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Experimental Study on Removal of Hg^0 from Flue Gas by Spraying Desulphurization Wastewater into Flue

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Abstract. Mercury in coal-fired power plants is a trace element, will be discharged into the atmosphere along with the smoke, endangering human health and ecological environment. Mercury removal from power plants has become a hot research topic at present. In this paper, combined with the existing conditions of mercury removal technology, focusing on the desulfurization wastewater spray into the flue synergistic removal of elemental mercury, and then proposed a new environmentally friendly mercury removal method.

Introduction

At present, China's energy structure is dominated by fossil fuels, of which coal resources are the most important fossil energy, and this energy structure will not be fundamentally changed for a long time. The composition of coal is extremely diverse, containing elements such as C, H, O, N, S, and trace elements such as Hg, As, Se, Pb and Cd which are toxic to the environment and human health[1]. The form of Hg in coal-fired flue gas is mainly Hg^0, Hg^{2+} and granular Hg. Hg^{2+} can be removed by adsorption and particulate Hg can be removed by electrostatic precipitators. Hg^0 is the most difficult to remove in the three forms of the part. It has insoluble in water, highly volatile, long residence time in the atmosphere, easily through the atmospheric diffusion of mercury pollution caused by the global[2-3]. Therefore, this paper will focus on the desulfurization wastewater Hg^0 removal efficiency.

Current mercury removal technology in power plants

The most common methods of mercury removal from coal-fired power plants are Adsorbent Injection Technology and Hg^0 Oxidation Technology. Firstly, the Adsorbent Injection Technology is the most mature and has been achieved at this stage of industrial application of mercury control technology. Activated carbon and modified activated carbon is the most widely used adsorbent. Activated carbon adsorption of mercury is a diversified process, which includes adsorption, condensation, diffusion and chemical reactions. Activated carbon is related to its physical properties, temperature, flue gas composition, residence time, mercury concentration in flue gas, carbon and mercury ratio and other factors. However, activated carbon mixed with fly ash can not be regenerated. Due to the existence of low capacity, poor mixing, low thermodynamic stability of the problem, and the utilization of activated carbon is low, large consumption, so that the direct use of activated carbon adsorption cost is too high. The US Department of Energy estimates that it would be difficult for coal-fired power plants to achieve a mercury removal rate of 90% and removal of 0.45 kg of mercury at a cost of $(2.5 \text{ to } 7.0)\times 10^4$ dollars[4]. Secondly, Hg^0 Oxidation Technology is mainly the use of a variety of strong oxidants on the oxidation of elemental mercury to make it into divalent mercury, which was adsorbed by the desulfurization equipment. Now the most widely used oxidants are $KMnO_4$, $K_2Cr_2O_7$, $K_2S_2O_8$ and H_2O_2. Qunfeng Ye[5] carried out the study of $KMnO_4$ removal of gaseous mercury, and the results showed that the initial concentration of $KMnO_4$ and the decrease of reaction temperature all promoted the removal of Hg^0. The presence of H_2SO_4 promoted the adsorption of Hg^0 by MnO_2, and the Hg^0 was indirectly oxidized by OH^- in strong alkaline solution. Therefore, strong acid or alkali Which is favorable to the removal of Hg^0. At

present, the main problem of oxidation technology is the introduction of new ions, may lead to equipment scaling, corrosion and removal of secondary pollution of wastewater problems.

Utilizing Desulphurization Wastewater to Remove Mercury from Flue Gas

Composition Analysis of Desulfurization Wastewater.

Desulfurization wastewater is mainly boiler flue gas wet desulfurization (limestone / gypsum method) in the process of absorption tower drainage water. Wastewater containing suspended solids, SO_3^{2-}, SO_4^{2-} and heavy metals and other substances, many of which are strictly required by the state environmental standards in the first category of pollutants. Now we are desulfurization wastewater component analysis, the results shown in the Table 1 below.(Desulfurization wastewater Source: Datang Baoding Thermal Power Plant, Baoding, Hebei Province)

Table1 Analysis of the Composition of Desulfurization Wastewater(unit: mg/L)

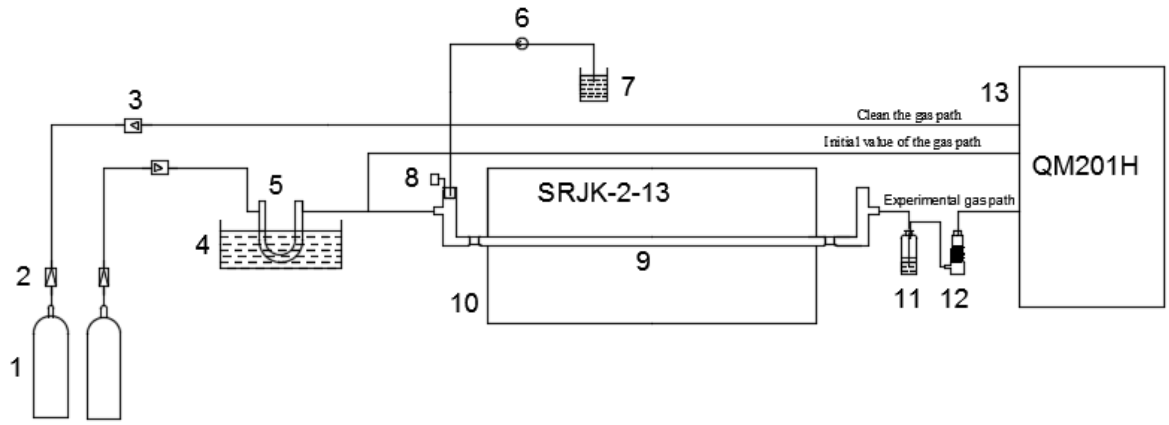
Project	Experimentally measured concentrations	Maximum allowable emissions
F^-	226	30
Cl^-	2422	250
Cr	3.01	1.5
Cd	0.32	0.1
Hg	0.15	0.05
SO_4^{2-}	4192.5	250
Cu^{2+}	0.893	5
CODcr	272	150
Suspended Solids	11900	400

From the table, we can see that the composition of desulfurization wastewater is very complex, many of which are seriously exceeded pollutants, conventional treatment desulfurization wastewater need to spend a greater human and material resources. If we can use desulfurization wastewater treatment Hg^0 in flue gas, is undoubtedly a "waste to waste" of the new method.

The construction of the experimental platform.

The experimental system is divided into four parts:flue gas simulation and flow control system, mercury generator system, simulated flue reaction system, mercury detection system. The experimental system diagram shown in Figure 1.

Nitrogen acts as a carrier gas, the elemental mercury at a uniform rate of blowing out. Desulfurization wastewater through a peristaltic pump at a constant flow rate drops into the atomizer, so the desulfurization wastewater is atomized. The desulfurization wastewater after atomization reacts with the elemental mercury in a tube resistance furnace, and the tube resistance furnace can adjust the reaction temperature. After the reaction of the gas, respectively, through the absorption bottle and drying bottles, and finally to the QM201H mercury analyzer.



1.Nitrogen cylinder 2.Pressure reducing valve 3.Rotor flowmeter 4.Constant temperature water bath 5.Mercury generating device 6.Peristaltic pump 7.Desulfurization wastewater 8.Atomizer 9.Simulated Flue Reactor 10.Tube resistance furnace 11.NaOH absorption solution 12.Desiccant 13.Mercury measurement of coal - fired flue gas

Figure1 Schematic diagram of the experimental system

The mercury removal rate is calculated by the following formula:

$$\eta(\%) = \frac{\text{Initial value} - \text{Final value}}{\text{Initial value}} * 100$$

Experimental results.

The experimental parameters are as follows: Experimental gas flow rate: 0.8L / min, clean air flow rate: 1.2L / min, water bath set temperature: 60 ℃ and at this temperature, Hg^0 production concentration: 101ng / L, peristaltic pump speed: 300uL / min, tubular resistance furnace temperature: 300-700 ℃.

Measurement of mercury content: 0.6L / min, carrier gas 0.8 L / min, measuring time: 2min, cleaning time: 2min, negative high pressure: -410V. The experimental results are shown in Table 2 below.

Table2 Experimental Results of Mercury Removal from Desulfurization Wastewater

reaction temperature	Initial value	Experimental measurements 1	2	3	Average measured value	Efficiency value
300℃	1200	0719	0723	0719	0720.3	39.98%
330℃	1192	0624	0620	0615	0619.7	48.01%
360℃	1200	0458	0462	0444	0454.7	62.11%
390℃	1195	0236	0242	0244	0240.7	79.86%
420℃	1203	0101	0094	0097	0097	92.00%

As it seen from the table, desulfurization wastewater can indeed remove Hg^0. Under the same conditions, the mercury removal efficiency increased with the increase of temperature. A large number of studies have found that desulfurization of Cl^- in the oxidation of Hg^0, making it into Hg^{2+}, but the specific reaction mechanism is under study.

After calculation, the desulfurization wastewater sprayed into the flue gas, the smoke humidity increased slightly from 7.14% to 7.56% and flue gas temperature dropped slightly from 142 ℃ to 136 ℃, but still higher than the acid dew point temperature, the flue gas is not saturated, will not produce flue and electrostatic precipitator low temperature corrosion. Therefore, there is no need to carry out modification treatment on the desulfurization waste water injection point follow-up

equipment. At the same time, the water consumption of the FGD system is reduced due to the decrease of the flue gas temperature and the increase of the moisture content of the flue gas.

Summary

Mercury is a trace element, great harm to the human body, and most of the mercury in the atmosphere is discharged in the power plant, so the power plant mercury removal become hot spots at this stage. Nowadays, the widely used mercury removal method has the disadvantages of high economic cost and the introduction of new metal ions. This experiment innovative use of coal-fired power plant desulfurization wastewater into the flue to remove Hg^0 flue gas exploration. And the surprise that it is effective, the average efficiency value of more than 60%. This method in the removal of Hg^0 at the same time, desulfurization wastewater also achieved zero emissions-To achieve the effect of two birds with one stone. This "waste control by waste" approach to achieve environmental sustainability, low cost, simple and convenient purposes.

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