Removal of Hg$^{2+}$ from flue gas by petroleum thioether

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Abstract. Petroleum thioether showed excellent flue gas de-Hg$^{2+}$ ability to control mercury reemission. Petroleum thioether was prepared with high-sulfur crude oil as raw materials and characterized by FT-IR. The thioether group content was 0.104 g/g by the potentiometric titration with lead acetate as titrant. The Hg$^{2+}$ removal performance of petroleum thioether was studied in simulated flue gas. The experiment results exhibited that petroleum thioether showed excellent Hg$^{2+}$ removal efficiency in flue gas without threat of mercury reemission, and the process for Hg$^{2+}$ capture by petroleum thioether was exothermic and went on smoothly below 60°C. 6 M HCl could be used to regenerate petroleum thioether trapped Hg$^{2+}$, and there acquired a regeneration of 89.6%, which meant this Hg$^{2+}$ removal treat showed low operation cost. Moreover, the regeneration of petroleum thioether captured Hg$^{2+}$ facilitated the centralized processing of mercury and prepared well for the full utilization of mercury resources.

1. Introduction
Mercury was the typical pollutant in flue gas, and it appeared in states of Hg$^0$, Hg$^{2+}$ and Hg$^p$. Traditionally, Hg$^{2+}$ and Hg$^p$ were captured by the pollutant treatment equipment (the WFGD system and the ESP system), and Hg$^0$ was the main mercury poured into the atmosphere [1-3]. Researches on mercury removal were mainly divided into two steps, Hg$^0$ was oxidated into Hg$^{2+}$ by oxidants firstly, and then Hg$^{2+}$ was removed by the pollutant treatment equipment. However, the WFGD system could remove Hg$^{2+}$ effectively, but it just kept Hg$^{2+}$ in desulphurization by-products, and it couldn’t change Hg$^{2+}$ into green products [4-6].

Many reports indicated that Cl$, Mg^{2+}$, NO$_2^-$ and SO$_3^{2-}$ could reduce Hg$^{2+}$ to Hg$^0$ obviously [7,8]. Hg$^{2+}$ in desulphurization by-products (such as gypsum and ammonium sulfate) could be easily reduced into atmospheric hazard Hg$^0$. Therefore, most researchers [1, 8-11] focused on keeping Hg$^{2+}$ in desulphurization by-products possibly, and there were scarcely reports about remove Hg$^{2+}$ from the desulfurization system radically. This Hg$^{2+}$ remove method can’t clear the Hg$^{2+}$ pollution completely, and it just resolve Hg$^{2+}$ pollution temporarily [12-16].

This work will concentrate on clearing Hg$^{2+}$ pollution form flue gas radically. A Hg$^{2+}$ removal absorbent was prepared, and its Hg$^{2+}$ capture ability, capture behavior and regenerability were also discussed.

2. Materials and methods

2.1. Preparation of petroleum thioether
Petroleum (support by Gudao oilfield in Shandong province, China) with a sulfur content of 2.3% (g/g) was used as the raw materials for the preparation of petroleum thioether. Petroleum was placed in the round-bottom flask and was distilled at atmospheric pressure until the temperature was elevated to 350°C, petroleum fraction of 275-350°C (diesel fraction) was collected. Then poured 1.5-fold benzene sulfonic acid into this petroleum fraction, stirring at room temperature for 3 hours and let it aside for stratification. Collected the bottom liquid, and benzene was added to this bottom liquid, stirring for 3 hours and let it aside for stratification. Collected the top liquid, then the top liquid was distilled at 50°C by the rotary evaporation equipment, and benzene was distilled out from the product of petroleum thioether. Then the petroleum thioether was washing throughout by deionized water.

2.2. Chemical characterization of petroleum thioether

Chemical characterization of petroleum thioether with the aim to detect thioether groups in petroleum thioether. FT-IR analysis was conducted with Fourier transform spectrophotometer (NEXUS 670, Nicolet Company, USA). Petroleum thioether was dropped onto the potassium bromide plates for this analysis, and the C-S-C in petroleum thioether was detected with wave numbers of 400-4000 cm⁻¹. Moreover, the thioether content in petroleum was characterized followed by potentiometric titration [17]. The details on assay for the thioether content were shown as follow: petroleum thioether was pretreated by 0.1 M AgNO₃ solution to remove petroleum thiol. The equal volume of methanol was added to petroleum thioether, and this mixture was poured through fixed extraction column (frits of porous polyethylene activated by methanol), pumped dry with vacuum pump. Then methylbenzene was used to elute the thioether absorbed in fixed extraction column. Collected the extract liquid and poured 8-fold potentiometric titration medium (a mixture of methylbenzene-acetic acid-deionized water with volume ratio of 50:43:7). Lead acetate was used as potentiometric titration agent and the thioether content in petroleum thioether was measured according to the consumed volume of lead acetate solution with a known concentration at the equivalent point.

2.3. Assay for the mercury concentration and the oxidation of Hg⁰

The determination of mercury concentration and the oxidation of Hg⁰ were refer to the reference [18].

2.4. Hg²⁺ removal by petroleum thioether

The schematic diagram of mercury absorption was showed in figure 1. The experiment was operated as follows, 60 ml petroleum thioether and 60ml deionized water was blended well by high-shear emulsifying machine (Fluko, German) with a high stirring speed, the mixture of petroleum thioether and deionized water were regarded as absorption solution and the absorbing pipette contained absorption solution was placed at magnetic stirring apparatus. Simulated flue gas contained 6% O₂ and 32.5 μg/m³ Hg²⁺ was prepared with N₂ as balance gas. The Hg²⁺ removal efficiency by petroleum thioether was calculated according to equation. (1). $H_{\text{out}}^{2+}$ represents the Hg²⁺ concentration in the inlet of absorption solution and $H_{\text{out}}^{2+}$ represents the Hg²⁺ concentration in the outlet of absorption solution.

$$E_r = \frac{H_{\text{out}}^{2+} - H_{\text{in}}^{2+}}{H_{\text{in}}^{2+}} \times 100\%$$ (1)
3. Results and discussion

3.1. Properties characterization of petroleum thioether

The thioether group content in petroleum thioether was determined by potentiometric titration with lead acetate as titrant [17]. Potentiometric titration results showed thioether group concentration was 0.104 g/g. Molecular weight of petroleum thioether was analyzed according to GB/T 17282-1998 and its mean relative molecular mass was 258 g/mol. FT-IR was used in the characterization of thioether group in petroleum thioether and the obvious absorption peak (698 cm\(^{-1}\)) about C-S was observed in figure 2. Moreover, Petroleum thioether showed dissolvability in aqueous phase, which prepared well for the separation of petroleum thioether and aqueous phase in pollutants removal system.
3.2. Effect of absorption time on $E_r$

$\text{Hg}^{2+}$ showed a good solubility in aqueous, which aroused mercury pollution, the distribution of $\text{Hg}^{2+}$ in aqueous and petroleum thioether was studied. The equal mixed solution of 60 ml petroleum thioether and 60 ml deionized water was used as absorbent and this set of experiments were conducted at 50°C with initial $\text{Hg}^{2+}$ concentration of 32.5 μg/m$^3$. The relationship between absorption time and absorption efficiency was showed in figure 3.

![Figure 3](image)

Figure 3. The relationship between absorption time and $E_r$.

According to figure 3, petroleum thioether showed excellent $E_r$. In detail, $E_r$ with 99.8% was acquired with 30 mins of time and $E_r$ decreased extremely slightly as the time went on, $E_r$ was high to 98.6% even prolonged the time to 5 hours. The reason might be attributed to the dissolution of $\text{Hg}^{2+}$ in the water or the chelation of petroleum thioether to $\text{Hg}^{2+}$ [19-21]. To verify the mechanism for the absorption, the equal mixed solution of 60ml petroleum thioether and 60ml deionized water was set at 50°C to absorb $\text{Hg}^{2+}$ for 2 hours, 1879.8 ng $\text{Hg}^{2+}$ was captured in this system and the mixture solution was set down for 2 hours. Then the mixture solution divided into the organic phase and the aqueous phase. 200 ml deionized water was used to scrub the mixture solution throughout, the scrubbing solution and aqueous phase was collected and analyzed for the mercury concentration. 20.7 ng mercury was detected in the total scrubbing solution and the elution rate was 1.1%. Which implied almost all $\text{Hg}^{2+}$ was captured in the petroleum thioether.

Petroleum thioether (as a soft base) could easily combine with $\text{Hg}^{2+}$ (as a soft acid) to capture $\text{Hg}^{2+}$ based on the hard-soft acid-base theory (HSAB). According to the HSAB theory [22,23], the capture of $\text{Hg}^{2+}$ consumed thioether groups in petroleum thioether and the thioether groups decreased in the system as the experiments went on, thus resulting in the $E_r$ drop. Petroleum thioether is water insoluble, while using petroleum thioether to remove $\text{Hg}^{2+}$ in flue gas could avoid $\text{Hg}^{2+}$ entering process water. Also, petroleum thioether shows insoluble to water, which means petroleum thioether could separate easily from the mixture of petroleum thioether and water. Thus benefit for the collection of petroleum thioether captured $\text{Hg}^{2+}$ and avoiding bringing new pollution of petroleum thioether to the system. Furthermore, sulfur appeared in the crude oil restricts its application and it need to be desulfurized before the further application. The preparation of petroleum thioether eased the burden of crude oil desulfurization, and made the effective utilization of sulfur resources.

3.3. Effect of treat temperature on $E_r$

To investigate the influence of treat temperature on $E_r$, 20 ml petroleum thioether was used as absorbent and this set of experiments were conducted at 30-70°C for 1 hour with the initial $\text{Hg}^{2+}$
concentration of 32.5 μg/m³. Effect of treat temperature on \( E_r \) was displayed in figure 4. There obtained \( E_r \) of 100%, 99.1%, 94.1%, 87.6% and 75.4% at 30, 40, 50, 60 and 70°C, respectively. \( E_r \) dropped as the temperature elevated. The results indicated that the combined reaction between \( \text{Hg}^{2+} \) and thioether belonged to exothermic process and the increase of temperature inhabited the bind of \( \text{Hg}^{2+} \) and thioether at a certain extent, which matched well with the previously report [24-26]. Petroleum thioether showed good \( E_r \) at temperature below 60°C, and the temperature in WFGD slurry pond was regarded as about 50°C [27], which implied that petroleum thioether was suitable to be used with WFGD slurry in desulfurizing tower.

3.4. The regeneration of petroleum thioether captured \( \text{Hg}^{2+} \)

The regeneration of petroleum thioether saves the \( \text{Hg}^{2+} \) operation cost, also, it turns waste into wealth. HCl was introduced to regenerate thioether groups in petroleum thioether [23, 28]. In the condition with high HCl concentration, on the one hand, \( \text{H}^+ \) and \( \text{Hg}^{2+} \) competitive binding with thioether groups, although \( \text{Hg}^{2+} \) exhibited higher affinity to thioether groups than \( \text{H}^+ \), the mount of \( \text{H}^+ \) far greater larger than \( \text{Hg}^{2+} \). On the other hand, \( \text{Cl}^- \) shows strong complex to \( \text{Hg}^{2+} \). Thus made \( \text{Hg}^{2+} \) reverse extracted from petroleum thioether to HCl solution and realized the regeneration of petroleum thioether. 89.6% regeneration efficiency (ratio of thioether groups in the regenerated petroleum thioether to thioether groups in the initial petroleum thioether) was acquired and the eluted \( \text{Hg}^{2+} \) appeared in the HCl solution by this process, which benefit for the centralized processing of mercury, such as ionizing \( \text{Hg}^{2+} \) eluted by the HCl solution to prepare mercury for the production of mercury thermometer. The missing petroleum thioether part might attribute to the dissolution of some small petroleum thioether molecular in HCl solution.

Figure 2 showed FTIR spectra of petroleum thioethers. Peaks at 698 and 682 cm⁻¹ assigned to the absorption of the stretching vibration of C-S [29], other peaks were mainly belonged to the vibration of \(-\text{CH}_3\) or \(-\text{CH}_2\). The crude petroleum thioethers displayed an absorption peaks at 698 cm⁻¹ for the stretching vibration of C-S. The capture of \( \text{Hg}^{2+} \) decreased electronegativity and stability of C-S bond, thus resulting red shift of C-S absorption to 682 cm⁻¹ [30]. Petroleum thioethers experienced regeneration showed almost the same absorption peaks as the crude petroleum thioethers, which implied there was no chemical change for the petroleum thioethers by the regeneration treatment. This regeneration process is easy to operate with low-cost, and contribute to the resource utilization for mercury without secondary pollution. Further, the regeneration process made petroleum thioether recycle capture \( \text{Hg}^{2+} \) from flue gas, which lead to the decrease the cost for \( \text{Hg}^{2+} \) removal.

Based on the discussion mentioned above, petroleum thioether showed strong capture ability of
Hg$^{2+}$. Diesel produced from high sulfur crude oil also contained high sulfur content [31], and the application of this diesel oil could discharge high concentration sulfur dioxide, which restricted its application. Various desulfurization treatment were introduced to remove sulfur content in diesel, thus made the high sulfur diesel to be clean diesel fuel [32]. Petroleum thioethers were the main contents in diesel [33], the production of petroleum thioether eased the burden of diesel desulfurization and contributed to changing the waste sulfur contents to the wealth and useful mercury capture agent (petroleum thioether), thus providing a new pathway for the utilization of diesel sulfur resource.

4. Conclusions
Petroleum thioether was a high-effective absorbent for Hg$^{2+}$ removal from flue gas. Its Hg$^{2+}$ removal efficiency from flue gas could above 87.6% at the temperature below 60°C. The petroleum thioether was regenerated by scrubbing with 6 M HCl successfully, and its regeneration rate reached up to 89.6%, which meant petroleum thioether absorbent was reusable. Considering its high economical efficiency and low pollution, the petroleum thioether could be used to remove Hg$^{2+}$ from flue gas during the WFGD system in real coal-fired power plants. Furthermore, the preparation of petroleum thioether eased the burden of crude oil desulfurization, and made the effective utilization of sulfur resources.

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