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Effect of additives on Hg^{2+} reduction and precipitation inhibited by sodium dithiocarbamate in simulated flue gas desulfurization solutions

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ABSTRACT

Mercury (II) (Hg^{2+}) ion can be reduced by aqueous S(IV) (sulfite and/or bisulfite) species, which leads to elemental mercury (Hg^0) emissions in wet flue gas desulfurization (FGD) systems. Numerous reports have demonstrated the high trapping efficiency of sodium dithiocarbamate over heavy metals. In this paper, a novel sodium dithiocarbamate, DTCR, was utilized as a precipitator to control Hg^{2+} reduction and Hg^0 emission against S(IV) in FGD solutions. Results indicated that Hg^{2+} reduction efficiency decreased dramatically while precipitation rate peaked at around 91.0% in consistence with the increment of DTCR dosage. Initial pH and temperature had great inhibitory effects on Hg^{2+} reduction: the Hg^{2+} removal rate gradually increased and reached a plateau along with the increment of temperature and initial pH value. Chloride played a key role in Hg^{2+} reduction and precipitation reactions. When Cl^- concentration increased from 0 to 150 mM, Hg^{2+} removal rate dropped from 93.84% to 86.05%, and the Hg^{2+} reduction rate remained at a low level (<7.8%). ${SO_4}^{2-}$, ${NO_3}^-$ and other common metal ions would affect the efficiency of Hg^{2+} reduction and precipitation reactions in the simulated desulfurization solutions: Hg^{2+} removal rate could always be above 90%, while Hg^{2+} reduction rate was maintained at below 10%. The predominance of DTCR over aqueous S(IV), indicated by the results above, has wide industrial applications in FGD systems.

1. Introduction

Over the past several years, rapid economic growth has created an extremely high energy demand, stimulating a wide expansion of coal combustion industry. However, lacking environmental awareness and adequate technology, China suffered from severe air pollution caused by coal-fired flue gas. Mercury was a major contaminant in the coal-fired flue gas and posed a serious threat to human health and the environment. Wu et al. reported that Hg emissions from coal combustion increased from 202 to 257 t from 1995 to 2003 [1]. In 2005, mercury emissions increased dramatically to a value of 334 t, and the annual average growth rate between 1995 and 2005 was amazingly high at 5.1% [2].

There has been a pressing need to develop effective strategies to cope with mercury emission in the flue gas from coal-fired plants. According to Hg species in the flue gas, some conventional pollution facilities were employed to remove specific mercury species. Particulate-bound mercury (Hg^p) is typically captured in a particulate control device. Compared to Hg^0, oxidized mercury (Hg^{2+}) is more soluble in water, less volatile at stack temperatures and more active with mineral matters, so Hg^{2+} could be easily removed in typical air pollution control devices (APCD) [3] such as scrubbers, electrostatic precipitators (ESP) and fabric filters. However, poor capture efficiency of the total mercury was often reported to be coupled with the observation that Hg^0 concentration in outlet gas was higher than that in inlet gas [4], which stimulated numerous investigations of novel methods. Yang et al. utilized a series of synthesized nanosized $(Fe_{3-x}Mn_x)_{1-\delta}O_4$ to oxidize Hg^0 to Hg^{2+} [5]. Yan et al. introduced RuO_2 to modify SCR catalyst for Hg^{2+} oxidation [6]. However, those novel approaches could be prohibitive when taking the economic factors and the stable operation into consideration.

In many coal-fired power plants, Hg^{2+} was removed by FGD systems together with SO_2. Several prior studies suggested that chemical reduction of Hg^{2+} to Hg^0 in the FGD systems was the major source for Hg^0 re-emission [7–10]. Thus, it was of/has been attached to great importance to exploring effective methods to inhibit reduction of Hg^{2+} from wet flue gas desulfurization (FGD). Among various techniques employed, the chelation/precipitation method has been widely adopted due to its convenience and high efficiency. Sodium sulfide, Na_2S, or sodium hydrogen sulfide, NaHS, was employed to form the compound HgS, which could be easily removed from aqueous solution [11]. A synthetic chelating ligand (K_2BDET) was shown to be able to remove mercury from groundwater [12], and the approach demonstrated its capability of removing Hg^{2+} in groundwater below 0.05 ppb at pH 4.7 and 6.4.

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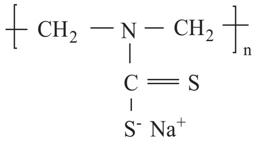
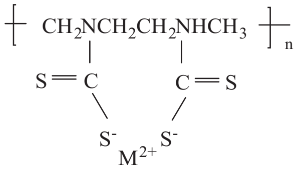
Sodium dithiocarbamates (DTC), which has been widely researched and utilized since 1850s, was obtained through the reaction between a primary or secondary amine and carbon dissulfide in basic media [13]. Due to their high stability, relatively low toxicity to human and low price, numerous studies have demonstrated the versibility and applicability of DTC in medical treatment, industrial production, food sterilization, pollution control, etc. [13,14]. One of sodium dithiocarbamates, DTCR, a new heavy metal macromolecule precipitator, was synthesized and could be coordinated with various heavy metals, such as Hg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, forming chelates with high stability constant. Tang et al. reported [15] that DTCR showed dramatic treatment effect on Hg^{2+} precipitation in simulated wet FGD solutions, the precipitation efficiency of which was about 87% at the stoichiometric ratio of 1.0. Other similar reports also indicated the unique structure of $Hg(DTCR)_2$ contributing to the high precipitation performance of DTCR over Hg^{2+}. Ito et al. analyzed the structure of $Hg(DTC)_2$ and found that the two species of Hg–S bonds coexisted as ionic bonds and coordinate bonds, which strengthened the stability of the chelate [16]. The structure of DTCR and $Hg(DTCR)_2$ could be represented as follows [14].

The mechanism of precipitation reaction was illustrated as below:

$$Hg^{2+}(aq.) + 2DTCR^{-}(aq.) \rightarrow Hg(DTCR)_2(s)$$





To better understand the performance of DTCR on inhibiting Hg^{2+} reduction and Hg^0 re-emission in the wet FGD solutions, a lab-scale batch-simulation apparatus was designed. Numerous factors related to the wet FGD properties were explored. The objective of this study was to evaluate the Hg^{2+} removal efficiency and reduction rate from the wet FGD solutions to determine the inhibition of Hg^0 re-emission in the presence of DTCR under different experimental conditions, so as to a theoretical basis for industrial applications.

2. Experimental

2.1. Materials

Sodium dithiocarbamate (DTCR) (30%) was purchased from the Prode Limited Co., Suzhou, China. Other chemicals including mercury chloride (>99.0%, AR), stannous chloride (98.0%, AR), potassium dichromate (99.95–100.05%, GR), sodium sulfite (>97.0%, AR), potassium permanganate (>99.5%, AR), sodium chloride (>99.5%, AR), calcium chloride (≥96.0%), magnesium chloride(≥98%), nitric acid (65–68%, GR), hydrochloric acid (36–38%, GR), sulfuric acid (95–98%, AR), etc. were all used as received without further purification. The gaseous Ar (99.95%) and N_2 (99.9%) were both purchased from Jingong Gas Co. Ltd.

2.2. Experimental apparatus

The laboratory-scale (or bench-scale) experimental design shown in Fig. 1 involved two sections: the Hg^{2+} reduction and precipitation reactor and the Hg^0 bubbling absorbing reactor. The former was carried out in a 1-L three-necked flask placed in a water bath at the desired temperature for 2 h. $HgCl_2$ and Na_2SO_3 were employed as the sources of Hg^{2+} and S(IV) respectively. The precipitating agent, DTCR, was added to the reactor. In order to prevent Hg^{2+} reduction by dissolved oxygen, the reaction mixture was stirred under a nitrogen environment. The bubbling reactors were made of two 100-ml washing-bottles attached to the end of the stem, and contained 10 mL solution composed of 10% (v/v) H_2SO_4–4% (w/w) $KMnO_4$ to absorb and oxidize outlet mercury (mainly Hg^0) to Hg^{2+}. This method was a standard protocol adopted by the US Environmental Protection Agency (EPA) [17].

2.3. Test methods

All samples obtained from the experiment were measured using QM201 cold vapor atomic fluorescence spectroscopy (CVAF) coupled with a fluorescence mercury analyzer (Qing'an Instrument Co., Suzhou, China). Prior to analysis, 7% (w/w) $SnCl_2$ solution was prepared as reducing reagent. During the reduction reaction, mercury vapors were flushed out by Ar gas and measured by cold vapor

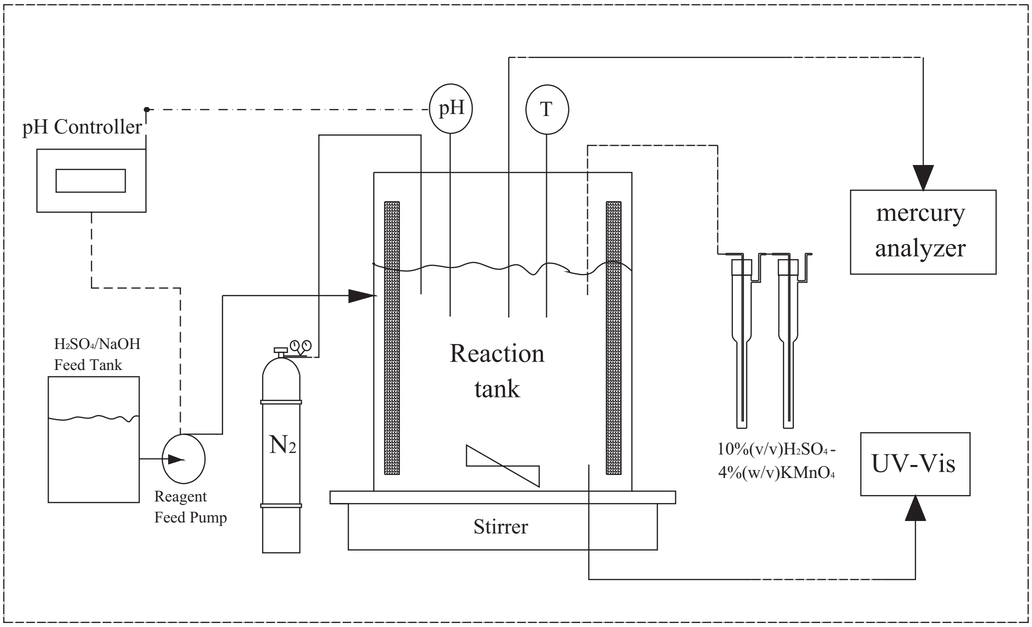


Fig. 1. Schematic representation of the bench-scale experiment layout for Hg^{2+} reduction and precipitation reactions.