

## Review Article

# Mercury Emission Abatement Strategies of China's Coal-Fired Power Plants

Li J<sup>1\*</sup> and Diao C<sup>2</sup><sup>1</sup>Beijing Municipal Institute of Labor Protections, PR China<sup>2</sup>College of Chemistry and Environmental Science, GuizhouMinzu University, PR China

**\*Corresponding author:** Jianfeng Li, Beijing Municipal Institute of Labor Protections, Taoranting Road 55#, Xicheng District, Beijing, PR China

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**Abstract**

Mercury and its compounds are highly toxic to humans and was identified mercury as a global pollutant. In the anthropogenic mercury emission, 65% comes from stationary combustion sources, in which the mercury emission from coal-fired power plants accounts for the largest proportion. The existence forms of mercury in flue gas mainly include the Hg<sup>0</sup>, RGM and Hg<sup>p</sup>. The oxidation degree of mercury in the coal-fired flue gas is influenced by many factors, such as burning condition, chemical composition of coal such as content of chlorine element, other compositions and contents in flue gas, temperature and contact time. For power plant, the characteristics of burning equipment and fly ash and air pollution control devices will both have an important influence on the form of mercury emission in the process of coal burning. Hg<sup>0</sup> in flue gas can be removed through homogeneous and heterogeneous oxidation. When the temperature is less than 450°C a d thermodynamic equilibrium is met, theoretically 100% of the Hg<sup>0</sup> can be transformed into Hg<sup>2+</sup> and washed out. Further, this paper analyzed the demercuration capacity of flue gas pollution control equipment for dust removal equipment, desulfurization system, and denitrification device. Also, there are two main methods to achieve control of the process: to utilize the absorbent and the catalyst. The paper discussed the performance of activated carbon absorbent, calcium-based absorbent, metals and its oxides and SCR Catalyst. It concluded that flue gas demercuration of coal-fired electric power plants may concentrate on based on existing SCR device, demercuration is to achieved by using (modified) SCR catalyst, which can reduce reconstruction fee and operation fee of site and device as well as, in addition, secondary release from by-products of power plants such as mercury-containing flying ash to realize centralized disposal.

**Keywords:** Atmospheric mercury; Emission abatement strategies; Coal-fired power plants

## Abbreviations

IARC: International Agency for Research on Cancer; Hg<sup>0</sup>: The Elemental Mercury; RGM Hg<sup>2+</sup>: Reactive Gaseous Mercury; Hg<sup>p</sup>: Particulate Mercury; IPPC: International Plant Protection Convention; CAIR: Clean Air Interstate Rule; MATS: Mercury and Air Toxics Standards; CAMR: Clean Air Mercury Rule; MEP-PRC: Ministry of Environmental Protection of the People's Republic of China; CCICED: China Council for International Cooperation on Environment and Development; SNCR: selective non-catalytic reduction; SCR: Selective Catalytic Reduction; ESP: Electrostatic Precipitator; FF: Fabric Filter; WFGD: Wet Electrostatic Precipitator; PAC: Powdered Activated Carbon; ACI: Activated Carbon Injection; FGD: Flue Gas Desulphurization

## Introduction

### Background

Mercury and its compounds are highly toxic to humans, especially to the developing nervous system. They are also harmful to ecosystems and wildlife populations. Microbial metabolism of deposited mercury can create methylmercury, which has the capacity to collect in organisms (bioaccumulate) and to concentrate up food chains (biomagnify), especially in the aquatic food chain. Methylmercury

is a well-documented neurotoxicant, which may in particular cause adverse effects on the developing brain. It readily passes both the placental barrier and the blood-brain barrier; therefore, exposures during pregnancy are of highest concern. It may also cause adverse effects on the cardiovascular system, thereby leading to increased mortality. Methylmercury compounds are considered possible carcinogenic to humans according to the International Agency for Research on Cancer (IARC, 1993). Furthermore, inhalation of elemental mercury vapour causes symptoms such as tremors, insomnia, memory loss, neuromuscular changes, and headaches. Kidney and thyroid may be affected.

Mercury in the atmosphere is divided into three inorganic forms [1], i.e. the elemental mercury (Hg<sup>0</sup>), reactive gaseous mercury (RGM, Hg<sup>2+</sup>) and particulate mercury (Hg<sup>p</sup>). Hg<sup>0</sup> is the main chemical speciation of atmospheric mercury, which constitutes the majority of the mercury in the atmosphere over 95% [2,3]. As Hg<sup>0</sup> has very low solubility in water and its chemical reaction rate is very slow with other components in the atmosphere such as the strong oxidant O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, OH and NO<sub>3</sub> radicals [4,5,6], Hg<sup>0</sup> has a long atmospheric lifetime (0.5~2 years) and can be transported through the atmosphere over thousands of kilometers [2,1]. In the long-distance transport, Hg<sup>0</sup> may have a chemical reaction with atmospheric oxidants such

as  $O_3$ ,  $H_2O_2$ , and halogen compounds and result in the formation of  $Hg^{2+}$ , which reaches the ground by dry and wet deposition and affects the global ecological environment.

About half of the mercury emission in the atmosphere comes from the natural emission source such as volcanic eruption, and the majority of the rest comes from the fossil fuel burning by human beings. In the anthropogenic mercury emission, 65% comes from stationary combustion sources, in which the mercury emission from coal-fired power plants accounts for the largest proportion (accounting for 40% of the mercury emission in the US, in 1999); 11% comes from gold production. The 3 sources of maximum mercury emission in the US, are 3 largest gold mines; 6.8% comes from the production of nonferrous metals, represented by metallurgical plants; 6.4% comes from cement manufacturing; 3.0% comes from waste treatment including municipal and hazardous waste, crematorium and sludge incineration; 3.0% comes from caustic soda production; 4.0% comes from other sources [7-12]. Bellanger M has made comments on the research on the mercury pollution cost in the Europe in the *Environmental Health*, saying that the research shows that there are up to 2 million newborn children of long-term mental deficiency every year in the European countries as they are exposed to unsafe mercury environment, causing losses of up to EUR 9 billion every year.

As a global pollutant, the mercury has been incorporated into the environmental diplomacy by UNEP. In the 25<sup>th</sup> European Council Meeting of UNEP held in February 2009, all countries agreed to establish the INC and enact a legally binding instrument concerning mercury problems. The 5<sup>th</sup> INC Meeting held on January 19, 2013 passed the *Minamata Treaty* aiming to control and reduce the mercury emission all over the world. The Treaty held that the coal-fired power plant was one of the largest sources of mercury pollution and every country in the world shall control the atmospheric mercury emission of various large coal-fired power plants. The *Minamata Treaty* will be signed in Japan on October 9, 2013.

The coal-fired power plant is the most important atmospheric mercury emission source in EU and US. In Europe, such regulations as *IPPC (2008/1/EC)* are the basic guarantee for controlling the atmospheric mercury pollution of coal-fired power plant and the implementation of optimal feasible technology is the main measure for reducing its mercury emission. In the US, *EPA* controls the atmospheric mercury pollution of coal-fired power plant by making legislation and setting standards. The *CAIR* promulgated in 2005 provides that the coal-fired generator unit shall be installed with desulfurization and denitration devices so as to reduce the mercury emission while further reducing the sulfur dioxide and oxynitride. The *CAMR* promulgated in 2005 is the first national regulation aiming at the mercury emission of coal-fired power plant in the world, which urges US to reduce the mercury emission by total quantity control and emission trading system. The *MATS* promulgated in 2011 imposes strict requirements on the mercury emission, making some power plant only use special mercury removal technology to meet the standard.

There are about 2503t mercury in the atmosphere, 1/3 of which comes from point source and confirmable anthropogenic source; and the rest 2/3 is attributed to the release of natural source, but human

activities (such as biomass burning) will deteriorate this process and most mercury discharged by natural source comes from anthropogenic source originally. At present, the estimates show that 1/3 of mercury discharged from natural source comes from the mercury discharged before industry and re-releasing of mercury deposited [13]. In the anthropogenic emission source, the rate of contribution of fossil fuel combustion is the highest. Pacyna [12] holds that the annual atmospheric mercury emission quantity in total in the world is 1930t, of which the atmospheric mercury emission caused by combustion of fossil fuel (mainly coal) is about 880.2t, accounting for 46% of the total emission quantity of anthropogenic source. The atmospheric mercury emission of China in 2005 was 825.2t, accounting for more than 42.85% of the total emission quantity in the world, among which the combustion of fossil fuel (mainly coal), gold extraction by amalgamation (indigenous method) and metal metallurgy were the largest atmospheric mercury emission sources [12].

According to the <*Technical Policy for Mercury Prevention and Control*> issued by *MEP-PRC* in January 2013, the data of 2007 shows that the annual atmospheric mercury emission quantity is about 643t. The mercury pollutants are discharged into the environment during the production of industries such as nonferrous metal metallurgy, cement production, color-alkali manufacturing and e-waste treatment in addition to coal firing. According to the <*Research on Policy of Mercury Management Topics in China*> undertaken by *CCICED* in 2007, the coal-fired boiler, coal-fired thermal power plant and nonferrous metal metallurgy account for more than half of the atmospheric mercury emission quantity of main industries in China, namely, 33%, 19% and 18% respectively.

In addition to mercury emission, the total mercury consumption in China is about 1000t, accounting for 50% of the total quantity in the world, so China has become the largest mercury product producer and user all over the world. China and Kyrgyzstan are the only two countries engaging in large scale mining of mercury mines in the world.

According to the pollution prevention and control objectives of mercury-related industry put forward by *MEP-PRC*, by 2015, the mercury-related industry will realize the overall process monitoring of mercury pollutant, including mercury exhaust gas, waste water to meet the emission standard. By 2020, the mercury-containing waste will be controlled comprehensively and the resource utilization, energy consumption and pollutant emission index will reach the international advanced level. The specific actions include the following two aspects:

### Form of flue gas mercury and its decisive factors

The oxidation degree of mercury in the coal-fired flue gas is influenced by many factors, such as burning condition, chemical composition of coal such as content of chlorine element, other compositions and contents in flue gas, temperature and contact time [14,15]. The existence forms of mercury in flue gas mainly include the  $Hg^0$ , RGM and  $Hg^p$  [16,17]. In the process of coal burning, the mercury is emitted mainly in the form of  $Hg^0$ . Due to different temperatures, flue gas compositions and pressure differences before and after burning in various pollution control equipment, there will also be a great change in form and the proportion in each form.

Different types of coal for burning will cause different morphological distributions of mercury in flue gas. In the flue gas generated by burning of *bituminous coal*, the form of mercury is dominated by  $\text{Hg}^{2+}$ , about 65%-70%, other 30-35% of the mercury exists in the form of  $\text{Hg}^0$  and few exist in the form of  $\text{Hg}_p$  [18,19]; in the flue gas generated by burning of *anthracite*, there is no large difference of proportion between  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  [19]; while in the flue gas generated by the burning of *lignite*,  $\text{Hg}^0$  is the main chemical form [14,20].

When different *burning methods and control pollution technologies* are adopted in the same industry, there might be a very large difference in atmospheric mercury emission and form. For power plant, the characteristics of burning equipment and fly ash and air pollution control devices will both have an important influence on the form of mercury emission in the process of coal burning.

**Influence from the characteristics of burning equipment and fly ash:** Both pulverized coal furnace and cyclone furnace operate in high temperature, morphological distributions of emitted mercury in flue gas are somewhat different. After burning in cyclone furnace, the content of  $\text{Hg}_p$  is higher than that in the pulverized coal furnace, this is mainly because there is a difference of quantity and characteristics of fly ash generated by burning and the mercury is absorbed [21]. In cyclone furnace, most of the incombustible mineral substances are converted into slag which is removed from the bottom of the combustion equipment in molten state; therefore, there are few incombustible mineral substances that are converted to fly ash or other mineral substances [4]. In pulverized coal furnace, 90% of the incombustible mineral substances are converted to fly ash. Compared with stoker and chain grate furnace, pulverized coal is more fully exposed to the air with higher burning efficiency; there is a relatively high content of gaseous mercury, while there are fewer remaining in the bottom. In addition, the low-NOX burner will also increase the content of carbon in fly ash and strengthen the absorption of fly ash to mercury, so as to increase the content of  $\text{Hg}_p$  entering in the lower-stream ESP or FF [22,23].

**Influence from Air Pollution Control Devices (APCD):** The main factors determining the emission and characteristics of atmospheric mercury are the morphological distribution of mercury entering the flue gas purification device, concentration of some compositions in flue gas (such as Cl, HCl and  $\text{NO}_x$ ), type and operation temperature of flue gas purification device etc. [14,24,25]. In flue gas, some  $\text{Hg}^0$  is oxidized, so the oxidative product is mainly  $\text{Hg}^{2+}$ , which is easy to solve in the water, and to be removed by wet-method washing system; some oxidative mercury can also be absorbed by the particulate matters in flue gas, then removed by the dust removal equipment from the flue gas.  $\text{Hg}^0$  has a relatively saturated steam pressure and is difficult to be dissolved in water with a relatively stable form. APCD has a relatively weak ability to remove  $\text{Hg}^0$ , so  $\text{Hg}^0$  removal must depend on additive absorption or transformation into  $\text{Hg}^{2+}$ , only in this way, can the total mercury emission be controlled effectively. In addition, as coal contains numerous chlorine elements, it is generally believed that the content of halogen in coal, especially the content of chlorine element is the most important factor to determine the distribution of mercury form in flue gas, because in the process of flue gas cooling,  $\text{Hg}^0$  can be oxidized by Cl into mercuric chloride [16,25].

**Removing mechanism of mercury in flue gas:**  $\text{Hg}^0$  in flue gas can be removed through homogeneous and heterogeneous oxidation. The reaction velocity of heterogeneous oxidation is far higher than that of homogeneous oxidation, so the research on  $\text{Hg}^0$  in the oxidized flue gas is mainly concentrated on the development of homogeneous catalyst. When the temperature is less than 450°C and thermodynamic equilibrium is met, theoretically 100% of the  $\text{Hg}^0$  can be transformed into  $\text{Hg}^{2+}$  [26]. Due to existence of halogen (mainly Cl), the  $\text{Hg}^{2+}$  is mainly mercuric chloride, but actually, the mercuric oxide, mercuric nitrate and mercury sulfate can all be formed in the flue gas [27-29].

## Homogeneous Oxidation

$\text{Hg}^0$  can react with many gas oxidants, such as chlorine, hydrogen chloride, chlorine radical and ozone [25,30,31]. Sliger et al. thought that  $\text{Hg}^0$  can be oxidized by chlorine radical in 400-700°C [32]. The activation energy in reaction of mercury and chlorine is very low; they can react in room temperature with reaction velocity far higher than that of the reaction between  $\text{Hg}^0$  and hydrogen chloride. The activation energy of reaction between mercury and hydrogen chloride is very high; it is difficult for them to react in normal temperature. The reaction between mercury and chlorine will generate an intermediate product  $\text{HgCl}$ .



The  $\text{HgCl}$  generated is further oxidized by hydrogen chloride or chlorine radical in the following. The research of Sligh et al. indicated that the oxidation degree of  $\text{Hg}^0$  presented a positive correlation with the concentration of HCl in flue gas (mainly depending on the content of chlorine element in coal) [15,32]. The mechanism proposed by Sligh et al. cannot explain the oxidation process of  $\text{Hg}^0$  in all conditions [32]. Niksa and Fujiwara found in the pilot research that the content of chlorine in coal was not the most necessary factor to decide the oxidation degree of  $\text{Hg}^0$  [33]. After comparing the previous two groups of research data, Wang and Anthony thought the velocity of direct reaction between  $\text{Hg}^0$  and Cl is very low, why there is a relatively high dynamic velocity is because heterogeneous reaction occurs on the container wall [26,34]. Within the normal flue gas temperature, the oxidation of  $\text{Hg}^0$  is influenced by the heterogeneous reaction. So the homogeneous oxidation of  $\text{Hg}^0$  is not only influenced by the content of oxidant chlorine, but is also inseparable with the content of volatile component and heterogeneous oxidation process [35].

## Heterogeneous Oxidation

Many mechanisms have been used to describe the heterogeneous oxidation mechanism of  $\text{Hg}^0$  [36,37]. Under a relatively high temperature (300-400°C), the reaction that hydrogen chloride is catalyzed by metal oxide to generate chlorine may occur in flue gas, i.e. Deacon Process [38], Deacon was once used to explain the oxidation of  $\text{Hg}^0$ :



In case of any suitable catalyst, the hydrogen chloride in the flue gas can be converted into chlorine and then  $\text{Hg}^0$  can be oxidized through Deacon Reaction. However, the hydrogen chloride concentration in the flue gas is generally less than 1%, so the  $\text{Cl}_2$  content in equilibrium is lower. Niksa and Fujiwara once had established a model to research

the heterogeneous oxidation of  $\text{Hg}^0$  and the research showed that only a small part of such oxidation was caused by gaseous reaction directly [14]. Therefore, other reaction mechanisms shall be established to explain the oxidation of  $\text{Hg}^0$ , such as the catalyst on the adsorption mechanism of  $\text{Hg}^0$ .

The bimolecular reaction of two substances adsorbed on the same surface can be described by Langmuir-Hinshelwood mechanism [39]:

In the above expression, A means  $\text{Hg}^0$  and B means the chlorine compounds, such as hydrogen chloride and the reaction rate is influenced jointly by the A and B concentration in the gas phase, adsorption equilibrium constant ( $K_i$ ) and surface reaction kinetics constant ( $K_{\text{surf}}$ ). The  $\text{Hg}^0$  can be adsorbed on the activated carbon and other adsorbents as well as carbon in the flying ash [35,39,40], so does the hydrogen chloride. Therefore, the Langmuir-Hinshelwood mechanism indicates that the substance which can absorb the  $\text{Hg}^0$  and hydrogen chloride is of catalytic oxidation  $\text{Hg}^0$  to make them form  $\text{HgCl}_2$ . Many researches find that the oxidation level of  $\text{Hg}^0$  is correlated to the hydrogen chloride concentration even under excessive hydrogen chloride [15,18,32]. Besides, the oxidation level of  $\text{Hg}^0$  will somewhat decrease in case of any adsorbent of hydrogen chloride, such as CaO [41].

The main gas components in the flue gas such as sulfur dioxide, nitrogen oxide and hydrogen chloride have an obvious influence on the adsorption mechanism of  $\text{Hg}^0$  and the main mechanism is to compete for activated carbon and active site on other adsorbents [42]. The research finds that the high-concentration sulfur dioxide in the simulated flue gas will restrain the conversion of  $\text{Hg}^0$  [14], which may be caused by its competition for adsorption site with hydrogen chloride. However, the existence of sulfur dioxide may also strengthen the oxidation of mercury or be of small influence [42]. Schofield et al put forward the mechanism of  $\text{Hg}^0$  oxidized as  $\text{HgSO}_4$  [43]. In the simulated flue gas with sulfur dioxide, the mercuric oxide and mercury sulfate would accumulate on the catalyst surface. This reaction obeyed first order kinetics for  $\text{Hg}^0$  and zero order kinetics for sulfur dioxide. In case of no sulfur oxide, mainly  $\text{Hg}^0$  would accumulate on the catalyst surface and then the  $\text{Hg}^0$  accumulating on the catalyst surface would be converted into mercuric chloride after adding hydrogen chloride. They thought the mercuric oxide and mercury sulfate were generated first in the reaction and then the mercuric chloride was generated by reacting with the hydrogen chloride. Besides, Granite and Pennline found the generation of mercuric oxide and mercurous sulfate in the photochemical oxidation of  $\text{Hg}^0$  under no oxide chloride [44]. Olson et al put forward another mechanism to describe the function of sulfur dioxide and nitrogen oxide in the oxidation of  $\text{Hg}^0$ , that is to say, the  $\text{Hg}^0$  and nitrogen dioxide could react on the activated carbon surface to generate mercuric nitrate [45]. In this reaction, the nitrogen dioxide is the electron acceptor. But when there was sulfur dioxide, the surface of some carbon would be of sulfation and the mercuric nitrate would not be generated, instead of mercuric bisulphate, in which the function of nitrogen dioxide was still electron acceptor. In the research on the adsorption of  $\text{Hg}^0$  in the simulated flue gas with manganese dioxide, Olson et al found that the mercuric bisulphate could react with nitrate to generate mercuric nitrate [45]. But Niksa et al held that when the hydrogen chloride was adsorbed on the catalyst surface, the  $\text{Hg}^0$  would be hard to or even not be adsorbed [46]. The

above researchers proposed that the oxidation and adsorption of the aforesaid  $\text{Hg}^0$  shall obey the Eley-Rideal mechanism, that is to say, the adsorbed hydrogen chloride reacted with gaseous  $\text{Hg}^0$ . In the formula, A means hydrogen chloride and B means  $\text{Hg}^0$ :



However, it is widely believed that the  $\text{Hg}^0$  can be adsorbed on many adsorbent surfaces. The Eley-Rideal mechanism and Langmuir-Hinshelwood mechanism are established by determining the reactant adsorbed on the catalyst surface such as hydrogen chloride or  $\text{Hg}^0$  etc. Besides, it is found that if the catalyst is pre-exposed in the oxidizer, such as hydrogen chloride and then the  $\text{Hg}^0$  is introduced under no gaseous hydrogen chloride, the  $\text{Hg}^0$  can still be oxidized. This further verifies the adsorption of hydrogen chloride on the catalyst surface described in the Eley-Rideal mechanism and Langmuir-Hinshelwood mechanism. Although the adsorption of reactant is complicated, the Langmuir-Hinshelwood mechanism can be demonstrated by chemical kinetics. The oxidation of  $\text{Hg}^0$  shall obey first order kinetics formula compared with the  $\text{Hg}^0$  concentration and hydrogen chloride concentration.

Similar to the above adsorption and oxidation process, Granite et al proposed that the oxidation of  $\text{Hg}^0$  shall follow the Mars-Maessen mechanism [39]. They thought the adsorbed  $\text{Hg}^0$  could react with the oxidizer (such as oxide and chlorine) in the catalyst lattice and the oxidizer consumed will be supplemented from the gas state. The oxidation of  $\text{Hg}^0$  on activated carbon with halogen pretreatment can be explained with this mechanism [39,47]. The following reactions describe the oxidation reaction of adsorbed  $\text{Hg}^0$  with the oxide in the catalyst lattice:



Wherein, A means  $\text{Hg}^0$  and  $M_xO_y$  means metallic oxide catalyst. So far, there is no mechanism that can expound the catalytic oxidation mechanism of  $\text{Hg}^0$ . The disadvantages of existing mechanisms are the inability to predict the catalytic oxidation level of  $\text{Hg}^0$  with different catalysts.

## Demercuration Capacity of Flue Gas Pollution Control Equipment

### Dust removal equipment

The electric precipitator and bag-type dust collector in good operation can effectively capture the grains in flue gas, so they can remove  $\text{Hg}_p$  in the flue gas with a high efficiency, some gas mercury can be absorbed in the flying ash and removed in the electric precipitator or bag-type dust collector. Hower et al. found in research that the flying ash containing various kinds of activated carbon had the most significant removal effect to gas mercury, while that containing inert carbon had seldom absorption effect on the mercury in flue gas [48]. In addition, the removal efficiency of flue gas mercury is also related

to the temperature of flying ash and operation temperature of bag-type dust collector (FF), the higher the temperature, the lower the removal efficiency will be. It was found in the experiment that when flue gas passed through the dust collector, about 5% of the  $\text{Hg}^0$  was converted into  $\text{Hg}^{2+}$  under the catalysis and oxidation of some metal oxidants in the flying ash, which was beneficial for the removal of mercury in the desulfurization system [49].

Bag-type dust collector is generally used to remove the high resistivity dust and fine dust; it particularly has a good effect in removal of fine dust. Some particles are rich in lots of mercury, so the bag-type dust collector has a great potential to remove the mercury in the flue gas. It is indicated through research that the average demercuration rate of bag-type dust collector is 58%, higher than that of the electric precipitator [50]. However, the work durability of bag-type dust collector depends on the temperature of flue gas and its resistance to some corrosive elements in the flue gas to a large extent. As the temperature of flue gas generally exceeds the temperature that can be borne by the bag-type dust collector, its application is limited. Wet dust collector and mechanical dust collector do not have high removal efficiency to the mercury in flue gas, respectively 6% and 0.1% [51]. Both dust collectors have relatively low dust removal efficiency and have a relatively poor removal effect to the fine particles containing rich mercury, resulting in that the mercury removal efficiency is not high.

### Desulfurization system

The flue gas desulfurization system is mainly classified into two categories, i.e. wet and dry flue gas desulfurization systems. The wet desulfurization device includes the common Limestone with Forced Oxidation (LSFO) and Magnesium Limestone Filter (MEL), which is used in about 1/3 of the coal-fired power plants in America. The dry flue gas desulfurization system is a typical Spray Drying Adsorption (SDA) method and mainly used in the power plant installed with bag-type dust collector. In the wet flue gas desulfurization system, the desulfurization adsorbent such as lime and limestone can be used to remove more than 90% of the  $\text{Hg}^{2+}$ , but of no obvious removal effect of  $\text{Hg}^0$ . In some common wet flue gas desulfurization (WFGD) systems, the  $\text{Hg}^0$  will not be adsorbed, but increase slightly, which may be caused by the reduction of partial  $\text{Hg}^{2+}$  [14].

The researchers had analyzed the mercury emission reduction effect in the wet desulfurization system of coal-fired power plant. As the  $\text{Hg}^{2+}$  adsorbed in the wet purifier may be converted into  $\text{Hg}^0$  to be discharged into the air again, NaHS is added in the testing to prevent the captured  $\text{Hg}^{2+}$  reduced as  $\text{Hg}^0$  [49]. The mercuric oxide removal rate of the desulfurization device of Endicott Power Plant (55MW, burning high sulfur coal, using limestone oxidation desulfurization) in Michigan, America can be up to 96% (accounting for 76-79% of the total mercury), therefore, the adding of NaHS can effectively prevent the captured mercury releasing into the atmosphere [49,52]. The mercury removal rate (51%) and  $\text{Hg}^{2+}$  removal rate (87%) of the desulfurization device of Zimmer Power Plant (1,300MW, burning high sulfur coal, using magnesian lime filtration and oxidation device) in Ohio, America are lower than that of Endicott Power Plant. Besides, the wet desulfurization system of Zimmer Power Plant makes the  $\text{Hg}^0$  concentration increase by 40% and cannot effectively prevent the  $\text{Hg}^0$  releasing even if the NaHS is added [49,52]. The

researchers conduct another experiment in the Mount Storm Central Power Plant (2,563MW, burning middle sulfur coal, using limestone oxidation method for desulfurization and selective catalytic reduction method for denitrification). Where the SCR unit is not opened and NaHS is not added, the desulfurization device can capture 90% of the  $\text{Hg}^{2+}$  (accounting for 71% of the total mercury), but which may be released into the atmosphere in the form of  $\text{Hg}^0$ . After adding NaHS, the desulfurization device can not only maintain a capturing rate of  $\text{Hg}^{2+}$  of 90% (accounting for 78% of the total mercury), but also effectively prevent the  $\text{Hg}^0$  releasing into the atmosphere. When the flue gas flows through the SCR unit, whether the NaHS is added, the capturing rate of  $\text{Hg}^{2+}$  is always more than 95% and the removal rate of total mercury is also up to about 90%, indicating that under certain operation conditions, the use of SCR unit and FGD unit can effectively reduce the mercury emission [52-55].

### Denitrification device

NOx control technology includes Selective Catalytic Reduction (SCR), Selective Non-Catalytic Reduction (SNCR) and low-nitrogen combustion technology etc. [14]. It is generally believed that the SCR device can oxidize partial  $\text{Hg}^0$  into  $\text{Hg}^{2+}$  by catalytic action while reducing NOx. The US EPA has measured the atmospheric mercury emission condition and mercury removal effect in the flue gas of some power plants installed with SCR and SNCR, the results of different power plants differ greatly and the advantages and disadvantages of the desulfurization effect of different denitrification technology are undetermined [52,53,56,57]. The catalytic oxidation efficiency of SCR device to  $\text{Hg}^0$  of coal-fired power plant varies between 45%-85% and the oxidation efficiency is influenced by the reaction temperature of catalytic reactor, ammonia concentration and chlorine concentration in the flue gas flow etc. The research finds that the 35%-50% of the  $\text{Hg}^0$  in the flue gas can be removed only with SCR device [58]. According to relevant report, the dust collector, desulfurization and denitrification control device can be used jointly to remove 65%-90% of the mercury [44,59,60].

Besides, the low-nitrogen combustion technology can also be used to remove the mercury. As the low-nitrogen combustion technology may increase the unburned carbon content in the flying ash in the flue gas, the mercury in the flue gas can be adsorbed and removed. The carbon content in the flying ash generated by different coal is different, so the demercuration efficiency is also somewhat different. For bituminous coal, the removal efficiency of mercury can be up to 85%; however, for subbituminous coal, that is relatively low, only 30%-50% [55,61]. Therefore, this technology is practical to the bituminous coal with large flying ash content. The development of pollutant combined removal technology, especially the use of SCR equipment to realize the combined removal of nitric oxide and mercury is economical and reasonable.

## Discussion

In the technological development of removal of  $\text{Hg}^0$  in flue gas, there are two main methods to achieve control of the process: to utilize the absorbent and the catalyst. From the research at home and abroad, we can find that one of the branch focuses on the development of efficient and economic absorbents, including activated carbon absorbent, modified activated carbon absorbent, calcium-based absorbent and flying ash absorbent; while the other branch focuses on

the research of oxidation of mercuric, including catalytic oxidation, photo-oxidation, plasma oxidation, and so on. All of those control methods perform differently in different coal-fired power plant and different flue gas mercury characteristics.

### Activated carbon as absorbent

Activated carbon is a common absorbent, and Activated Carbon Injection (ACI) can absorb both  $Hg^0$  and  $Hg^{2+}$  [39, 62-64]. It can not only absorb  $Hg^{2+}$ , but also  $NO$ ,  $SO_2$ ,  $HCl$ , etc. [42,65-69]. Mercury adhered to activated carbon will react with hydrogen chloride which is also on it to oxidize mercury; as a result, activated carbon can be both absorbent and catalyst to remove mercury. Many of the studies find that mercury can be absorbed on the carbon in flying ashes [35,40,70,71]. Furthermore, the oxidation degree of mercury depends on the unburned carbon in the flying ashes [35,46].

Researchers add activated carbon absorbent in flue gas from coal-fired power plant to control the emission of mercury. It is the key for the control technology to add powder absorbent before the dust collector [72]. TOXECON™ is one of the equipments. It has small bag-type dust collector, which is installed at the end of electrostatic precipitator. Electrostatic precipitator will remove most of the Particulate Matter (PM). After this process, absorbent is added and the bag-type dust collector downstream will absorb all of the rest absorbent and PM. In the end, flying ash and absorbent will be separate effectively [51,52,57,72].

The most common absorbent is Powdered Activated Carbon (PAC). Generally speaking, more PAC is added, the mercury removal efficiency will be higher. Since enough halogen ensures the function of PAC in flue gas, more PAC must be added while burning low grade coal with low chlorine concentration. The effect of mercury removal of PAC is largely affected by the structure and type of existing flue gas pollution control equipment. For instance, small bag-type dust collector is installed behind the electrostatic dust collector; the mercury removal efficiency will be largely improved after adding large dose of PAC. However, if the PAC with mercury is collected by electrostatic dust collector, the PAC size will influence the mercury removal rate. While using bag-type dust collector, the influence can be subtle.

Generally speaking, with the increase of  $Hg^{2+}$  in flue gas, the absorption effect for mercury will be improved. What's more, the content of halogen in flue gas will directly influence the content of  $Hg^{2+}$ . However, the effect of PAC is not so obvious in the coal-fired and pollution control equipment of the three kinds of plants as below: first, the plant burning low grade carbon and adopting electrostatic dust collector, which will result in a low content of chlorine, second, the plant burning low grade carbon and adopting spray drying desulphurization and bag-type dust collector, with the result similar to that in the first kind of plant mentioned above, and third, the plant burning sulphur coal, where the large quantity of sulphur trioxide will cover the surface of PAC, as a result of which, mercury cannot be absorbed [14]. However, those kinds of plants can use both Selective Catalytic Reduction (SCR) and Flue Gas Desulphurization (FGD) to control the emission of mercury.

The absorptive ability of PAC to mercury is a very complicated process, and the cognition of the specific principle is still not enough.

Judging from the experimental results, it is likely to be a combined result with both physical and chemical absorption. From this perspective, to develop better technology of demercuration effect by PAC, we need to add halogen or other nonmetal elementary or component substances which can react with mercury to the surface of PAC. Uddin et al find that the absorptive ability of PAC will be largely improved if PAC is disposed by  $SO_2$  or  $H_2SO_4$ , and soaked by  $MnO_2$  or  $FeCl_3$ . This is because the absorptive process of  $Hg^{2+}$  includes both physical and chemical absorption. In addition, after the processing with  $SO_2$ , PAC assisted by  $SO_3$  or  $H_2SO_4$  which are formed by  $O_2$  and  $H_2O$  in the flue gas completes the oxidation removal of mercury [73-75].

Chi et al also reported that the absorption rate of simulated flue gas mercury by PAC absorbent modified by Iodide ( $I_2$ ) is 70% at 393K. What's more, the oxidizing ability of Iodide-PAC to mercury element soars to 90% after adding flying ash or PAC [76]. Zhuang et al paid close attention to the corrosion of additives like halogen on flue gas equipment [77]. For example, mercury removal effect is better after adding  $Br_2$  to flue gas to oxidize mercury, but this also corrode equipment badly. It is required to replace some part of the flue gas pipeline every six months under the supervision of safety standard. Therefore, it's not suggested to use high density  $Br_2$  as additive to modify PAC.

Some researchers have done relevant studies on the grain diameter and dosage of activated carbon as well as the economic feasibility of mercury removal. The experiment of Miller et al showed that removing 1.0g mercury elements in the flue gas in which the mercury elements content is  $10\mu g/m^3$  (removal rate is above 90%) needed 3,000g PAC with the diameter of 4um or 18,000g PAC with the diameter of 10um [14,78,79]. The most common evaluation of absorption capability of PAC at experiment is C/Hg. The effect of PAC to remove flue gas mercury is obvious, but it is not able to tell the distinct removal efficiency of mercury elemental and  $Hg^{2+}$ , PAC can absorb mercuric chloride. As a result, it is very difficult to measure the oxidation rate of mercury element. EPA believes that mercury removal rate can reach 60%-90% through adding PAC and improving cooperative mercury removal ability of existing equipment [52,53]. It also believes that the mercury removal rate can reach 90%-95% if adding halogen PAC and other chemical agents. And, at least, some of the key technology in mercury control field can be put into business during 2010-2015. Those optimized mercury removal technologies include absorbent and optimized combined SCR and FGD system [55,80]. PAC and other modified technologies discussed above are still under further study. Based on the present technological level, the operating cost of coal-fired power plant and the *Bill of Contamination Control* have not reached an agreement yet. Therefore, it is not appropriate to be put into use in a large scale.

### Calcium-based substances and flying ash

US EPA has studied the effect of calcium-based substances in mercury removal. It shows that the removal rate of calcium-based substances, such as  $Ca(OH)_2$  to  $Hg^{2+}$  is about 85%. And other calcium-based substances, such as  $CaO$  can also absorb the chloride of mercury effectively, but the removal efficiency of mercury element is very low [52, 81,82]. Calcium-based substances, which are quite common in power plant and can be obtained easily with little cost, are

a kind of effective sulphur remover in flue gas. Therefore, it becomes the highlight in studying sulphur removal. Flying ash from pulverized coal furnace has certain economic value. In addition, we find flying ash is a potential absorbent in the study of the absorptive ability of mercury adsorbent.

The flue gas mercury removal ability of flying ash to different coal-fired power plants differs greatly. And it is mainly depends on the quantity of magnetite and iron oxide in spinal structure it contains. The experiment also shows that the oxidation functional group and the existing of halogen on the surface of flying ash can improve absorption of flying ash to mercury; the superficial area, however, has little impact on it [83-85]. It is always regarded that the oxidation of  $Hg^0$  occurs on the place of carbon, as a result, there are researchers establishing the correlation of the unburned carbon and the efficiency of mercury removal [28,72]. However, using loss on ignition to evaluate the unburned carbon will usually over estimate the carbon concentration in flying ash [82].

Mercury removal ability of flying ash is strongly influenced by the components of flue gas. Galbreath et al found that improving the concentration of HCl or HBr in flue gas with flying ash could promote the generation of  $Hg^{2+}$  [86]. Kellie et al also found that concentration of HCl in flue gas would increase while there was a large quantity of chlorine in flying ash, which favored the generation of oxidized mercury [87]. Laudal et al found that oxynitride could react with flying ash, but this reaction was affected by the proportional control of NO and  $NO_2$  [19,88].  $NO_2$  could heterogeneously oxidize  $Hg^0$ , but the effect was much less than that of chlorine. Norton et al found that  $NO_2$  could deepen the degree of oxidation of mercury, but NO would retard oxidation of mercury [89]. The influencing mechanism of NO and  $NO_2$  to mercury removal is still not so clear. According to other researches of Laudal et al, other components in flue gas will retard oxidation of mercury. For example,  $SO_2$  will retard oxidation of mercury [19]. Serre and Silcox found that  $SO_2$  would reduce the efficiency of oxidation of mercury for it restrains absorption of mercury in flying ash [71]. Kellie et al believed that the sulphur content in flying ash was related to the content of  $Hg^{2+}$  in flue gas in some extend [87]. Still, the reaction mechanism of sulphur dioxide is not so clear.

Hassett et al measured catalytic and oxidizing ability of various flying ash by fixed bed reactor in 150°C, and found that different flying ash had different catalytic and oxidizing ability to mercury. Many kinds of bituminous coal and sub-bituminous coal could transform 20%-50% of  $Hg^0$  to  $Hg^{2+}$  in simulated flue gas. However, the ability of flying ash burning lignite was very bad and the conversions were less than 10% [70,71]. Similarly, some scholars researched on mercury removal effects of different flying ash and carbonic catalyst in different coal flue gases (lignite, sub-bituminous and bituminous coal). They also got different results [70]. The conventions of flying ash and carbonic catalyst to mercury while burning lignite reduced from 100% to 0 after 18 weeks; while, the catalytic ability of burning sub-bituminous coal would lose activity after 12 weeks. In addition, when applying a kind of carbonic catalyst, which can keep conversions above 80% in two months, to lignite flue gas, the conversions reduced below 80% before long [90].

Taking economic costs into consideration, flying ash is cheaper

than ACI. But it still needs a long time to research its mercury removal prospect [91]. Research shows that the cost efficiency of halogen activated carbon is much higher than that of others [92,93], but it has been questioned recently as some scholars think it has the possibility to promote formation of PCDD/Fs (Polybromine dibenzo-p-dioxins/furan) and PBDD/Fs (polychlorinated dibenzo-p-dioxins /furan) [94,95].

### Metals and its oxides

Many metals and metallic oxides can serve as catalyst in the process of  $Hg^0$  oxidation. While using metals and metallic oxides as catalyst, coal-fired power plants need to load grouped metals and metallic oxides in the carriers, such as honeycomb ceramics. Kamata et al summarized the mercury oxidization performance [96] of metallic oxides such as  $V_2O_5$ , NiO, CuO,  $MoO_3$ ,  $Fe_2O_3$ , and  $WO_3$  loaded with 1-15% metal content, with  $TiO_2$  being the carrier of the mercury oxidization process. The research found that  $V_2O_5$  and CuO loaded in the carrier,  $TiO_2$ , with 10% metal content, would present the best mercury oxidization performance. Under the condition of 423K, after 20ppm HCl were added in the experiment, approximately 80% of the mercury was oxidized into  $Hg^{2+}$ , which was related to the form of  $V_2O_5$  and  $SO_2$  concentration in the simulated flue gas and the use of low concentration mercury resource.

Similarly, Lee et al. reported that  $V_2O_5/TiO_2$  in nano-particles could bring about better effect in the process of the removal of  $Hg^0$  from the simulated flue gas. The research indicated that  $V_2O_5/TiO_2$  in nano-particles had better demercuration effect, removing 96% high content  $Hg^0$  in the simulated flue gas through oxidation into  $Hg^{2+}$  under the condition of 100-200°C. As  $V_2O_5/TiO_2$  in nano-particles are denitration catalyst with excellent sulfur resisting and water-resisting performance, researches on the demercuration of denitration catalyst has attracted widespread attention [97].

Qiao et al conducted the experiment of catalyzed oxidation demercuration of  $Hg^0$  in flue gas using  $MnOx/Al_2O_3$ . The demercuration efficiency would be the best 90% under the condition of 600K [25]. Impacted greatly by the  $Cl_2$  concentration and gaseous HCl concentration, the demercuration efficiency changed with the load of  $M_n$  and the demercuration effect would be the best with the  $M_n$  load of 3%. Yamaguchi et al found that, from the simulated oxidation experiment of  $Hg^0$  in flue gas by using metallic oxide, CuO that low HCl concentration would promote the oxidation of  $Hg^0$  and the oxidation efficiency would decline with the rise of the temperature and there would be a negative correlation between the demercuration efficiency and the size of CuO particles [98]. Hrdlicka et al conducted the catalyzed oxidation experiment of  $Hg^0$  in the flue gas put on the bag-type dust collector by using  $Au/TiO_2$  and  $Pd/Al_2O_3$ . He found that the demercuration efficiency of the two groups was 40%-60% and 50%-80% respectively and there was still room for improvement in demercuration efficiency of the  $Pd/Al_2O_3$  group [99]. Tian et al achieved low temperature demercuration effect by injecting  $CeO_2$  onto the surface of activated carbon [100]. The research indicated that the demercuration efficiency of  $Hg^0$  could reach 70% with 1%  $CeO_2$  load under the condition of 100°C, while it could reach as high as 90% with the best 3%  $CeO_2$  load under the best condition of 100°C as  $CeO_2$  could decompose the HCl in the flue gas into highly active Cl atom, which removed  $Hg^0$  by oxidizing  $Hg^0$  into  $Hg^{2+}$ .

In the experiment of simulated flue gas atmosphere, many metallic oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{CaO}$  and so on were found influencing the catalyzed oxidation of  $\text{Hg}^0$  to different degrees. For example,  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$  both could highly effectively catalyze and oxidize the  $\text{Hg}^0$  in the simulated flue gas. At the same time, in the research on the influencing factors of metallic oxides removing  $\text{Hg}^0$  in the gas, Uddin et al found that  $\text{SO}_2$  obviously had inhibitory effect on the oxidation removal of  $\text{Hg}^0$  [101]. However, Li et al.'s research indicated that  $\text{SO}_2$  had certain facilitating effect on the oxidation of  $\text{Hg}^0$  in the gas [102,103]. He also summarized that  $\text{O}_2$ ,  $\text{HCl}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$  would have facilitating effect or inhibitory effect on the demercuration of  $\text{Hg}^0$  in the gas for the first time in his research, which contributed a lot in the research of the relationship between the main components and the demercuration efficiency conducted by the following scholars. However, the result in scale and measurement of this research did not present as obvious as other research results [102,103].

Other metals and metallic oxides like iron and iron oxides could also promote the process of catalyzed oxidation of  $\text{Hg}^0$  in the flue gas [14]. Dunham et al founded that under the condition of  $120^\circ\text{C}$  and  $180^\circ\text{C}$ , the oxidation efficiency of  $\text{Hg}^0$  would be proportional to the magnetite concentration in the fly ash [78]. Ghorishi et al found that under the condition of  $250^\circ\text{C}$  with  $\text{HCl}$ , the fly ash containing  $\text{Fe}_2\text{O}_3$  could make 90% of the  $\text{Hg}^0$  oxidized, while the fly ash without  $\text{Fe}_2\text{O}_3$  could just make 10% of the  $\text{Hg}^0$  oxidized into  $\text{Hg}^{2+}$  [41]. This indicated that  $\text{Fe}_2\text{O}_3$  could promote the catalyzed oxidation of  $\text{Hg}^0$  in the flue gas. Galbreath et al spurted hematite and megahemite into the flue gas containing fly ash. As a result, the form of mercury in the flue gas would not change by spurting hematite into the flue gas, while the oxidation efficiency of  $\text{Hg}^0$  would be improved by spurting megahemite into the flue gas [86]. These results all indicated that iron oxides like  $\text{Fe}_2\text{O}_3$  imposed good demercuration effect on the  $\text{Hg}^0$  in the Precious metals like copper, gold, silver, palladium and so on were used to be catalyst in the process of catalyzed oxidation of  $\text{Hg}^0$  in the flue gas. A ten-month long pilot scale research on palladium catalyst indicated that palladium catalyst could maintain good catalyzed demercuration performance for a long time and the oxidation efficiency of  $\text{Hg}^0$  had not changed much, just declined from the initial over 90% to 80%. Furthermore, short-term experiment of palladium catalyst on site indicated that no matter the flue gas was produced by bitumit, subbitumimous coal or brown coal, the oxidation efficiency of  $\text{Hg}^0$  in the flue gas could always be approximately 90% [99]. The ten-month experiment also indicated that the reason for the decline catalyst activity was that the catalyst was put into the lower reach of ESP leading to the existing accumulation of fly ash, which would cover the active material on the surface of the catalyst, thus causing the decline of the catalyst activity. The author suggested making some post disposal of the catalyst, like blowing into  $\text{N}_2$  or  $\text{CO}_2$  for cleaning, to regenerate the catalyst activity.

Other precious metals like gold, uranium, iridium, silver, and copper could also achieve the same demercuration effect. Meischen and Van Pelt made use of the compounds mixed by gold, silver, platinum and their compounds by certain proportion in the process of catalyzed oxidation of  $\text{Hg}^0$  in the flue gas and found that the demercuration efficiency within 45h under the condition of  $70^\circ\text{C}$  could reach as high as over 95% using gold catalyst [104]. Zhao et al.

also reported recently that under the condition of  $175\text{-}225^\circ\text{C}$  with chlorine gas, gold catalyst could make 60%-90% of  $\text{Hg}^0$  oxidize, and at the same time he also found that while using gold catalyst,  $\text{Cl}_2$ , as oxidant, had better effect than  $\text{HCl}$ . Ghorishi et al's research on copper catalyst indicated that when the fly ash contained  $\text{CuCl}$ , the  $\text{Hg}^0$  in the flue gas could be partially oxidized without  $\text{HCl}$  in the flue gas [105].

### SCR catalyst

Due to the expensive cost of activated carbon injection method, the Department of Energy of the United States estimates that the cost is between USD 25,000-70,000 to remove 1 pound (around 0.4536g) of  $\text{Hg}$  to control the 90% of  $\text{Hg}$  discharge in the flue gas of coal-fired electric power plant [14]. It is difficult to accept such price for many coal-fired electric power plants so that numerous researchers start to pay attention to a more economic and practical flue gas demercuration method such as catalytic oxidation removal of flue gas mercury. They try to seek for a more excellent and economic demercuration catalyst to achieve efficient mercury removal. In fact, one of the most optimized demercuration methods of coal-fired electric power plants is to achieve combined removal pattern by  $\text{Hg}^0$  in the flue gas and controlled nitric oxide on existing SCR device which can reduce reconstruction fee and operation fee of site and device as well as, in addition, secondary pollution from by-products of electric power plants such as mercury-containing flying ash to realize centralized control.

The major component of present commercial SCR catalyst is  $\text{V}_2\text{O}_5/\text{WO}_3$  with titanium dioxide as the carrier [33]. Research aiming at such SCR catalyst to catalytic oxidize the  $\text{Hg}^0$  in the flue gas is not limited in conducted operational testing at pilot-scale test model in the laboratory scale, among which it investigates the main factors to influence demercuration such as major gas components in the flue gas (concentration of  $\text{HCl}$ , concentration of  $\text{NO}$  and the specific value of  $\text{NO}/\text{NH}_3$ , etc.) as well as its temperature and coal-fired types [106-109]. Laboratory investigation manifests that SCR catalyst can effectively catalytically oxidize  $\text{Hg}^0$  in the flue gas with most distinct influence on demercuration efficiency by components of flue gas. Studies have found that there is a great relation between the oxidation degree of  $\text{Hg}^0$  in the simulated flue gas and the concentration of chlorine content there among which the demercuration efficiency has a positive correlation with the concentration of chlorine in the flue gas and increase of the ammonia concentration shall decrease the oxidation efficiency of  $\text{Hg}^0$  [96,110,111]. Laudal et al discovered in pilot-scale study that when it was  $340^\circ\text{C}$ , concentration of  $\text{Hg}^0$  at the exit of SCR shared a negative correlation with concentration of hydrogen chloride and sulfur dioxide, whose result was consistent to the research results on the stationary bed of laboratory by Straube et al [19,112]. In addition, it is found that decrease of specific value of  $\text{NO}/\text{NH}_3$  and concentration of  $\text{HCl}$  will reduce the oxidation efficiency of  $\text{Hg}^0$ .

The components of flue gas will influence not only the demercuration efficiency of SCR, but also the product of demercuration. Study by Eswaran and Stenger finds that when the temperature of flue gas including 10-20ppm hydrogen chloride is higher than  $300^\circ\text{C}$ , the oxidation degree of  $\text{Hg}^0$  only can achieve 95% with the end product of  $\text{HgCl}_2$ , but with the end product of  $\text{HgSO}_4$  in case of any sulfur dioxide or sulfuric acid [106].

There are also some research results about the disposal of demercuration regeneration of SCR catalyst. Straube et al made a test towards the demercuration performance and regeneration disposal of the SCR catalyst  $V_2O_5/TiO_2$  in the  $NH_3$ -SCR system whose result indicates that  $V_2O_5/TiO_2$  catalyst has a good oxidation effect towards  $Hg^0$  in the simulated flue gas and oxidized mercury is adsorbed on the surface of  $V_2O_5/TiO_2$  as in the form of (Hg-O) and then can be recycled after washing by the mixed dilute solution of acetic acid and hydrochloric acid [112].

Many studies also investigate the oxidation effect of  $Hg^0$  in the flue gas of the electric power plants installed with SCR catalytic device, finding that not only gas composition and gas concentration, but also the parameters such as airspeed and fire coal type will influence the demercuration effect of SCR catalyst [108]. The study finds that when the airspeed of boiler flue gas fired with subbituminous coal increase from  $3,000h^{-1}$  to  $7,000h^{-1}$ , the oxidation effect of  $Hg^0$  decreases from 30% to 15%. Senior et al reported the effect on catalytic oxidation of the flue gas by some commercial SCR catalyst in an electric power plant firing 87% subbituminous coal and 13% anthracite [111]. In case of normal condition of this electric power plant, the conversion efficiency of  $Hg^0$  generally is between 60%-80%. Benson et al also make an investigation on the oxidation effect of  $Hg^0$  by using SCR catalyst in the electric power plant firing anthracite and lignite [109], finding that just a small quantity of  $Hg^0$  is oxidized in the flue gas (350-360°C) generated by firing lignite; the proportion of  $Hg^0$  converting into  $Hg^{2+}$  is higher in the flue gas (315-345°C) generated by mixed firing the bituminous coal and subbituminous coal which can reach 60%-80% [109].

Except studies on demercuration effect and influence factors, parts of scholars make some reports aiming at demercuration mechanism of SCR catalyst. Because the mechanism of catalytic oxidation of  $Hg^0$  by SCR catalyst is still not clear, some scholars put forward several possibilities, but many studies find  $Hg^0$  can be adsorbed on the surface of SCR catalyst. Generally, SCR catalyst deoxidizing oxynitride and oxidizing  $Hg^0$  respectively is conducted in two areas. One is nearby the entrance, in which there is relatively much  $NH_3$ , so the active site on the surface of SCR is mainly occupied by ammonia. It is the place to make reduction reaction of NO; during the latter half process of SCR catalyst, most  $NH_3$  has been used up, so that the one to occupy the surface of catalyst is HCl or  $Cl_2$ . Oxidation reaction of  $Hg^0$  is achieved in this area.

Niksa and Fujiwara think that oxidation mechanism of  $Hg^0$  on the SCR catalyst is similar to that of the catalytic reduction of NO, in which, firstly, HCl is adsorbed on the surface of  $V_2O_5$  and reacts with the  $Hg^0$  in the gas phase or adsorbed on the surface of  $V_2O_5$  physically, which results ammonia to compete for the active site on the surface of catalyst against hydrogen chloride [33]. Hocquel thinks that ammonia, hydrogen chloride compete for the active site on the surface of catalyst against  $Hg^0$  at the same time and the oxidation of  $Hg^0$  is achieved through the reaction between the adsorbed  $Hg^0$  on adjacent sites and hydrogen chloride (Langmuir-Hinshelwood mechanism), which can explain why the increase of the concentration of ammonia can reduce the oxidation efficiency of  $Hg^0$  [113]. The chlorine detected on the SCR catalyst by Guberlet et al explains that it may be the action of Deacon Reaction for the oxidation of  $Hg^0$  [114].

Meanwhile, many studies report that components of flue gas

play the inhibition mechanism role in the demercuration efficiency of catalyst. Studies find that increase of ammonia concentration will result in desorption of  $Hg^0$  from the surface of catalyst, but there is no specific introduction to the desorption process. Senior, recently, puts forward a pattern to explain the inhibition mechanism of the  $Hg^0$  on the SCR catalyst, which deems that oxidation of  $Hg^0$  complies with the Eley-Rideal mechanism (adsorbed  $Hg^0$  reacts with gaseous hydrogen chloride, but compete to adsorb against ammonia [111]). This model can predict the temperature and airspeed of flue gas, the concentration of hydrogen chloride, the structure of catalyst and the specific value of  $NH_3/NO$  and the influence relation between  $Hg^0$  and oxidation efficiency, but no explanation is given on its reasons. Because of the complication about the reaction mechanism of  $NH_3/SCR$  system and kinetics and unclear influence of adding mercury on the denitration effect of catalyst, besides, the related research work is not thorough enough, study in this aspect shall be strengthened and it is required to have a deeper research on the catalytic oxidation of the  $Hg^0$  in the flue gas with SCR catalyst and its inhibition mechanism.

Although laboratory researches find SCR catalyst can oxidize almost 95% of  $Hg^0$ , the real oxidation efficiency in flue gas suffers a decline obviously. Pilot-test demercuration studies find that after a long time of operation, the oxidation efficiency of  $Hg^0$  decreases from 70% to 30% which may result from the plug of catalyst by flying ash [19]. Due to the mass alkaline substance contained in flying ash, the flying ash containing alkaline substance is adsorbed on the surface of SCR catalyst to decrease the surface acid site of SCR catalyst so as to further reduce the efficiency of catalytic oxidizing  $Hg^0$ . The experiments of three electric power plants find that the duct of SCR catalyst is blocked by alkaline substance, therefore, to lead to the decrease of conversion efficiency of  $Hg^0$  and oxynitride.

## Conclusion

*MEP-PRC* declares that China is still in the initial stage in the aspect of coal-fired mercury pollution control, and most coal-fired power plants are not equipped with specialized mercury pollution control equipment. In western countries, coal-fired fuel gas is of desulfurization and denitration treatment first and then of demercuration treatment, whose process is to add some AC to absorb the gaseous mercury. However, there is still some gaseous mercury unable to be removed and the by-products after desulfurization and denitration are generally coal ash and gypsum. If the gypsum and coal ash are reused, the mercury is likely to be released again.

In case of demercuration, the corresponding industry will bear higher costs. The Division of Air Pollution Control, Tsinghua University has estimated the price and the results showed that the mercury emission control by using AC involves investment cost, adsorbent cost and disposal cost, of which the investment cost is about USD 3.6/kw; the AC is about USD 0.39-0.95/pound and the disposal cost is about USD 19/t; besides, the cost of sales loss of flying ash caused by activated carbon pollution is about USD 20/t. Considering the sales loss of flying ash, for a unit with a capacity of 500MW, the annual operation and maintenance expenses of ACI demercuration system exceed USD 2 million. Also, the US Department of Energy estimates that the ACI cost is between USD 25,000-70,000 to remove 1 pound Hg (around 0.4536g) by coal-fired electric power plant [14]. It is unaffordable for most coal-fired power plants.

It is a relatively economical and practical method to remove the mercury in the flue gas while controlling the oxynitride and sulfur dioxide by SRC combining with FGD unit. Existing SCR position is not much appropriate for the combined removal of oxynitride and Hg<sup>0</sup> because present SCR catalyst mostly is located on the upstream of PM (particulate matter) control device so that SCR catalyst generally is exposed in the high-concentration flying ash which needs some improvements. At present, some researchers try to put the SCR catalyst on the downstream of PM control device and FGD to specifically control the discharge of mercury by running in the low temperature (150°C). As SCR catalyst generally runs above 300°C, the high temperature can enable the desorption of the Hg<sup>0</sup> adsorbed on the surface of catalyst, so that the oxidation degree of Hg<sup>0</sup> will be limited.

All the studies above manifest that it is practical and feasible to realize simultaneous denitration and demercuration by NH<sub>3</sub>-SCR system but some reformation is needed for the existing SCR device. Even so, it is still of practical and feasible significance for combined demercuration by existing denitration device. There is no mature and applicable demercuration technology in present coal-fired electric power plants and a lot of problems exist in the application of mercury removal technology in the coal-fired electric power plant flue gas, most of which is still under laboratory research period. Research aiming at flue gas demercuration of coal-fired electric power plants may concentrate on how to effectively utilize existing pollution control device to improve the removal efficiency, taking the combined typed pollution control path. Thus, there are evident advantages to apply flue gas denitration control device to realize synergized demercuration with a vast application prospect.

All in all, for China, it is of practical and feasible significance for combined demercuration by existing denitration device. *MEP-PRC* declares that flue gas demercuration of coal-fired electric power plants may concentrate on how to effectively utilize existing pollution control device aiming at typical SNCR/SCR + ESP/FF + WFGD to improve the removal efficiency.

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