



Full Length Article

Recyclable CuS sorbent with large mercury adsorption capacity in the presence of SO₂ from non-ferrous metal smelting flue gas

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ABSTRACT

Gaseous elemental mercury (Hg⁰) is difficult to dispose using traditional sorbents when co-existed with high concentration of SO₂ from non-ferrous smelting gas. CuS was selected for Hg⁰ removal from non-ferrous metal smelting flue gas due to large Hg⁰ uptake capacity under SO₂ condition. Hg⁰ removal experiments indicated that CuS has the largest Hg⁰ adsorption capacity compared to that of ZnS, CdS, MnS and SnS. The Hg⁰ adsorption rate and capacity of CuS at 50 °C was 0.0716 mg/(g·min) and 50.17 mg/g with 50% breakthrough threshold, respectively. In addition, the effects of reaction factors such as reaction temperatures and gas components (O₂, SO₂, H₂O, SO₃) on Hg⁰ removal performances were investigated. O₂, H₂O and SO₂ showed negligible influences on Hg⁰ capture. However, SO₃ competed with mercury for adsorption sites, resulting in a decrease of mercury adsorption capacity. The XPS analysis and Hg-TPD results indicated that the adsorbed mercury mainly existed as HgS on the material surface. CuS exhibited high mercury adsorption capacity under SO₂ atmosphere at low temperature, appeared to be a promising material for Hg⁰ capture from non-ferrous metal smelting flue gas. They can be used co-benefit with electrostatic demister (ESD), upstream entering the acid plant for SO₂ recovery.

1. Introduction

Mercury is one of the most hazardous global pollutants due to its high toxicity, long-rang atmospheric transportation and bio-accumulation performance [1]. After decades of negotiations, the *Intergovernmental Negotiating Committee (INC)* had adopted the *Minamata Convention on Mercury* in January 2013, aiming at controlling anthropogenic mercury emissions globally [2]. And this convention had come into force on August 16, 2017. Previous researches indicated that mercury emission from nonferrous metal smelters accounted for approximately 27.6% of the total in China, particularly in zinc, copper, lead and industrial gold production processes [3–6]. Therefore, it is significant to control mercury emission from non-ferrous metal smelters.

Generally, mercury is released from sulfides ores to flue gases during the pyrometallurgical processes of non-ferrous metals, and primarily exists in three forms: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particle-associated mercury (Hg_p) [7]. Generally speaking, gaseous mercury is primarily coexisted with high concentration SO₂ and SO₃ in flue gas. Before entering the acid plant, acid mist/SO₃ and particles are removed for avoiding V₂O₅ catalyst poisoning in a series of air pollution control devices (APCDs) including

cyclone (CC), electrostatic precipitator (ESP), wet flue gas scrubber (WFGS) and electrostatic demister (ESD). Using these APCDs can achieve a co-benefit removal of mercury. For example, most of Hg_p can be simultaneously collected by CC or ESP. Hg²⁺ can be captured by WFGS or ESD due to its high solubility in water and sulfuric. However, it is difficult to effectively remove Hg⁰ by APCDs due to its highly volatility and insolubility [8]. Therefore, to meet the strict regulation for mercury emissions, it requires additional Hg⁰ removal techniques after the purification system.

Currently, the control methods for Hg⁰ emissions from non-ferrous metal smelters mainly contains two categories: the one is adsorption technique which first oxidize Hg⁰ with strong oxidants and then remove oxidized mercury, or to capture Hg⁰ with specific adsorbents [9]. Another one is absorption technique, such as the Boliden–Norzink and Bolchem processes. Absorption technique is limited for widely application due to high operation cost, serious corrosion and potential environmental risk [10]. Meanwhile, various types of sorbents, such as activated carbon, selenium, have been used for the adsorption of mercury [11]. However, most of these sorbents are not suitable for usage due to low mercury capacities. Some chemicals such as sulfur, halogen, and noble metals were applied for the modification of sorbents [12–15].

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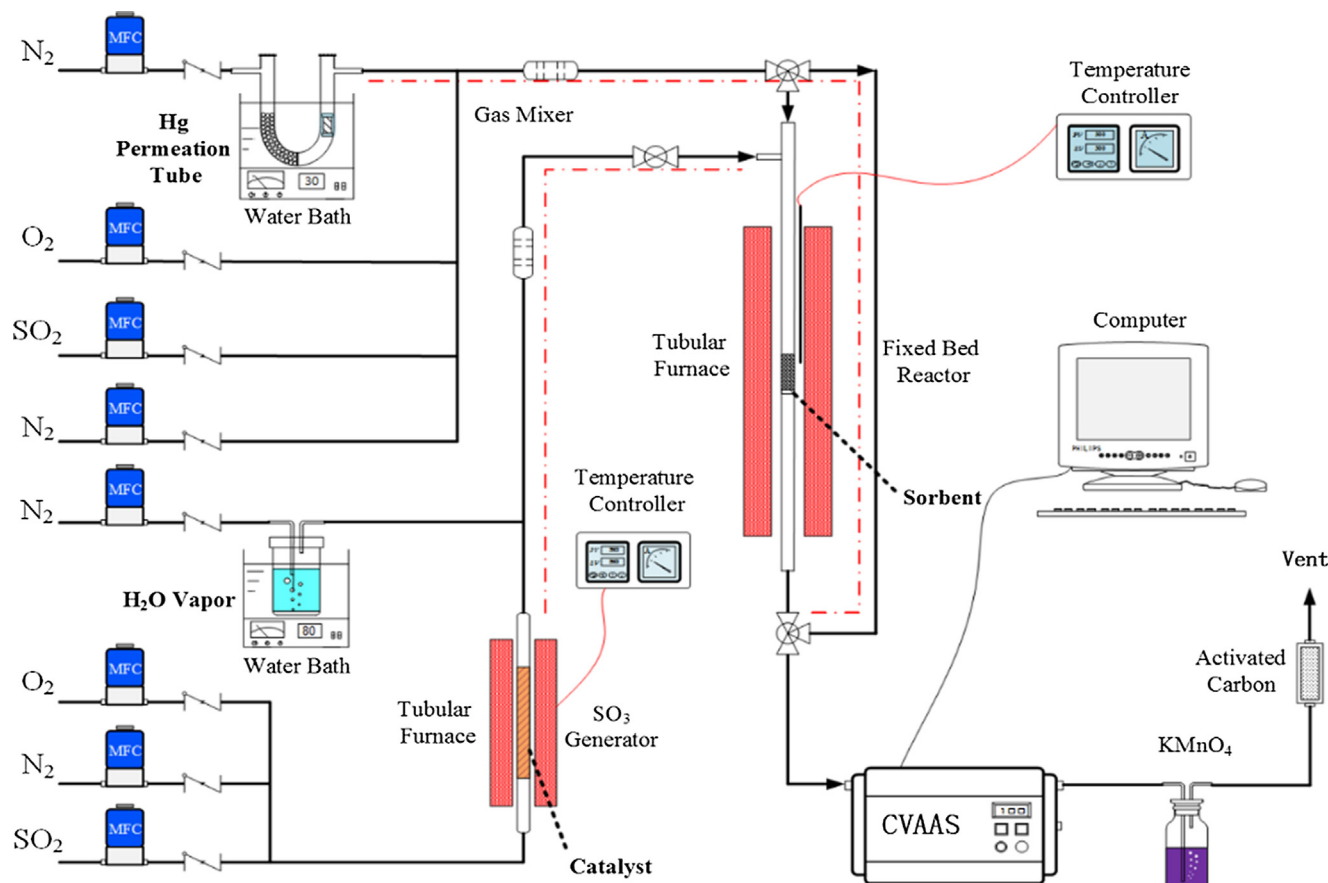


Fig. 1. Schematic diagram of lab-scale Hg^0 adsorption evaluate system.

Although mercury adsorption capacities were enlarged, most of them were easily suffered from the poisons of H_2O and SO_2 [16]. Therefore, developing novel sorbents to remove Hg^0 in flue gas containing high concentration SO_2 is important.

Chemical functionalization by sulfur is an important method to enlarge mercury adsorption capacity, resulting from the fact that surface sulfur compounds provide sufficient binding sites for mercury, forming stable mercuric sulfides (HgS) [14,17]. Metal sulfides are treated as promising adsorbents for Hg^0 due to its extensive active sulfur sites, low cost and environmental friendliness. Compared with some traditional sorbents, metal sulfides exhibit excellent Hg^0 capture performances and super resistances to H_2O and SO_2 . Li et al. prepared nano-ZnS with a huge surface area, which exhibited a superior mercury adsorption capacity ($497.84 \mu\text{g/g}$) than that of commercial activated carbons [18,19]. Liao et al. chose magnetic pyrrhotite as a recyclable sorbent to remove Hg^0 from the flue gas because of the excellent resistance of H_2O and SO_2 at low temperature [20]. However, mercury adsorption capacities of these metal sulfides are still too low to use in real industrial applications. Therefore, developing metal sulfides sorbents with larger mercury adsorption capacity is the key for controlling mercury emission from nonferrous metals smelting.

Copper sulfides (CuS) has been widely investigated for its potential application in Li-ion rechargeable batteries, gas sensors, photovoltaic devices, and catalysis. CuS composed abundant active sulfur sites is promising to remove Hg^0 effectively. In addition, literatures indicated that Cu-terminated active sites have strong adsorption performance for mercury [21]. Moreover, CuS is a cheap raw material in non-ferrous metal melting industry. Taking these advantages into account, we consider that using CuS to remove Hg^0 in smelting off-gas may be a scientifically sound and economically feasible technique.

In this study, CuS was prepared by precipitation method to remove

Hg^0 in non-ferrous metal smelting flue gas. The influences of flue gas components such as O_2 , SO_2 , H_2O and SO_3 on mercury adsorption performances, were investigated in a fixed-bed reactor. The potential application of CuS accompany with WFGS and EDS systems was discussed. Additionally, the mechanism for Hg^0 adsorption was also investigated.

2. Experimental section

2.1. Preparation of materials

Sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) was purchased from Shanghai Macklin Biochemical Company. Zinc nitrate ($\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2\cdot x\text{H}_2\text{O}$), tin chloride ($\text{SnCl}_2\cdot 2\text{H}_2\text{O}$), cadmium chloride (CdCl_2), copper nitrate ($\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Company. All reagents were used as received without further purification. All the chemicals were of AR grade. Distilled water used for all dilutions and sample preparations.

Synthesis of metal sulfide. Metal sulfide sorbents were synthesized using simple precipitation method. In a typical procedure, 1 M aqueous solution of metal nitrates ($\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2\cdot x\text{H}_2\text{O}$ etc.) and 1 M aqueous solution of Na_2S were prepared using distilled water. Then Na_2S solution was added dropwise to the metal nitrates solution under vigorous stirring for 2 h at room temperature. The resulting turbid dispersion was aged for 2 h. The products were separated from the solution by centrifugation. Then, the samples were washed several times with distilled water and centrifuged, dried under vacuum at 65°C for 12 h. Finally, the collected samples were ground and sieved through 120/180 meshes before used in Hg^0 removal tests.

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