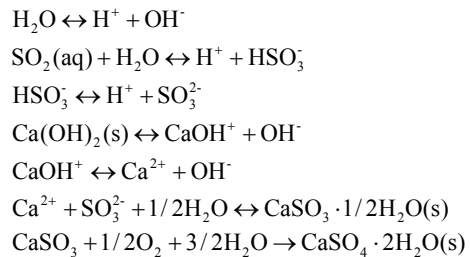
(b) The Effect of Oxidative Additive on Specific Surface Area of Absorbent

Fig. 15 The nature of additive effect on specific surface area

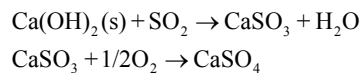
3.3 Simultaneous Removal Using Semi-dry Flue Gas Cleaning Technology

Composite absorbent with multi-component and high activity combined with multi-stage humidifier were used in semi-dry flue gas cleaning technology to control multi-pollutants simultaneously.

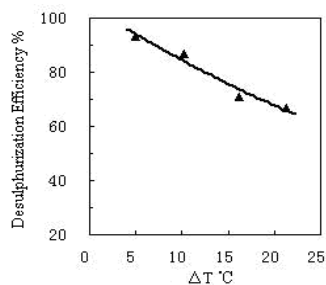
The main ionic reactions of SO₂ in absorber are listed below:



There are some deceleration reactions happened near the outlet of the top of absorber.



Results in Figs. 16 and 17 imply that operating condition affects the purification efficiency and utilization ratio of semi-dry flue gas cleaning technology for multi-pollutants simultaneous removal a lot. The results indicate the lower adiabatic saturation temperature (ΔT) the higher DeSO₂ efficiency. DeSO₂ efficiency was above 96% in experiment while 95.7% in practice project.



Flu-gas Volume 1156 Nm³/h, Inlet Temperature 160□, Inlet SO₂ Concentration 2288 mg/Nm³, Ca/S=1.5

Fig. 16 The effect of adiabatic saturation temperature (ΔT) on DeSO₂ efficiency

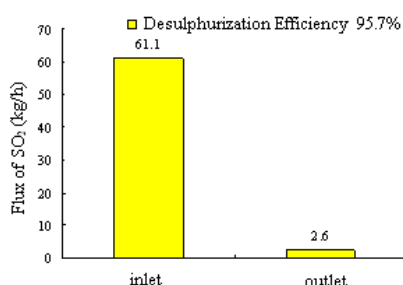


Fig. 17 DeSO₂ efficiency in practice project.

In absorber, NO are oxidized to NO₂ through the adsorption and catalysis of composite additives with high activity, and then absorbed by ash, additives and calcium-based absorbent. Key NO_x removal reactions are listed hereinafter.

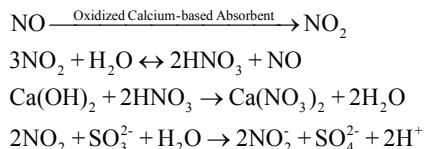


Fig. 18 shows the effect of oxidizing additive on DeNO_x. In a certain range, the DeNO_x efficiency increases with the high oxidizing additive ratio. Fig. 19 shows that the DeNO_x efficiency of practice project has reached 41.11%.

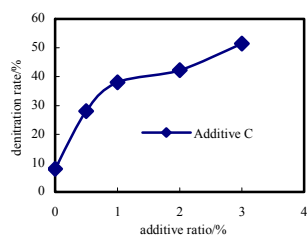


Fig. 18 The effect of oxidized additive on DeNO_x

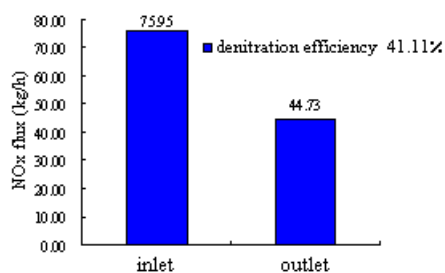
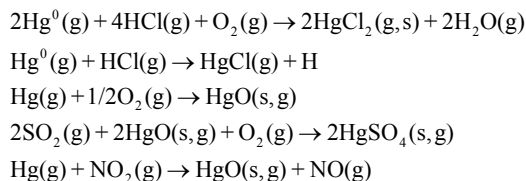


Fig. 19 DeNO_x efficiency in practice project

Earlier researches indicate that HCl is a key material effecting the transformation of mercury. There are also other influencing factors, such as O₂, NO_x and SO₂. Main reactions of mercury after combustion are as follow:



There are none ways suitable for the removal of all three phases of mercury. In semi-dry flue gas cleaning technology for multi-pollutants simultaneous removal, calcium-based absorbent was sprayed into absorber to control mercury phases. Adsorption efficiency of zero-valence mercury in gaseous phase increases by multi-stage humidifier. Divalent mercury is absorbed into liquid drops. Both gaseous phases of mercury are converted into particles, which is beneficial to three phases of mercury removal simultaneously.

Fig. 20 shows mercury reduction varying with time in the different temperature. As shown in Fig. 21, the removal efficiency of divalent mercury efficiency has been to 89.11%, the removal efficiency of total mercury efficiency has reached to 73.1%.

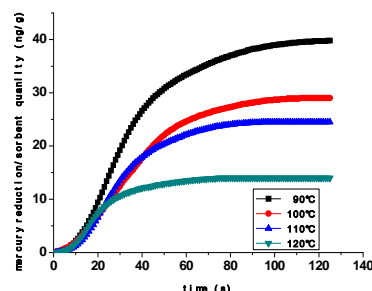
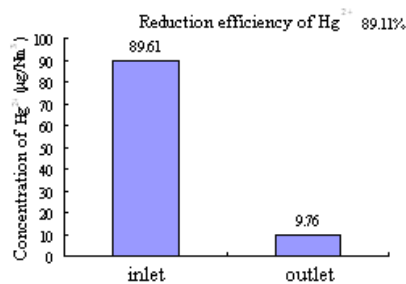
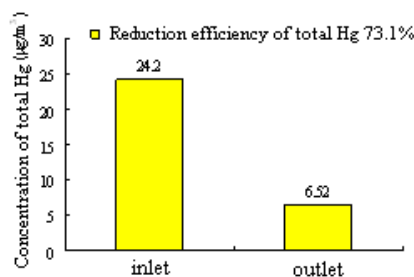


Fig. 20 Mercury reduction varying with time in the different temperature



(a) Removal efficiency of divalent mercury



(b) Removal efficiency of total mercury

Fig. 21 Removal efficiency of mercury in practice project

4 CONCLUSIONS

The flue gas multi-pollutants simultaneous removal is an inevitable trend in the field of flue gas purification. The CRS plasma technology and multi-stage humidifier semi-dry technology appears a good foreground for flue gas multi-pollutants simultaneous removal according to our previous research. The CRS of ammonia as additional gas can obtain high DeSO_2 removal efficiency and medium DeNO_x removal efficiency. Additionally, the CRS of oxygen as additional gas combining alkali solution can achieve high DeSO_2 and DeNO_x removal efficiencies. Furthermore, it is very fit of the reconstruction of primary WFGD. The semi-dry flue gas cleaning technology using circulating suspension and multistage humidification has realized large-scale industry application. It can achieve high multi-pollutants removal efficiency through multistage humidification and improving additive.

ACKNOWLEDGEMENTS

The work is supported by 973 Program of China (2006CB200303), 863 Project of China (2007AA061804), NSF of Zhejiang (Y507079), EOP of Zhejiang (Y200702725) and PSF of China (20080431325).

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