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Dielectric Barrier Discharge Non-thermal Plasma for NO-removal from Coal-combustion Flue Gas

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ABSTRACT

In this paper, the removal of NO and SO_2 from flue gases using the dielectric barrier discharge (DBD) non-thermal plasma (NTP) generator was studied. The DBD generator could be used in two modes, one in which the flue gas was directed through the discharge zone (direct oxidation), and another in which the produced ozonized air was injected into the flue-gas stream (indirect oxidation). The results showed that the denitration efficiency was higher than the desulfurization efficiency in both the cases (direct and indirect oxidation). It was also observed that indirect oxidation could greatly reduce the power consumption. The effect of factors (reactor medium thickness) on denitration efficiency was investigated. Following the approach of increasing energy efficiency, it can successfully seek a measure to increase denitration efficiency and reduce reactor energy consumption, so as to realize the purpose of saving energy and actual value of DBD plasma-based denitration.

INTRODUCTION

Recently, the use of coal has been rising at the rate of 2.2% annually, and this rise is faster than that of any other fuel. The use of coal is expected to increase between today and 2030, and as per the forecast, its usage will overstep 70% of the reserves. Developing countries contribute to 97% of the share. By 2030, the proportion of coal in global power generation is expected to improve by 40 to 45%. Enormous amounts of SO_2 and NO_x are produced during coal combustion, which degrade the air quality, cause haze, produce acid rain, harm human health and pollute the environment (Gao et al. 2013). Effective and economical control of the content of SO_2 and NO_x in the emitted smoke becomes an important strategic problem for sustainable development (Ding et al. 2008, Liu et al. 2006). Studies on non-thermal plasma (NTP)-control of atmospheric environmental pollution, especially the researches on denitration and desulfuri-zation based on NTP, are gradually turning into topics of great importance. Wang et al. have researched and analyzed the influence of the gaseous components on denitration in dielectric barrier discharge (DBD) (Wang et al. 2012). Cai Yixi et al. have used NTP for denitration in diesel engines using nano catalysis technology (Cai et al. 2012). Yu Qinqin, et al. researched and analyzed the NTP selective catalytic reduction of NO by B_2O_3/g-AL_2O_3 (Yu et al. 2012). Wang Chuan et al. investigated the NTP influence on the decomposition of NO in DBD by changing the DBD parameters (discharge voltage, dielectric material, discharge gap, etc.) (Wang et al. 2013). NTP is mainly produced by gas discharges, which includes corona discharge, glow discharge, DBD, photo ionization or laser radiation ionization, radiation, etc. While the DBD and pulsed corona discharge, both control pollution, DBD can produce more NTP stably under normal temperature and pressure. Shi Yunxi et al. researched the surface temperature at the discharge area, discharge voltage, discharge frequency, and air-flow rate, which are four factors affecting the NTP generation that produces a concentration of active substances (Shi et al. 2013). Controlling NTP is easy in DBD, and it helps in broadening the prospects of denitration and desulfurization (Wei et al. 2001, Clements et al. 1989, Kim et al. 2004, Wang et al. 2009).

MATERIALS AND METHODS

Plasma Generator

The generator is made of stainless steel. The length of the discharge region is 150 mm and the discharge gap is 3 mm (on one side). The discharge voltage supplied is lower when the DBD gap is smaller. Moreover, the thickness of the blocking medium influences the electrode discharge. The diameter of the corundum tube is 10 mm, and that of the convex platform is 14 mm. The generator is shown in Fig. 1.

Experimental Platform

Distribution system: The simulated flue gas in the

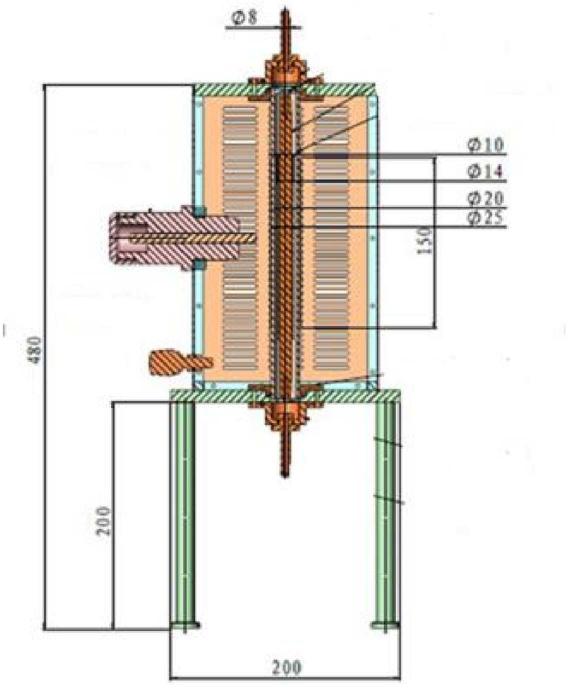

Fig. 1: Structure of the plasma generator.

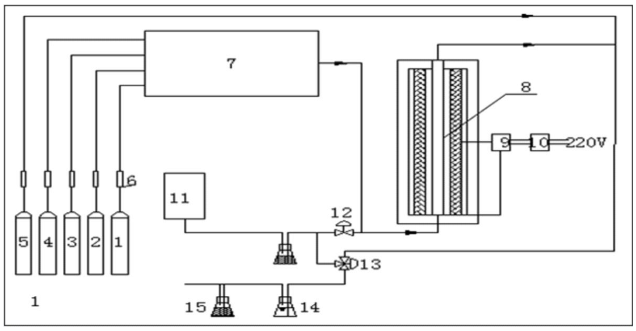

Fig. 2: System used for direct NTP desulfurization and denitration. The numerals used in the figure are: 1: O_2 bomb, 2: SO_2 bomb, 3: N_2 bomb, 4: NO bomb, 5: NH_3 bomb, 6: flow counter, 7: gas mixer, 8: plasma generator, 9: plasma electric source, 10: voltage transformer, 11: gas analysis equipment, 12: valve, 13: three-way valve, 14: inverted bottle, and 15: dry bottle.

experiment consists of N_2, O_2, NO, SO_2 and NH_3. NO accounts for more than 95% of the NO_x generated in power stations burning coal. The content of NO_2 is only 5% (Svachula et al.1993, Liu et al. 2004). Its content is relatively less and has little influence, and therefore, can be neglected. Hence, NO is generally used in experiments to represent the NO_x in the flue gas from power stations. The flow of gas in each steel cylinder is controlled by a rotameter. The gases are first mixed in a commingler, then the uniformly mixed gas enters the tabulation to preheat. The basic information about the simulated flue gas is presented in Table 1.

$$\eta \text{ (The efficiency of removing NO or } SO_2 \text{ \%)} = \frac{\text{The concentration of NO or } SO_2 \text{ at entrance} - \text{The concentration of NO or } SO_2 \text{ at exit}}{\text{The concentration of NO or } SO_2 \text{ at entrance}} \times 100\%$$

Definition of the Efficiency of Removal

All the gases enter the commingler, and are mixed thoroughly. Then, they pass through to the plasma generator. This gas mixture can be desulfurized and denitrated in the plasma generator by reactions. This process is called desulfurization and denitration using non-thermal plasma by direct. The system is shown in Fig. 2.

The gases are mixed thoroughly on entering the commingler. They are then made to react with the free radicals, which are produced when O_2 and steam react, by passing through the plasma generator at the exit of generator. This process is called desulfurization and denitration using non-thermal plasma by indirect. The system is shown in Fig. 3.

Gas analysis system: German MRU's MGA-5 flue gas online analyzer was used to measure the concentration of NO, NO_2, SO_2, NH_3, CO and O_2, and the test accuracy was ±1 ppm. The instrument's built-in gas sampling pump extracts the flue gas sample from the flue pipe through the sampling tube and the sampling line. The flue gas sample is dehydrated and filtered by the steam separator, and the concentrations of the gases within the sample gas are measured by the electrochemical sensor within the instrument. The oxygen content in the sample gas is measured using two electrode electrochemical sensors, and toxic gases such as CO, NO, NO_2, SO_2 and H_2S are measured using three electrode sensors. The electrochemical sensors use the gas diffusion technique. The advantage of this technique is that the output signal is linearly proportional to the gas concentration (ppm). The three electrodes are: S (measuring electrode), C (negative electrode) and R (reference electrode). When the measured gas reaches the measuring electrode, an oxidation or reduction reaction happens on the surface of the electrode; the concentration of the measured gas can be obtained by measuring the current (in μA) involved in the reaction, and using microprocessor processing.

Reaction mechanism: Plasma is a gas ionized at high voltage (Zhu et al.2008), especially, the gases ionized through electric discharge, heat release, etc., when the number of particles reaches a certain value. It is formed by particles

Table 1: Basic information about the experimental flue gas.

Parameter	Numerical value
Temperature	20°C
Initial concentration of NO	380 ppm
Initial concentration of SO_2	500 ppm
Flow of the simulated flue gas	500 mL/min

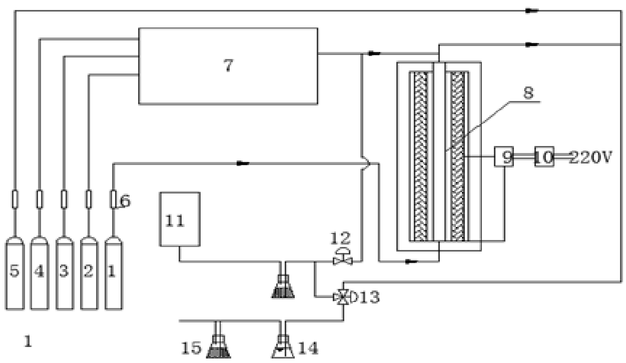

Fig. 3: System used for indirect NTP desulfurization and denitration. The numerals used in the figure are: 1: O_2 bomb, 2: SO_2 bomb, 3: N_2 bomb, 4: NO bomb, 5: NH_3 bomb, 6: flow counter, 7: gas mixer, 8: plasma generator, 9: plasma electric source, 10: voltage transformer, 11: gas analysis equipment, 12: valve, 13: three-way valve, 14: inverted bottle, and 15: dry bottle.

such as electrons, ions and atoms. The total positive charge is equal to the total negative charge, and it is an electrically conductive fluid. The plasma has characteristics of conductive and electromagnetic effects, and its activity is very strong. In many ways, it is different from solid, liquid and gas. Therefore, it is also known to be the fourth state of matter (Zhang et al. 2015). DBD-NTP is a high-pressure, low-temperature and non-equilibrium plasma. Because it can be generated at atmospheric pressures or higher, it can obtain the active particles required for the chemical reaction without any vacuum equipment. It possesses special light, heat, sound, electrical and other physical and chemical properties. The distance between the DBD electrodes is several mm, and it generates high concentrations of high-energy electrons, ions and free radicals (O•,OH•,HO_2•), and O_3. Plasma O_3 reacts with NO and SO_2, resulting in denitration and desulfurization; the chemical reactions are as follows (Hu et al. 1999, Francis et al. 2002, Yan et al. 2005):

1. O_2, water vapor and NH_3 react through the plasma reactor:

   $O_2 + e \rightarrow 2O + e$

   $H_2O + e \rightarrow H + OH + e$

   $O_2 + O \rightarrow O_3$

   $H + O_2 \rightarrow HO_2$

   $NH_3 + e \rightarrow NH + H_2 + e$

   $H_2 + e \rightarrow 2H + e$

   $H + NH_3 \rightarrow NH_2 + H_2$

2. Reaction mechanism of free radicals (O, OH, HO_2), ozone O_3 and NO:

   $NO + OH\bullet \rightarrow HNO_2$

   $NO + HO_2\bullet \rightarrow NO_2 + OH\bullet$

   $NO + O\bullet \rightarrow NO_2$

   $NO + O_3 \rightarrow NO_2 + O_2$

3. Further reaction of free radicals, ozone O_3 and the NO_2 generated by the reaction of free radicals and ozone O_3:

   $NO_2 + OH\bullet \rightarrow HNO_3$

   $NO_2 + O_3 \rightarrow NO_3 + O_2$

4. Reaction mechanism of high-energy electrons, free radicals (O, OH, HO_2), ozone O_3 and SO_2:

   $SO_2 + OH\bullet + e \rightarrow OHSO_2 + e$

   $O\bullet + SO_2 + e \rightarrow SO3 + e$

   $SO_2 + O_3 \rightarrow SO_3 + O_2$

RESULTS AND DISCUSSION

Analysis of the direct denitration and direct desulfurization performances of low-temperature plasma: The denitration efficiency of the low-temperature plasma generator at different input powers is shown in Fig. 4. The simulated flue gas contains N_2 and NO and has a flow rate of 500 mL/min. The NO concentration at the inlet is generally controlled at 380 ppm. When the plasma generator input voltage is 15 V, the DBD-NTP generator starts discharging. It ionizes all kinds of gases and produces high-energy electrons, ions and free radicals. The chemicals react with each other, and NO starts being removed; the removal efficiency is about 25%. With increase in the input voltage and input power, the denitration efficiency increases rapidly,with increase in the input power from 17 W to 28 W, the denitration rate rose to 71.2%. For further increase in the NTP generator input power, the denitration efficiency improvement tends to be gentle. For the pursuit of a small amount of denitration efficiency, paying a huge price for energy consumption, the economic performance is relatively low and it has no practical value. However, it can be observed from the experimental curve that, with increase in the input power of the plasma reactor, the denitration activity increases. This is because the formation of the free radicals, which are responsible for the oxidation and removal of NO, is proportional to the energy density and O_3. The highest voltage is 40 V, and current is 1.3 A. When the input voltage and current continue to improve, the denitration efficiency also contin-

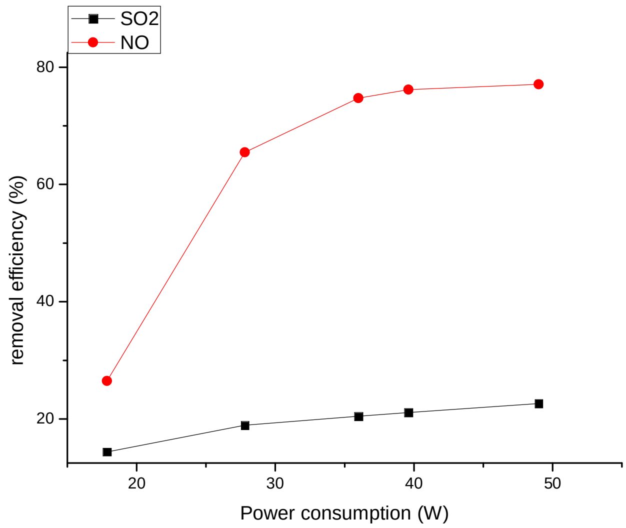

Fig. 4: Analysis of NO_x^- and SO_2^- removal from flue gas by direct oxidation.

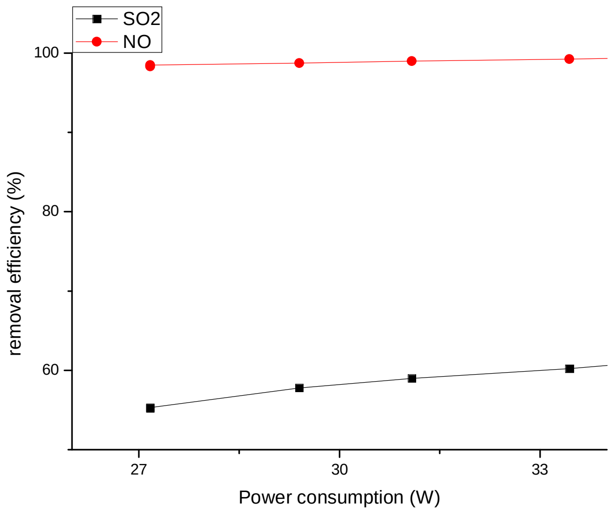

Fig. 5: Analysis of NO_x^- and SO_2^- removal from flue gas by indirect oxidation.

ues to improve; however, the improvement is not obvious until the voltage increases to a certain value. When the DBD breaks down, and generates an arc discharge, the denitration efficiency decreases sharply.

Fig. 4 also shows the desulfurization efficiency of the low-temperature plasma generator at different input powers. In this case, the simulated flue gas contains N_2 and SO_2 with a flow rate of 500 mL/min. The SO_2 concentration at the inlet is generally controlled at 600 ppm. From the experiment, it is observed that the ionization of SO_2 is more difficult than that of NO and the efficiency is only about 20%. From the chart, it can be inferred that the removal rate of SO_2 is far lower than the removal rate of NO. Moreover, the removal and decomposition processes are not stable and the SO_2-concentration fluctuation is very large.

When the input voltage and current continue to increase, the desulfurization efficiency also continues to improve; however, the improvement is not obvious until the voltage increases to a certain value. When the DBD breaks down, and generates an arc discharge, the desulfurization efficiency decreases sharply.

Analysis of the indirect denitration and indirect desulfurization performances of low-temperature plasma: When the simulated flue gas contains N_2 and NO, and flows at 500 mL/min, the NO concentration at the inlet is generally controlled at 380 ppm. When the simulated flue gas contains N_2 and SO_2, and flows at 500 mL/min, the SO_2 concentration at the inlet is generally controlled at 600 ppm. The O_2 passes into the low-temperature plasma reactor. The denitration and desulfurization efficiencies of the low-temperature plasma generator, at different input powers, is shown in Fig. 5.

The removal efficiency of NO is very high, reaching over 95%. Even at the minimum input trigger-voltage of the plasma generator that produces plasma, the removal efficiency is as high as 95%. At that point, the plasma generator's input power is the lowest and it can be assumed that the denitration efficiency and power consumption have reached optimum values and that the effect is ideal. However, the process of removal of NO results in a certain amount of NO_2 generation. In this experiment, before the reaction, the concentration of imported NO was 397 ppm and the concentration of NO_2 was 55 ppm. The concentration of exported NO_2 reached 125 ppm. Because NO_2 is easily soluble in water and can easily participate in other oxidation reactions, the removal of NO_2 was not considered here. As can be observed in Fig. 5, the removal efficiency of SO_2 can reach 58%. Compared to direct desulfurization, the removal efficiency is greatly improved; however, this process is not stable. The concentration fluctuates greatly, and it is difficult to oxidize. As the input power increases, the removal rate of SO_2 decreases. In the initial stages of the desulfurization process, a certain amount of H_2S was generated along with the reaction process. This H_2S reacted by oxidation and the concentration decreased to zero. Compared to the other desulfurization methods that have been developed, the decomposition and oxidation effects of desulfurization and the economy are not very good in the case of using low-temperature plasma. Hence, the DBD-NTP is not recommended for desulfurization.

From the experimental results, the removal efficiency is quite satisfactory. We speculate that the high-energy elec-

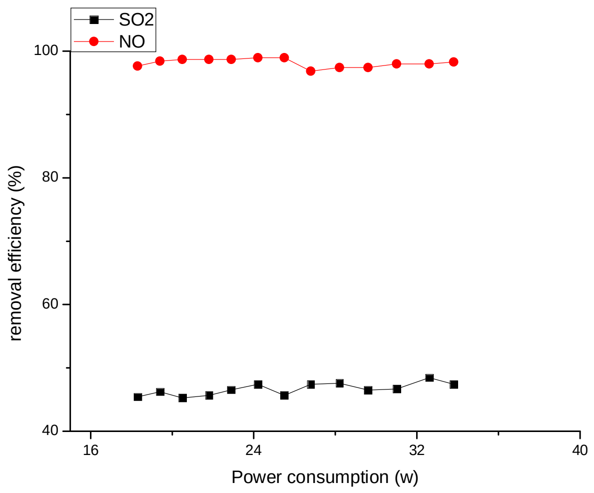

Fig. 6: Analysis of the removal efficiencies of simultaneous indirect desulfurization and denitration.

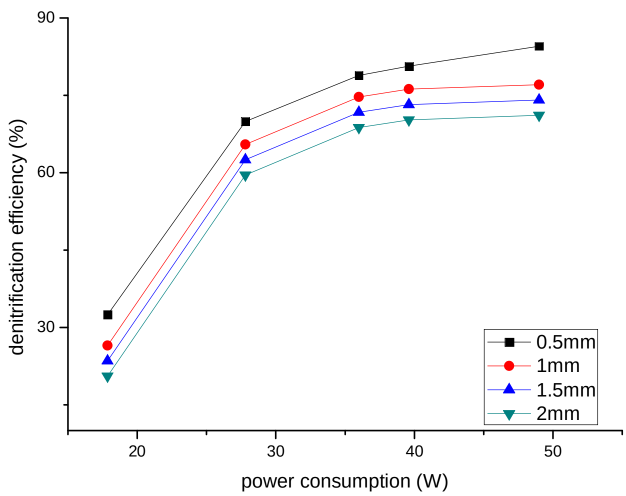

Fig. 7: Analysis of NOx removal from flue gas by the different thickness of the plasma generator.

trons, ions and free radicals, generated by the DBD-NTP generator, react with NO and SO_2. The major factor, the plasma generator, produces a large amount of O_3, and causes strong oxidation of NO and SO_2. Thus, it plays an important role in the removal process. Some literature mentions that the plasma cannot be transported across distances. High-energy electrons, ions, and radicals are transported through a certain distance, and chemical reactions occur between each other.

Analysis of simultaneous indirect desulfurization and denitration: The results of the denitration-efficiency experiment for simultaneous indirect desulfurization and denitration are shown in Fig. 6. For a 15-V input voltage, the discharge plasma reactor begins the reaction at a reactor input power of 18.9 W. Then the input voltage is changed to 23 V, at an input power of 33.81 W. The flow rate of the reactor is 500 mL/min, the NO import concentration is 380 ppm, and concentration of SO_2 import is 500 ppm. The denitration efficiency must be kept high to maintain high desulfurization-denitration efficiency.

As can be observed from the chart, from the beginning of the reaction, the denitration efficiency is very high, reaching more than 94%, and the desulfurization efficiency can reach up to 46%, distinct from the direct simultaneous desulfurization and denitration effect in which desulfurization efficiency is very low. Regardless of the increase in input power, until the low-temperature plasma reactor achieved a high-voltage, discharge breakdown of desulfurization-denitration efficiency does not play a significant role. While, indirect desulfurization and denitrification require only input voltage supplied to DBD, and even if the input power is small, can achieve very efficient denitration efficiency and certain desulfurization efficiency. And with increasing the input power of plasma generator from 18W to 33W, the removal efficiency remained a same, which shows that the minimum power input can obtain the same removal efficiency. The efficiency of the experimental results is ideal, which can greatly reduce the input power and energy consumption, and has practical application value and significance. From the reaction mechanism, indirect simultaneous desulfurization and denitration is caused by the reaction of the plasma generator O_3 and SO_2 with NO and SO_2, and the NO removal. However, in the indirect desulfurization and denitration process, no O_3 oxidation to NO_2 and O_2 occurs, leading to the generation of a large amount of NO_2, and NO_2 activity is strong. In the subsequent experiments, measures must be taken (such as adding a reducing agent or adsorbent) to remove NO_2, and thus, perform real denitration. Individual desulfurization is more efficient than simultaneous desulfurization and denitration, but indirect oxidation can meet the requirements of simultaneous desulfurization and denitration. The process is simplified and has high practical value.

Exergy analysis of changing dielectric barrier thickness in plasma generator: The experimental fuel gas is made up of N_2, O_2 and NO. The structure of NTP reactor has the discharge zone of 150 mm long, alundum tube of 25 mm × 20 mm, tooth-shaped electrode core of 10 mm and boss diameter of 14 mm and discharge space of 3 mm. This part is to change the dielectric barrier thickness of 0.5 mm, 1 mm, 1.5 mm and 2 mm. The results are shown in Fig. 7.

Results show that when the dielectric barrier thickness was 0.5 mm, NTP reactor with input power of 9 V could discharge and generate free radicals with highest value of denitration efficiency. Therefore, the thicker the dielectric barrier is, the lower the denitration efficiency would be. The denitration efficiency, when the dielectric barrier thickness was 2 mm, is about 20% lower than that of 0.5 mm, showing that the thinner the dielectric barrier is, the smaller the entropy generation and the larger output profit energy would be.

CONCLUSIONS

According to the analysis of the experimental study, the following conclusions could be drawn regarding the low-temperature plasma desulfurization and denitration:

1. Both, direct desulfurization and removal of nitrate or indirect desulfurization and denitration, extrusion efficiency and plasma generator input power are in a linear relationship. The denitration efficiency is better than the desulfurization efficiency. It indicates that the oxidation of NO is stronger than the oxidation of SO_2, in the plasma generated by the DBD-NTP. Decomposition and ionization of NO in the DBD-NTP is better than the SO_2 decomposition and ionization. Depending on the number of DBD-NTPs produced by the DBD-NTP plasma generator input power, the plasma power determines the number of decompositions and oxidations of NO and SO_2 degree, and reflects the degree of the removal rate.
2. In the case of direct separate denitration, the denitration efficiency is relatively ideal. With an increase in the power consumption of the plasma generator, the removal efficiency can reach 80%. In the case of direct desulfurization, the desulfurization efficiency and denitration efficiency are not ideal. In the case of direct simultaneous desulfurization and denitration, the differences from the case of denitration or desulfurization alone are very obvious. The efficiency of SO_2-removal is much lower, but it also affects the performance of NO-removal to a large extent, resulting in a denitration efficiency that can reach only about 20%. In addition, the low-temperature plasma reactor discharge is very large, the input voltage increases in a lot of cases to produce the experimental results that the direct discharge, to achieve simultaneous desulfurization and denitration and the removal of NO from flue gas SO_2 is not realizable.
3. In the indirect simultaneous desulfurization and denitration process, the denitration efficiency can be very high, and the desulfurization efficiency is also quite good. This is because, in addition to the reactions of free radicals with NO and SO_2, O_3 has also played a major role. In addition, in the indirect process, just ionization of O_2 or H_2O, by a very small trigger voltage can produce plasma. Because of the low power consumption, the energy-saving effect is very obvious. For applications that need simultaneous desulfurization and denitration, the indirect method is worth popularization, because of its economic performance, namely under low input powers, and good desulfurization-denitration efficiencies. Indirect desulfurization and denitration, regardless of the de-NO_x efficiency and desulfurization efficiency, indirect oxidation is more efficient, but a certain amount of NO_2 generation occurs in the oxidation process. Free radicals, including O_3, react with N_2, forming NO_2. This is a serious problem, and requires corrective measures to remove the NO_2; thereby, achieving the true capability of denitration.

The visible NO-removal using NTP technology is still in the experimental stage. Researchers need to increase their research efforts on reducing energy consumption, improving the efficiency of denitration, and achieving practical application value, so as to realize industrialization, there is a way to explore.

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