



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.

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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

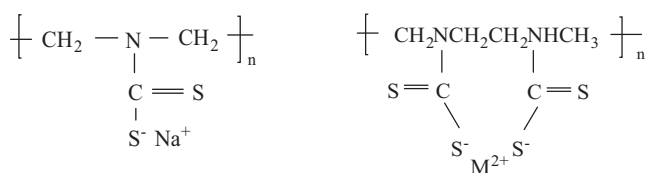
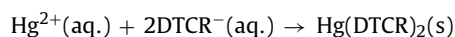
typical air pollution control devices (APCD) [3] such as scrubbers, electrostatic precipitators (ESP) and fabric filters. However, poor capture efficiency of the total mercury was often reported to be coupled with the observation that Hg^0 concentration in outlet gas was higher than that in inlet gas [4], which stimulated numerous investigations of novel methods. Yang et al. utilized a series of synthesized nanosized $(\text{Fe}_{3-x}\text{Mn}_x)_{1-\delta}\text{O}_4$ 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/had 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 disulfide in basic media [13]. Due to their high stability, relatively low toxicity to human and low price, numerous studies have demonstrated the versatility 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 $\text{Hg}(\text{DTCR})_2$ contributing to the high precipitation performance of DTCR over Hg^{2+} . Ito et al. analyzed the structure of $\text{Hg}(\text{DTC})_2$ 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 $\text{Hg}(\text{DTCR})_2$ could be represented as follows [14].

The mechanism of precipitation reaction was illustrated as below:



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 ($\geq 96.0\%$), magnesium chloride ($\geq 98\%$), 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 (CVAAS) 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

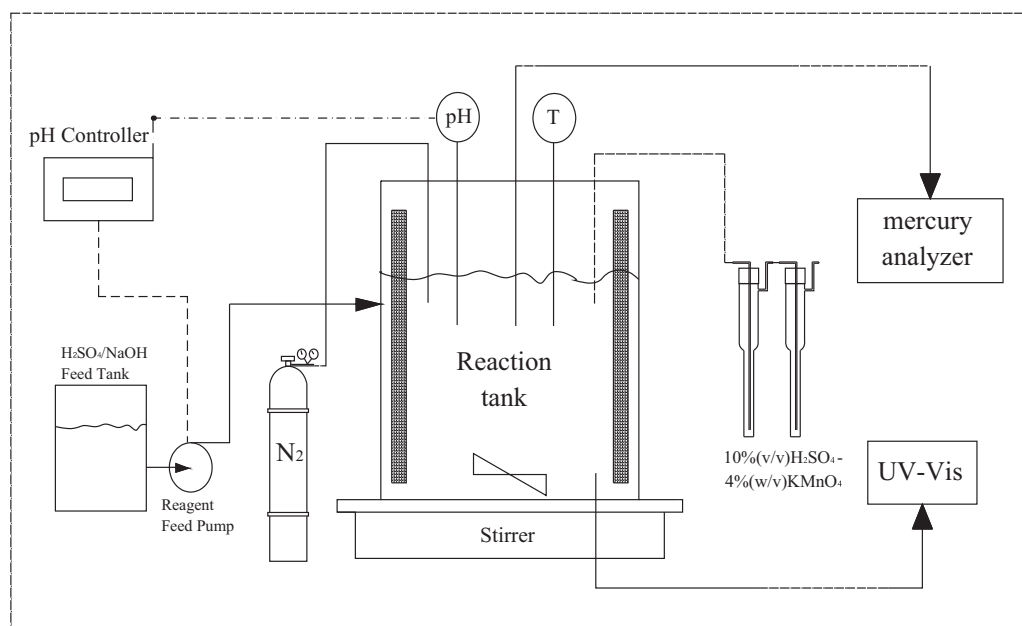


Fig. 1. Schematic representation of the bench-scale experiment layout for Hg^{2+} reduction and precipitation reactions.

generation atomic absorption spectrometry. Before initiating the reaction, all reactant solutions were adjusted to a desired pH value with diluted H_2SO_4 and NaOH through a digital pH meter (Mettler-Toledo Co., Shanghai, China), but no further adjustments were made during the reaction processes. The reaction temperature was controlled by a water bath with a temperature controller.

In this study, the reaction efficiency of Hg^{2+} reduction and precipitation was calculated as follows:

$$\eta_{Hg^{2+}rm} (\%) = \frac{C_{Hg^{2+}rm}}{C_{Hg^{2+}in}} \times 100 \quad (1)$$

$$\eta_{Hg^{2+}rd} (\%) = \frac{C_{Hg^{2+}out}}{C_{Hg^{2+}in}} \times 100 \quad (2)$$

$$\eta_{Hg^{2+}p} (\%) = \left(1 - \frac{C_{Hg^{2+}rm}}{C_{Hg^{2+}in}} - \frac{C_{Hg^{2+}out}}{C_{Hg^{2+}in}} \right) \times 100 \quad (3)$$

where $C_{Hg^{2+}out}$ (mM) is the Hg^{2+} concentration in the outlet gas, $\eta_{Hg^{2+}rd}$ (%) is the Hg^{2+} reduction rate, $\eta_{Hg^{2+}p}$ (%) is the Hg^{2+} precipitation rate, $C_{Hg^{2+}in}$ (mM) is the inlet Hg^{2+} concentration, and $C_{Hg^{2+}rm}$ (mM) represents the concentration of Hg^{2+} that remains in solution after the reaction.

3. Results and discussion

3.1. Effect of the precipitator's dosage

The performance under different precipitator dosages was analyzed to study the inhibition of Hg^{2+} reduction and Hg^0 re-emission. Results shown in Fig. 2 indicated that the Hg^{2+} reduction ratio was 33.62% in the absence of the precipitator in simulated wet FGD solution. When DTCR dosage increased from 0 to the theoretic dosage ($Q_{th} = 0.14 \text{ mg l}^{-1}$), Hg^{2+} reduction rate decreased sharply while the precipitation efficiency increased rapidly. When DTCR dosage ranged from $1.0Q_{th}$ to $3.0Q_{th}$, the Hg^{2+} precipitation rate reached a plateau of around 91.0% while the Hg^{2+} reduction rate was controlled below 7.0%.

Based on the results presented above, the outstanding precipitation efficiency might have a close relationship with its structure. It could be deduced that the precipitation reaction of Hg^{2+} was dominated by the formation of water-insoluble chelate $Hg(DTCR)_2$. Apart from the ionic bonds between Hg^{2+} and DTCR, another

coordinate bonds existed in the complex and formed a bidentate chelate, which ensured the stability of $Hg(DTCR)_2$ [16]. Research also indicated that two $-CSS-$ legends in DTCR could chelate with Hg^{2+} to form insoluble polymer matrices with a cross-linked network structure [18].

When DTCR dosage was $1.0Q_{th}$, 91.1% of Hg^{2+} was precipitated, and therefore $1.0Q_{th}$ was chosen as DTCR dosage in the subsequent experiments.

3.2. Effect of the reaction temperature

The performance under different reaction temperatures (30–60 °C) was tested to study the temperature effect on Hg^{2+} reduction and Hg^0 re-emission inhibited by DTCR. As shown in Fig. 3, the Hg^{2+} reduction efficiency varied from 9.14% to 5.53% by adding DTCR when reaction temperature increased to a certain extent. Other experimental conditions such as an initial pH value of 5.0, S(IV) concentration of 5.0 mM, and reaction time of 2 h remained the same as previous study. When the temperature rose to 50 °C, the reduction rate decreased to 6.29% from initial 8.45% while the precipitation efficiency reached 92.72% compared to 86.08% at 30 °C, achieving good inhibition performance. Since the temperature of 50 °C was obtained in the practical desulfurization solution, that solution was chosen in the subsequent experiments.

The observation that precipitation rate saw a slight increase along with the temperature rise might be attributed to the thermodynamics of the reaction. High temperature accelerated collisions between Hg^{2+} and DTCR, which in macro-phenomenon indicated the increment of the reaction rate. Furthermore, the increment of temperature produced more confirmations of DTCR owing to the multiple polymer chains. Thus, the structure of $Hg(DTCR)_2$ was more cross-linked and stable.

3.3. Effect of initial pH values

The initial pH value of the reaction solution was a critical factor on Hg^{2+} reduction and precipitation since the reactivity of precipitators could be influenced by pH value. Binding capacities between Hg^{2+} and DTCR were weakened due to the protonation of sulfur atoms in functional groups of DTCR at low pH values, which was in accordance with the results shown in Fig. 4. Along with the increase in pH value, the Hg^{2+} reduction efficiency declined from 11.27% to 2.30% while the Hg^{2+} precipitation efficiency increased

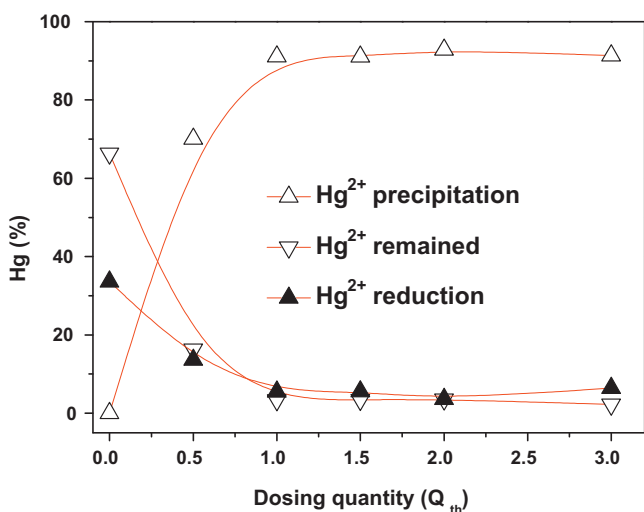


Fig. 2. Effect of dosing quantity on Hg^{2+} reduction and Hg^0 re-emission inhibited by the introduction of DTCR ($Hg^{2+} = 0.1 \text{ mg l}^{-1}$, S(IV) = 5 mM, $T = 50 \text{ }^\circ\text{C}$, and pH value = 5).

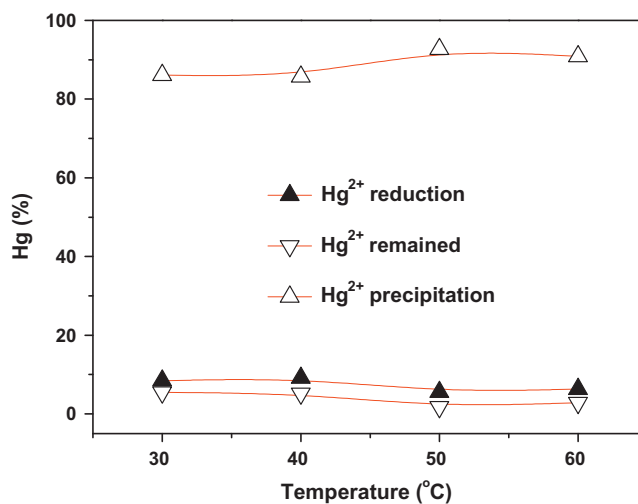


Fig. 3. Effect of the reaction temperature on Hg^{2+} reduction and Hg^0 re-emission inhibited by DTCR ($Hg^{2+} = 0.1 \text{ mg l}^{-1}$, S(IV) = 5 mM, DTCR = 0.14 mg l^{-1} and pH value = 5).

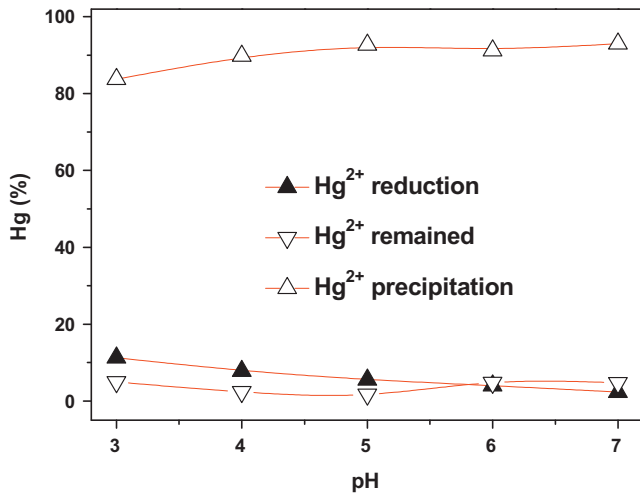


Fig. 4. Effect of initial pH values on Hg^{2+} reduction and Hg^0 re-emission inhibited by DTCR ($\text{Hg}^{2+} = 0.1 \text{ mg l}^{-1}$, $\text{S(IV)} = 5 \text{ mM}$, $\text{DTCR} = 0.14 \text{ mg l}^{-1}$ and $T = 50^\circ \text{C}$).

gradually and was ultimately maintained at a relatively high level (about 90%). At an initial pH value of 3.0, the sulfur atoms in functional groups of DTCR were protonated and those positively charged functional group generated Coloumbic repulsion against Hg^{2+} , which would reduce their binding capacities with Hg^{2+} [15]. On the contrary, the presence of OH^- with increasing pH value would greatly strengthen the transformation of Hg^{2+} to Hg(OH)^+ , and then to Hg(OH)_2 , which settled down in the form of a precipitate. Thus the concentration of Hg^{2+} remaining in solution decreased [15], consequently leading to higher efficiencies in inhibiting Hg^{2+} reduction.

3.4. Effect of Cl^- concentration

Effect of Cl^- concentration on inhibiting Hg^{2+} reduction and Hg^0 re-emission by DTCR was shown in Fig. 5. Results indicated that the Hg^{2+} precipitation efficiency gradually declined with increase in Cl^- concentration. The results might be due to the reaction between Hg^{2+} and Cl^- and the formation of HgCl_x^{2-x} complex, which reduced Hg^{2+} exposure to organic sulfur and thereby lowered Hg^{2+} precipitation efficiency by DTCR [19]. The mercury

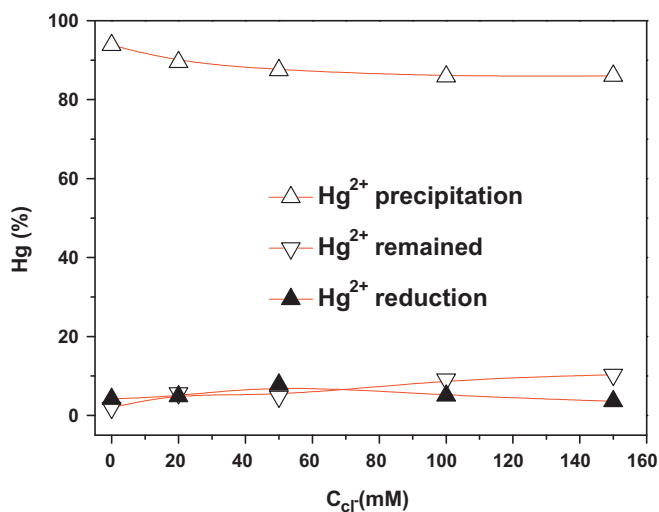


Fig. 5. Effect of Cl^- concentration on Hg^{2+} reduction and Hg^0 re-emission inhibited by DTCR ($\text{Hg}^{2+} = 0.1 \text{ mg l}^{-1}$, $\text{S(IV)} = 5 \text{ mM}$, $\text{DTCR} = 0.14 \text{ mg l}^{-1}$, $T = 50^\circ \text{C}$ and pH value = 5).

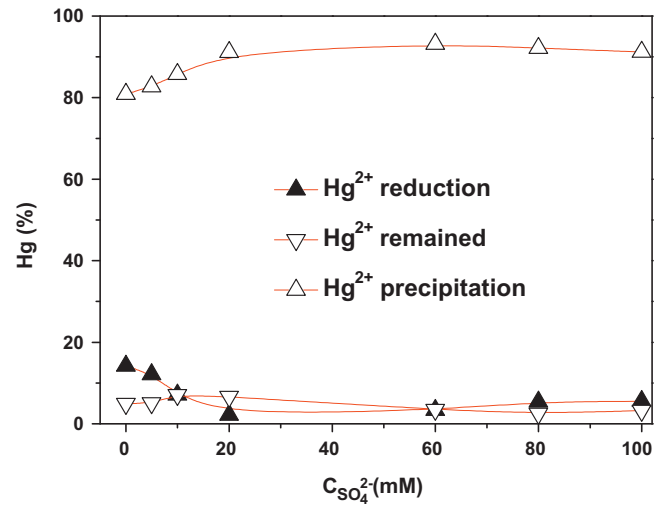


Fig. 6. Effect of sulfate concentration on Hg^{2+} reduction and Hg^0 re-emission inhibited by DTCR ($\text{Hg}^{2+} = 0.1 \text{ mg l}^{-1}$, $\text{S(IV)} = 5 \text{ mM}$, $\text{Cl}^- = 100 \text{ mM}$, $\text{DTCR} = 0.14 \text{ mg l}^{-1}$, $T = 50^\circ \text{C}$ and pH value = 5).

reduction rate was dependent on Cl^- concentrations as shown in Fig. 5. It was worth noting that the Hg^{2+} reduction rate increased slightly first and then decreased. It was likely that in the absence of Cl^- , the mercury precipitation was predominantly controlled by Hg-S complex to form insoluble chelates, while the introduction of Cl^- to desulfurization solutions led to the competition against DTCR and generated HgCl_x^{2-x} complexes. Subsequently, due to the instability of HgCl_x^{2-x} complexes, more and more Hg^{2+} was released from the complexes, which became available for the reaction with S(IV) . However, higher Cl^- content decreased the Hg^{2+} reduction efficiency. According to Wo et al. [9], with increasing Cl^- concentration, several intermediates including ClHgSO_3^- and $\text{Cl}_2\text{HgSO}_3^{2-}$ were produced. Since $\text{Cl}_2\text{HgSO}_3^{2-}$ was very stable and Hg^{2+} was steadily combined in the complex, further Hg^{2+} reduction reaction was inhibited from the complex, which led to a decrease in Hg^{2+} reduction rate at higher Cl^- concentrations.

3.5. Effect of sulfate concentration

The SO_4^{2-} concentration had a significant effect on inhibiting Hg^{2+} reduction and precipitation reactions by DTCR (as shown in Fig. 6). When the concentration of SO_4^{2-} increased from 0 to 20 mM, Hg^{2+} precipitation gradually increased while the Hg^{2+} reduction ratio decreased from 14.18% to 2.18%. The efficiency of Hg^{2+} precipitation remained steady when SO_4^{2-} concentration further increased. Consequently, more than 90% of Hg^{2+} was precipitated by DTCR. Liu et al. had reported the inhibition of Hg^{2+} reduction by SO_4^{2-} . In the presence of S(IV) , SO_4^{2-} would react with Hg^{2+} to generate $\text{HgSO}_3\text{SO}_4^{2-}$ and thereby damping the formation of HgSO_3 , whose decomposition was assumed to be the critical step of Hg^{2+} reduction [20].

3.6. Effect of nitrate concentration

Results shown in Fig. 7 indicated that NO_3^- concentration had an adverse effect on Hg^{2+} precipitation while Hg^{2+} reduction rate saw a slight increase in the circumstance of DTCR. More specifically, with NO_3^- concentration increasing from 0 to 100 mM, Hg^{2+} precipitation efficiency decreased from 89.7% to 83.3%. The strong oxidation potential of NO_3^- in acid solutions might be a contributing factor for precipitation decrease. When pH value was at 5 and the NO_3^- concentration was 100 mM, the electrode potential calculated was 0.7794 V, showing relatively strong oxidation ability. Thus, large

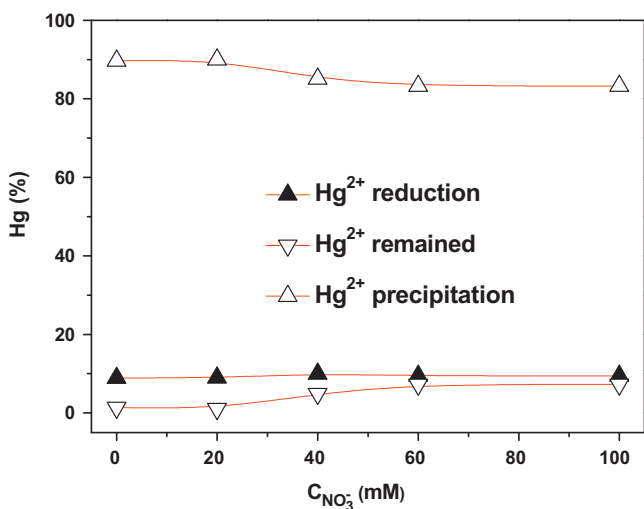


Fig. 7. Effect of nitrate concentration on Hg²⁺ reduction and Hg⁰ re-emission restrained by DTCR (Hg²⁺ = 0.1 mg l⁻¹, S(IV) = 5 mM, Cl⁻ = 100 mM, DTCR = 0.14 mg l⁻¹, T = 50 °C and pH value = 5).

quantities of functional groups in DTCR were prone to be oxidized by NO₃⁻, which inhibited the precipitation performance over Hg²⁺. Therefore, Hg²⁺ remaining in the FGD solution benefited from the hampered precipitation rate and rose dramatically to over 5 times the initial residual rate, which had a positive effect on the increase of Hg²⁺ reduction. However, the rate of Hg²⁺ reduction did not have a similarly tremendous growth with Hg²⁺ that remained. This phenomenon could be ascribed to the strong oxidation potential of NO₃⁻ which could react with S(IV) to inhibit Hg²⁺ reduction. Furthermore, from those data obtained above, there existed an urgent need for denitrification during flue gas desulfurization to prohibit further Hg⁰ re-emission.

3.7. Effect of Ca²⁺ concentration

As shown in Fig. 8, low concentrations of Ca²⁺ (<10 mM) had an adverse effect on inhibiting the Hg²⁺ reduction by DTCR while high concentrations of Ca²⁺ stimulated the reduction rate. The increase in Ca²⁺ concentration led to the gradual increase in Hg²⁺ precipitation rate by DTCR. More specifically, when Ca²⁺ concentration rose

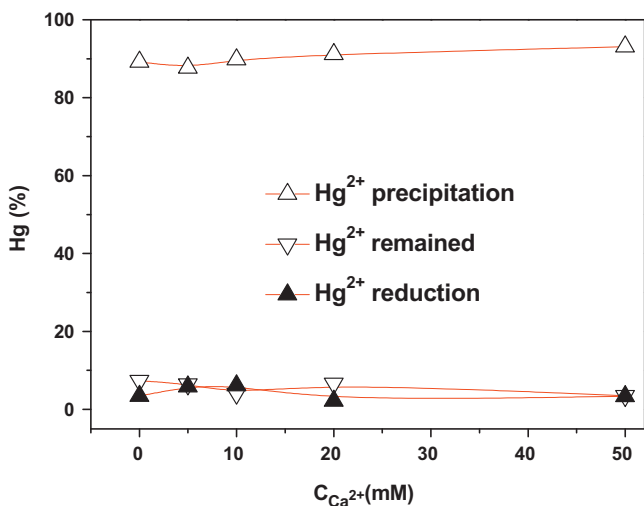


Fig. 8. Effect of Ca²⁺ concentration on Hg²⁺ reduction and Hg⁰ re-emission restrained by DTCR (Hg²⁺ = 0.1 mg l⁻¹, S(IV) = 5 mM, Cl⁻ = 100 mM, DTCR = 0.14 mg l⁻¹, T = 50 °C and pH value = 5).

from 0 to 10 mM, Hg²⁺ reduction rate increased from 3.42% to 6.15%, indicating that low concentration of Ca²⁺ promoted the removal of Hg²⁺. The hypothesis was that the change in Ca²⁺ concentration affected numerous factors in the desulfurization solutions (such as SO₃²⁻, pH value), which in turn affected Hg²⁺ reduction efficiency. When Ca²⁺ and SO₃²⁻ coexisted in the desulfurization solutions, some chemical reactions could be expressed as follows:



Ca²⁺ reacted with SO₃²⁻ to form slightly soluble CaSO₃, and the precipitation reaction made the equilibrium (3-3) move towards the left and reduced the chance of generating Hg(SO₃)₂²⁻. As a result, more HgSO₃ was produced to shift the equilibrium (3-2) to the left, which in turn raised Hg²⁺ reduction rate.

In contrast, when Ca²⁺ concentration was higher than 10 mM, Hg²⁺ reduction rate gradually decreased and white particles that could be seen with naked eyes were formed. The strengthened sedimentation effect was probably due to the acceleration of formation of less soluble CaSO₃ along with increase in Ca²⁺ concentration. Because of the low solubility of CaSO₃ in water, most CaSO₃ was suspended in the solution. Hg²⁺ in the FGD solutions might be adsorbed to the surface of CaSO₃ particles [21], which weakened Hg²⁺ reduction. Meanwhile, Ca²⁺ could not easily react with coordinated sulfur atoms in DTCR, leading to non-competition against Hg²⁺. Furthermore, the chelation between DTCR and Hg²⁺ could carry a certain amount of negatively charged groups, resulting in mutual exclusion in the formed chelate and a decrease in flocculation. However, Ca²⁺ played a key role in double-layer compression and thereby accelerated flocculation during Hg²⁺ reduction and precipitation reaction, which ultimately contributed to the improvement of the Hg²⁺ precipitation rate [22].

4. Conclusion

DTCR was shown to be an effective agent to inhibit Hg²⁺ reduction and Hg⁰ re-emission in FGD liquors. More than 80% of Hg²⁺ was captured by DTCR, and Hg²⁺ reduction efficiency decreased to less than 10%. The experimental results indicated that increasing the precipitator dosage, the temperature (≤60 °C), the initial pH value, or SO₄²⁻ concentration could contribute to inhibition of Hg²⁺ reduction in simulated wet FGD solutions and Hg⁰ re-emission across a wet FGD scrubber by DTCR. Effects of Cl⁻, NO₃⁻, and Ca²⁺ concentration on Hg²⁺ reduction and Hg⁰ re-emission in FGD solutions in the presence of DTCR were complicated but still consistent with the law of conservation of mass. The general mechanism and control methods for Hg²⁺ reduction and Hg⁰ re-emission was discussed, and such exploration would provide a profound theoretical basis for industrial applications such as mercury restraint in wet FGD systems.

Acknowledgments

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