Fuel 140 (2015) 136–142

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# Process migration and transformation of mercury in simulated wet flue gas desulfurization slurry system

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## HIGHLIGHTS

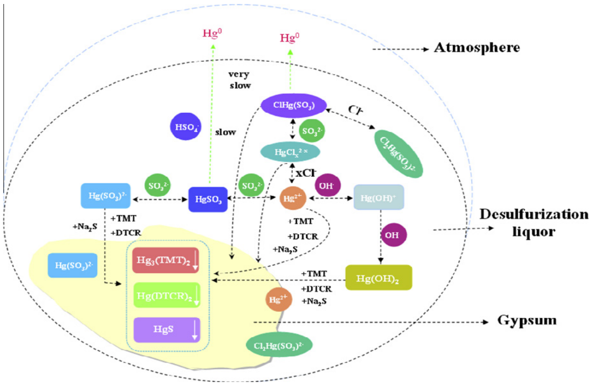
- Hg distribution in gaseous–liquid–solid phase in simulated WFGD system was studied.
- Lower temperature and pH were desirable for Hg capture via decrease Hg reduction.
- Higher S(IV), $Cl^-$ and $NO_3{}^-$ concentration was found to inhibit Hg reduction.
- DTCR and TMT were found to be effective in preventing Hg reduction and re-emission.
- The amount of Hg in FGD gypsum may increase, which need to be treated in future.

## ARTICLE INFO

*Article history:*
Received 17 July 2014
Received in revised form 24 August 2014
Accepted 18 September 2014
Available online 7 October 2014

*Keywords:*
Mercury
$Hg^0$ re-emission
Distribution
WFGD
Additives

## GRAPHICAL ABSTRACT



## ABSTRACT

Wet flue gas desulfurization (WFGD) system has been increasingly recognized to be effective in Hg removal. But the generated secondary pollution due to Hg re-emission from desulfurization solutions or solid byproducts has received researchers' attention. In this paper, the distribution of captured $Hg^{2+}_{(L)}$ in the simulated WFGD slurry was studied as a function of various environmental factors. Experimental results indicated that the pH value had a strong effect on $Hg^{2+}$ reduction but had negligible influence on the $Hg^{2+}$ retention by the grained fraction of gypsum. Increasing in pH value resulted in higher $Hg^{2+}$ reduction and over 46% of $Hg^{2+}$ was found to be reduced into $Hg^0$ at pH 5.0. Besides, increased slurry temperature also promoted the $Hg^{2+}$ reduction and $Hg^0$ re-emission as well as the $Hg^{2+}$ retention efficiency by gypsum. Other factors including S (IV), $Cl^-$ and $NO_3^-$ concentration was found to inhibit $Hg^{2+}$ transformation into $Hg^0$ but slightly promoted the $Hg^{2+}$ retained in gypsum. Moreover, the addition of sodium sulfide ($Na_2S$), 2,4,6-trimercaptotiazine, trisodium salt nonahydrate (TMT), and sodium dithiocarbamate (DTCR) prevented the $Hg^{2+}$ reduction and precipitated out as insoluble HgS, $Hg_3(TMT)_2$ and $Hg(DTCR)_2$ on gypsum. The findings presented in this study could provide theoretical basis for Hg removal in coal-fired power plants.

## 1. Introduction

Mercury is increasingly known as an extreme toxic pollutant distributed worldwide. It has been reported to cause various neurodegenerative diseases [1], to damage the immune system and kidneys [2], as well as to pose threat to the cardiovascular and nervous systems [3]. Therefore, Hg is regarded as a leading hazardous substance of environmental health concern by the US Environmental Protection Agency (EPA), which issued the Clean Air Mercury Rule (CAMR) on March 2005 to reduce Hg emissions.

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http://dx.doi.org/10.1016/j.fuel.2014.09.094
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Then in 2011, the national forms of Mercury and Air Toxics (MATs) was finalized by the EPA Administrator for reducing Hg emissions from coal-fired power plants. Mercury is emitted into the atmosphere through both natural occurring and anthropogenic processes. Anthropogenic mercury releases are known to be dominated on national scale mainly by coal combustion process that release Hg into the atmosphere [4]. As a consequence, research related to Hg control technology for coal-fired power plants received growing attention.

To remove Hg, the nature of Hg in coal derived flue gas was firstly studied. Mercury emissions from coal-fired power plants varied in total amount and speciation depending on coal types, boiler operating conditions, and presence of air pollution control devices [5]. Generally, the predominant forms of Hg in flue gases are elemental ($Hg^0$), oxidized ($Hg^{2+}$) and particle-bond ($Hg^p$). During combustion, Hg is liberated from coal as $Hg^0$. As the flue gas cools down, $Hg^0$ can undergo homogeneous and heterogeneous oxidation by forming $Hg^{2+}$, such as $HgCl_2$ and HgO [6]. Based on the aforementioned studies, numerous efforts have been made to develop control technologies to reduce Hg emissions in flue gases of coal-fired power plants. For example, activated carbon injected (ACI) method, a proven and effective $Hg^0$ removal technology has been widely investigated [7]. However, higher operating costs and negative effects on fly ash quality limited its wide application. Thus, great efforts have been devoted to develop cost-effective and ultrafine sorbents with highly effective sorption capacities and rapid reaction kinetics [8,9]. Considering the attractive economical factors, wet flue gas desulfurization (WFGD), a selective technology for sulfur dioxide ($SO_2$) removal adopted by US coal-fired power plants was recommended for removal of Hg [7]. Laboratorial, pilot and full-scale tests showed that WFGD units could remove nearly 90% of the received $Hg^{2+}$, but essentially none of $Hg^0$ due to its insoluble nature in water [7,10–12]. In order to increase the capture efficiency of Hg in flue gas, the combination of a wet scrubber and a catalyst has attracted research attention. During this process, the catalyst converts $Hg^0$ to $Hg^{2+}$, then the $Hg^{2+}$ is subsequently captured by the wet scrubber solution. To date, the conducted studies fall into three main catalyst areas: selective catalytic reduction (SCR) catalysts [13], carbon-based materials [14], and metal oxides [15]. SCR catalysts which are used for $NO_x$ reduction are composed of vanadium pentoxide ($V_2O_5$)/tungsten trioxide ($WO_3$) supported on titanium dioxide ($TiO_2$). The oxidation of $Hg^0$ across SCR catalysts possibly occurs via such reaction: HCl present in the flue gas adsorbs to the catalysts and reacts with either gas-phase or weakly bound $Hg^0$. Carbon-based materials are general sorbents that are used to remove $Hg^0$ in flue gas. In addition to adsorbing $Hg^0$, the materials also adsorb other different species from flue gas, such as HCl, NO and $SO_2$. Similar to SCR catalysts, the presence of adsorbed HCl in carbon-based materials opens the possibility for the heterogeneous oxidation of mercury. However, Hg reduction in aqueous solution containing sulfur species was found to decrease the overall Hg removal efficiency, which could be one of the limitations of WFGD method [16,17]. $Hg^0$ even appeared to increase in some tests, possibly due to the chemical reduction of ionic mercury by sulfite in scrubber solution followed by re-emission as $Hg^0$. The possible reaction is as Eq. (1) [18–20]:

$$Hg^{2+} \underset{-SO_3^{2-}}{\overset{+SO_3^{2-}}{\rightleftarrows}} HgSO_3 \overset{+H_2O}{\rightarrow} Hg^0\uparrow + SO_4^{2-} + 2H^+ \tag{1}$$

Some efforts have been made to find out the exact mechanism and the specific conditions under which this process has taken place. S (IV) was identified as the main species that affecting Hg reduction and re-emission [17,12]. Besides, effect of pH, temperature, and concentration of $Cl^-$ on Hg reduction in simulated wet flue gas desulfurization liquors was also studied by Wo et al. [16]. However, little work had been done to study the partitioning of $Hg^{2+}$ onto solid phase and the subsequent re-emission of $Hg^0$, which made it difficult to predict the exact Hg removal efficiency in WFGD units. Wang et al. [21] conducted an experiment by assuming that there was 100% $Hg^{2+}$ in flue gas to study the effects of slurry conditions on gas phase $Hg^{2+}$ removal and its reduction. Unfortunately, the aqueous phase $Hg^{2+}$ retained in FGD gypsum was not calculated in that paper.

In this paper, the ionic reactions of aqueous Hg in a typical simulated WFGD slurry was studied. The objective of this study was to investigate the partitioning of Hg onto solid phase and also its reduction in the solution under a range of operating slurry conditions (pH value, and slurry temperature and ion strength). Moreover, we intend to provide a theoretical basis for the removal of highly soluble oxidized Hg in WFGD units.

## 2. Experiments and methods

### 2.1. Chemical reagents

The gases ($N_2$ and Ar) stored in the steel cylinders were purchased from Jingong Gas Co. Ltd., Mercury chloride (>99.0%, AR) was purchased from Pharmaceutical Group Shanghai Chemical Reagent Company, China. Other chemicals including anhydrous sodium sulfite ($\geqslant$97.0%, AR), potassium dichromate (99.95–100.05%, GR), potassium permanganate (>99.5%, AR), sulfuric acid (95–98%, AR), calcium sulfate (>98.0%, AR), calcium carbonate (>99.0%, AR), potassium chloride (>99.5%, AR), hydroxylammonium chloride (>98.5%, AR), potassium borohydride (>97.0%, AR), as well as sodium chloride (>98.5%, AR) were purchased from Aladdin Co. Ltd., China.

### 2.2. Experimental apparatus and procedures

The experiments were designed to describe the transformation and migration of $Hg^{2+}$ in the simulated WFGD slurry. As shown in Fig. 1, the simulated experiment was processed in a 1 L three-necked flask surrounded with water at 50 °C to react for 3 h, while the pH was controlled using $H_2SO_4$. The simulated slurry composed of a solid mixture of gypsum (95%) and unreacted limestone (5%). In order to remove the production $Hg^0$, the flask was saturated with the continuous flow of nitrogen gas. With the continued stirring during the process, $HgCl_2$ (100 μg/L) aqueous solution were added to the WFGD slurry. Beside the reactor, a series of impinges were prepared in sequence of KCl and $H_2SO_4/KMnO_4$, so the $Hg^0$ atoms and $Hg^{2+}$ came from the reaction solutions could be absorbed separately. Compared to the standard method provided by the US Environmental Protection Agency [22], there was no $Hg^P$ collector in the equipment because particles would not exist in the simulated experiment. Considering the influences caused by different factors, $Na_2SO_3$, NaCl, $NaNO_3$ were selectively added to the system to simulate the source of $SO_3^{2-}$, $Cl^-$ and $NO_3^-$, as shown in Table 1. Each experiment was treated in double.

### 2.3. Test method

Concentration of $Hg^{2+}$ in the aqueous solutions could be measured with the cold-vapor atomic fluorescence spectroscopy (AFS-230E, Beijing Kechuanghaiguang Instrument Co., Ltd.). $KBH_4$ (guaranteed reagent, Aladdin Reagent Co., Ltd., Shanghai, China) was used as a reducing reagent. Ar was the carrier gas which flush mercury vapor out to the analyzer.

Moreover, $Hg^0$ was absorbed by the $KMnO_4/H_2SO_4$ solution which could oxidize $Hg^0$ to $Hg^{2+}$. After that, the $KMnO_4/H_2SO_4$ solution was titrated with $HONH_2{\cdot}HCl$ until the color faded to