Effect of heavy metals on the stabilization of mercury(II) by DTCR in desulfurization solutions

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ABSTRACT

Several heavy metals, including Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, were investigated in simulated desulfurization solutions to evaluate their interferences with Hg^{2+} during the reaction with dithiocarbamate type chelating resin (DTCR). Appropriate DTCR dosage and the effect of pH were also explored with respect to restoration of high Hg^{2+} precipitation efficiency and reduction of mercury concentrations. The experimental results suggested that increasing heavy metal concentration inhibited Hg^{2+} precipitation efficiency to a considerable extent and the inhibition order of the four heavy metals was $Cu^{2+} > Ni^{2+} > Pb^{2+} > Zn^{2+}$. However, the coordination ability was closely related to the configuration and the orbital hybridization of each metal. In the cases of Cu^{2+} and Pb^{2+}, increased DTCR dosage was beneficial to Hg^{2+} precipitation, which could lay the foundation of practical applications of DTCR dosage for industrial wastewater treatment. The enhanced Hg^{2+} precipitation performance seen for increasing pH might have come from the deprotonation of sulfur atoms on the DTCR functional groups and the formation of metal hydroxides $(M(OH)_2, M = Cu, Pb, Hg)$.

1. Introduction

The high toxicity of mercury to the human central nervous system and the strong bioaccumulation in human bodies through the food chain has triggered public concern over mercury contamination [1]. For instance, Minamata disease, caused by severe mercury poisoning, made thousands of victims suffer from a neurological syndrome in Japan. Mercury emission from anthropogenic activities is usually blamed for pollution and threats to human safety. Combustion utilities, such as coal-fired power plants and incinerators, constitute the major anthropogenic mercury sources [2,3].

In the flue gas emitted from coal combustion, mercury occurs in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-bound mercury (Hg^p). Based on the unique physical and chemical properties of the three forms of mercury, research has been conducted to prevent mercury emission to the environment. Conventional mercury control technologies, such as electrostatic precipitators (ESPs), fabric filters (FFs) and flue gas desulfurization (FGD) systems, have been applied to remove Hg^{2+}, but none effectively remove elementary mercury. However, a novel technology, which involves the use of activated carbon injection upstream of a particulate control device (ACI), was reported to be able to remove both elemental and oxidized mercury [4]. Among the varieties of mercury control devices, FGD could capture nearly 90% of Hg^{2+} and was also considered to be cost-effective [5,6].

In the FGD system, alkaline sorbents capture pollutants like Hg^{2+} and SO_2 and ions like Cl^-, NO_3^-, F^-, and Ca^{2+} [7]. SO_2, however, which is absorbed by the alkaline sorbent and not entirely oxidized to SO_4^{2-}, has a high potential to reduce Hg^{2+} and to further generate Hg^0 [8]. Wo et al. reported that the pH, reaction temperature and ions in desulfurization solutions had a profound effect on Hg^{2+} reduction [8]. Other similar work has also discussed the reduction and reemission of mercury to the atmosphere. For example, Kirk et al. reported a rapid reduction and reemission of mercury deposited into snowpacks [9]. The residence time of the resulting Hg^0 in the atmosphere ranged from 0.5 to 2 years [10], so urgent steps need to be taken to develop novel technologies to inhibit Hg^{2+} reduction and Hg^0 reemission.

Dithiocarbamates (DTCs) are a versatile class of monoanionic 1,1-dithio ligands with a strong coordination and stabilization ability for transition metals [11]. Since the synthesis of dithiocarbamic acid was reported by Debus in 1850 [12], much attention has been focused on their applications and on structural identification of metal dithiocarbamates. Currently, a wealth of structural data for metal dithiocarbamates has demonstrated the strong affinity of dithiocarbamate ligands for metals. This strong affinity has boosted their use as pesticides in agriculture, industry and antidotes for metal poisoning, such as Pb poisoning [13–15].

Burgeoning interest in transition metal chemistry has also broadened their wide utilization in industrial applications. To meet increasingly stringent environmental regulations, DTCs were

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Table 1
Characteristics of the simulated FGD solution.

Element	Simulated FGD solution
Temperature (°C)	50
pH value	5.0
Cl^- (mM)	100
SO_4^{2-} (mM)	50
S(IV)(mM)	1
Ca^{2+} (mM)	10
Mg^{2+} (mM)	10
NO_3^- (mM)	50
Hg^{2+} (mg l^{-1})	0.1

employed as chelating agents to precipitate various heavy metals in industrial waste, including Hg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, and Cr^{3+}. Ito and co-workers demonstrated the stability of $Hg(DTC)_2$ by measuring the Hg–S bonds and electron distributions [16]. Furthermore, numerous studies have reported the utilization of DTC derivatives to precipitate aqueous Hg^{2+}. Say et al. elaborated that mercury adsorption depended on the solution pH, mercury concentration and mercury speciation by DTC derivatives [17]. Tang et al. reported the precipitation efficiency of Hg^{2+} and the inhibition of Hg^{2+} reduction by one DTC derivative (DTCR) in desulfurization solutions [18]. Nevertheless, demonstrating that DTCR could be a promising precipitant to inhibit Hg^0 release in FGD solutions is important. For this purpose, Lu et al. illustrated the high precipitation performance of DTCR for Hg^{2+} under varied conditions (e.g., initial pH value, SO_4^{2-} concentration, Cl^-, NO_3^-, and Ca^{2+} concentration) in FGD solutions [19].

Trace heavy metals, such as Cu^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}, have been shown to be retained in FGD materials and fly ashes [7]. In spite of the outstanding Hg^{2+} precipitation efficiency and the inhibition potential of Hg^{2+} reduction, it was reported that coexisting heavy metal ions in FGD solutions had a negative influence on DTCR precipitation efficiency. The adverse effect of Cu^{2+} and Pb^{2+} on Hg^{2+} precipitation was studied by Tang et al., and the results showed that the Hg^{2+} removal rate decreased by 12.6% and 5.0%, respectively, in the presence of 1.0 mg l^{-1} Cu^{2+} and Pb^{2+} [18]. The decrease of Hg^{2+} removal rate with increasing Hg^{2+} concentration in FGD solutions enhanced Hg^{2+} reduction and Hg^0 reemission. Thus, it is very important to explore the effect of trace heavy metals on Hg^{2+} reduction inhibition under the presence of DTCR.

In this paper, the effect of four trace heavy metal ions, Cu^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}, on DTCR Hg^{2+} precipitation efficiency and Hg^{2+} reduction inhibition was studied. Furthermore, the optimal DTCR dosage and pH value were determined in simulated FGD solutions after adding Cu^{2+} and Pb^{2+}. These studies will provide further insight into the proposed application of DTCR as a precipitant for stabilizing dissolved Hg^{2+} to prevent reemission of Hg^0 in FGD solutions.

2. Experiments and methods

2.1. Simulated FGD solutions and heavy metal precipitants

The concentrations in the simulated FGD solutions were based on the concentration of elements in practical FGD solutions (Table 1). The DTCR (30%) solution was purchased from Prode Limited Co., Suzhou, China. The molecular structure of the precipitant is described for better understanding.

$$\left[CH_2 - N - CH_2 \right]_n$$
$$| $$
$$C = S$$
$$| $$
$$S^- \ Na^+$$
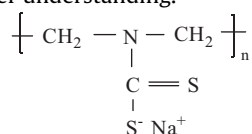
2.2. Effect of trace heavy metals on Hg^{2+} stabilization and reduction inhibition by DTCR

The batch experiments for stabilization and reduction inhibition of mercury in simulated FGD solutions were conducted in a 500 mL three-necked flask in a water bath at 50 °C. A specified amount Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+} or Ca^{2+} (Table 1) was added to the flask with 500 mL deionized water. A predetermined number of trace heavy metal ions were then added to the flask with continuous nitrogen flushing to prevent S(IV) oxidation. Next, S(IV) was added and the pH was adjusted to 5.0. Then, Hg^{2+} and the theoretical dosage of DTCR (Q_{th} = 0.70 mL of 0.01% DTCR) were added to the flask. The flush nitrogen then acted as a carrier to prohibit the accumulation of Hg^0 in the solution. A 10% (v/v) H_2SO_4 and 4% (w/w) $KMnO_4$ solution in two impingers in series was employed to adsorb Hg^0. After 2 h of reaction, the solutions in the flask and the two impingers were diluted and the mercury concentrations were determined.

2.3. Effect of DTCR dosage and pH on Hg stabilization and reduction inhibition

The batch experiments for DTCR dosage and pH value were carried out in 250 mL beakers containing 150 mL simulated FGD solutions with 0.1 mg l^{-1} of Hg^{2+} and 100 mM of Cl^-. After adding the heavy metal ions, the solution pH was adjusted and the temperature held at 50 °C. The solution was rapidly mixed using a quadruple magnetic stirrer for 15 min after the DTCR dose was added. Afterwards, 100 mg l^{-1} of polyaluminum chloride (PAC) and 2 mg l^{-1} of polyacrylamide (PAM) were added and the solution was slowly stirred. After standing for 30 min, the solution was centrifuged and 5 mL of the supernatant was diluted to 50 mL in a volumetric flask in which 5 mL of the stationary liquid (a solution with 0.5 g l^{-1} K_2CrO_4 and 5% HNO_3, v/v) had already been added. The Hg^{2+} concentration in the sample was detected and the remaining Hg^{2+} in the beaker was calculated.

2.4. Analysis

Mercury concentrations were determined by a QM201 cold vapor Atomic Fluorescence Spectrometer coupled with a Mercury Analyzer (Qing'an Instrument Co., Suzhou, China). Mercury (Hg^{2+}) in the samples was reduced with a 7% (w/w) $SnCl_2$ solution to generate elementary mercury vapor. Mercury vapor was then flushed out with argon as carrier gas and pumped into the mercury analyzer. A digital pH meter (Mettler-Toledo Co., Shanghai, China) was used to measure pH values in the FGD solutions.

The Hg^{2+} concentrations in the simulated FGD solutions were calculated directly from the data obtained from the mercury analyzer, while the concentrations of released Hg^0 were extrapolated according to the adsorption equilibrium.

3. Results and discussion

3.1. Effect of trace heavy metal concentration

Trace heavy metals, such as Hg, Cu, Pb, Zn and Ni, were captured considerably by FGD chemistry and simulated in the water streams during re-circulation [7,20]. Because DTCR has the ability to strongly chelate many transition metals, Hg^{2+} might compete against other heavy metals in the reaction for DTCR, which could inhibit the stabilization of Hg^{2+} in the desulfurization solution. Thus, investigating the effect of the four heavy metals mentioned earlier on mercury stabilization and reduction inhibition is critical. The measured concentrations of the four investigated heavy metals in desulfurization solutions from four coal-fired power plants ranged from 0.46 to 0.72 mg l^{-1} for Pb^{2+}, 0.05 to 0.20 mg l^{-1} for