New insights into synergistic effects and active species toward Hg\(^0\) emission control by Fe(VI) absorbent

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**Highlights**

- Fe(VI) is a promising agent for Hg\(^0\) control.
- Removal of Hg\(^0\) was optimized with the response surface methodology.
- Synergic effect of pH and temperature is considerable.
- Species analysis and thermodynamics revealed Hg\(^0\) removal mechanism.

**Abstract**

With the timelines for implementation of the U.S. Environmental Protection Agency’s mercury emission control rules approaching soon, finding an innovative and cost-effective mercury removal technology has become increasingly important. The most challenging species in all the mercury forms is gaseous elemental mercury (Hg\(^0\)). The objective of this work is to inspect the absorption behavior and removal of Hg\(^0\) by Fe(VI). The synergistic effects of various factors were investigated and the optimization for Hg\(^0\) removal by Fe(VI) was achieved based on the response surface methodology. The speciation of Fe(VI) and Hg reaction species was emphatically analyzed in the entire pH range in order to clarify the possible Fe(VI)-based Hg\(^0\) removal mechanism in depth. According to the thermodynamics calculation, the Gibbs free energies for the reaction between Fe(VI) and Hg\(^0\) in the weak alkaline/acid medium are determined as −120.03 kJ/mol and −235.42 kJ/mol, respectively, implying the oxidation of Hg\(^0\) by Fe(VI) is spontaneous and thorough. Finally, industrial feasibility analysis indicates that Fe(VI) has the practical potential to be a promising removal agent for Hg\(^0\) emission control from coal-fired flue gas, which might be integrated into the existing mainstream flue gas desulfurization scrubber to achieve the removal of multi-pollutants simultaneously, in prospect.

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With the breakneck development of the energy industry in the last few decades, mercury emission has become more problematic to the atmosphere, water and soil [2]. The Global Mercury Assessment reported that approximately 1,960 tons of mercury was emitted to the atmosphere in 2010 as a direct result of human activity. In order to cope with the serious environmental and health issues incurred by the increase in mercury emission, a global treaty for mercury emission control was recently signed in Geneva in early 2013. Coal combustion is responsible for about 475 tons of annual mercury emissions [3]. Mercury emission regulation will be implemented in the United States soon [4].

Mercury in coal-derived flue gas exists in three forms: particulate-bound mercury (Hg\textsubscript{0}), vapor-phase oxidized mercury (Hg\textsuperscript{2+}), and vapor-phase elemental mercury (Hg\textsuperscript{0}) [5,6]. The majority of Hg\textsubscript{0} and Hg\textsuperscript{2+} can be easily captured by existing pollution control technologies including electrostatic precipitators (ESP) or fabric filters (FF) [7], activated carbon injection [7,8] and wet flue gas desulfurization (WFGD) systems [9]; however, the removal of Hg\textsubscript{0} is challenging due to its high volatility and low solubility [10]. Clearly, the strategy for effective removal of Hg\textsubscript{0} is to quickly convert Hg\textsubscript{0} to Hg\textsuperscript{2+} since the latter is soluble and hence can be easily absorbed by WFGD. Many oxidizing absorbents, including KMnO\textsubscript{4}, K\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, NaClO\textsubscript{2}, and H\textsubscript{2}O\textsubscript{2} have been investigated [11–15]. Unfortunately, these classical oxidants either have lower economical efficiencies or may generate hazardous byproducts which can lead to secondary pollution. Specifically, KMnO\textsubscript{4}, K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and NaClO\textsubscript{2} are often considered as the effective reagents for removal of Hg\textsubscript{0}, but they will bring a large number of heavy metal, manganese, chromium and chlorine species that remain in the removal products from the process, which can bring serious threats to the environment and human health [16,17]. Although H\textsubscript{2}O\textsubscript{2} is an environmentally benign reagent, this approach is very inefficient without UV radiation, and as such its commercialization application is seriously restricted. Therefore, the development of efficient and environmentally friendly technologies for the removal of Hg\textsubscript{0} from flue gas is imperative.

Ferrate(VI), or Fe(VI), because of its strong oxidation and coagulation ability, has been used to treat wastewater [18–20], particularly in removing heavy metals such as As\textsuperscript{3+}, Mn\textsuperscript{2+}, Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, Cr\textsuperscript{6+}, and Hg\textsuperscript{2+} in water and wastewater [21]. Recently, limited efforts have been devoted to introduce this emerging green multifunctional chemical, Fe(VI), into flue gas treatment [22–24]. An Fe-based absorbent shows more potential to simultaneously control multi-pollutants including mercury [24–26], however, to the best knowledge, the study focused on Hg\textsubscript{0} removal by Fe(VI) is not thorough, especially with regards to the synergistic effects on the Hg\textsubscript{0} absorption behavior by Fe(VI) absorbent, which is crucial for further optimizing to suit a wide range of industrial applications. Meanwhile, the Hg\textsubscript{0} removal mechanism of Fe(VI) is far from being clearly studied and analyzed. This work aimed at filling this gap. In conventional multifactor experiments, optimization is usually performed by varying a single factor while keeping all other factors fixed at a specific set of conditions. It is not only time-consuming, but also usually incapable of reaching the true optimum due to ignoring the interactions among factors. Compared with other statistical experimental design methods, the main advantage of response surface methodology (RSM) is the reduced number of experiment trials needed to evaluate multiple parameters and their interactions [27,28]. For this reason, RSM was employed to investigate the independent and synergistic effects of main operating conditions on the Hg\textsubscript{0} removal capability, respectively, in order to optimize the process and provide parameters suitable for a pilot-scale trial. In addition, the Hg\textsubscript{0} removal mechanism of Fe(VI) was explored in detail by species analysis and thermodynamics calculation under various pH conditions. Finally, the industrial implementation and its feasibility were discussed and analyzed.

2. Experimental

2.1. Materials

Potassium ferrate (K\textsubscript{2}FeO\textsubscript{4}, purity 92%) was supplied by the Tianshun Chemical Co. in Xi’an, China. All the other reagents were analytical grade and purchased from the Tianjin Chemical Reagents Co., in Tianjin, China. Ferrate(VI) solutions were prepared by mixing predetermined amounts of K\textsubscript{2}FeO\textsubscript{4} powder and deionized water along with a pH regulator, in which 0.2 M KOH or 0.1 M H\textsubscript{2}SO\textsubscript{4} solution acted as a pH regulator to control the initial pH of the reaction solution.

2.2. Apparatus and methods

The experimental apparatus used for removal of Hg\textsubscript{0} with Fe(VI) is illustrated in Fig. 1. It has three units: inlet flue gas simulation, removal of Hg\textsubscript{0}, and outlet gas analysis and treatment, corresponding to parts 1–7, 8–12, and 13–14 in Fig. 1, respectively. Teflon (PTFE) lined tubing and fittings were employed to connect all parts in the apparatus. The first step of mercury removal test is to flow N\textsubscript{2} from its cylinder (1) at 1 L/min controlled by a regulator (2) and a meter (3, LZN, Tianjin Flow Meter Co.) into the Hg\textsubscript{0} generator, which consists of glass beads (4a), a membrane veneer (4b), and a mercury permeation tube (4c, VICI Metronics Co.). The temperature of the Hg\textsubscript{0} generator was controlled by a HD120-T12 thermostatic water bath with the four-bit LED display (5, ±0.02 °C, Prima Co., British). Then the gas from the Hg\textsubscript{0} generator set was mixed with the balance N\textsubscript{2} controlled by a flow meter (3°) in a gas mixer (6). The gas mixture passed through a valve (7) and then entered the Hg\textsubscript{0} removal reactor (10), through a gas diffuser (8), and the Hg\textsubscript{0} reacted with Fe(VI) loaded through an injector (9). In order to improve the applicability, the reactor was designed with a reduced scale ratio of 1:40 to mimic a pilot-scale bubble column tower in an actual power plant (600 MW, MATOU power plant, Hebei, China). The capacity and the height of the reactor were determined as 1 L and 15 cm, respectively, in accordance with the E-S1 and E-S2 (Supplementary data).

The gas velocity in vacant reactor was kept down to 4.5–6 cm/s, to avoid back-mix flow. The pH values of the reaction solution were tested by a waterproof pH meter (±0.01, PHS-3G type, Shanghai LEICI Co., China). Part of the outlet gas from the reactor (10) was monitored with a PHSJ-5 Hg\textsubscript{0} analyzer (11, Suzhou, Qijing Instrument Co.) and a computer (12), while the remaining part passed through a three-way-valve (13) for complete removal of Hg\textsubscript{0} with a solution containing 10 wt.% H\textsubscript{2}SO\textsubscript{4} and 4 wt.% K\textsubscript{2}MnO\textsubscript{4} in a scrubber (14) before it was vented to hood.

2.3. Experimental design

Considering many unparalleled advantages, including miniimization of the number of experiments and analysis of potential interaction of factors [27,28], response surface methodology (RSM) was applied to find out the relationship between the removal efficiencies of Hg\textsubscript{0} and the associated factors, to evaluate the significance of each factor and their synergistic effects, and therefore to determine the optimal industrial operating conditions for the Hg\textsubscript{0} removal. The output response is the removal efficiency of Hg\textsubscript{0} (%), which was calculated as below:

\[
\eta_{\text{Hg}_0} = \left(1 - \frac{C_{\text{Hg}_0}}{C_{\text{Hg}_0}}\right) \times 100\%
\]

(E1)

where \(C_{\text{Hg}_0}\) and \(C_{\text{Hg}_0}\) stand for the inlet and outlet concentrations of Hg\textsubscript{0}, respectively. Many factors will affect the removal efficiency of
Hg\(^0\) in an industrial application. The oxidation by Fe(VI) is sensitive to pH, temperature and concentration, so these were the primary factors chosen as the main operating variables. In this work, the effects of these three variables, i.e., the initial concentration of Fe(VI) \((C_{Fe(VI),0})\) between 0.1 mM and 0.6 mM, the initial pH of the reaction solution from 4.3 to 12.7, and reaction temperature \((T)\) from 25 °C to 75 °C, were investigated using a central composite design (CCD) at 3 factors and 5 levels (the arranged tests are listed in Table S1 of Supplementary data), and the experimental results were analyzed with statistical graphics Design-Expert 8.0.5b software.

3. Results and discussion

3.1. Significance of various factors and synergistic effects on Hg\(^0\) removal

To reveal the significance of various factors and to find the synergistic effects of multiple factors on Hg\(^0\) removal, twenty tests based on central composite experimental design were conducted, consisting of eight orthogonal design points along with six star points to form a central composite rotatable design with \(\alpha = \pm 1.682\) and 6 center points for replication. The CCD matrix and Hg\(^0\) removal efficiencies under various experimental conditions are summarized in Table S2 (Supplementary data), and the experimental results were analyzed and are discussed in detail below.

3.1.1. Initial concentration of Fe(VI)

The removal efficiency of Hg\(^0\) changing with the initial concentrations of Fe(VI) are presented in Fig. 2. Fe(VI) demonstrates remarkable removal of Hg\(^0\). It can be seen that higher initial concentrations of Fe(VI), \(C_{Fe(VI),0}\), result in higher removal efficiencies of Hg\(^0\). The increases in the total oxidative removal of Hg\(^0\) at lower Fe(VI) concentration range is larger than those at higher Fe(VI) concentration range. Under the moderate Fe(VI) concentration condition, 0.35 mM, 82.75% removal efficiency of Hg\(^0\) was obtained. After the Fe(VI) concentration exceeds 0.35 mM, with the further increase of the initial concentration of Fe(VI) in the bubble reactor, the removal efficiency of Hg\(^0\) increases slowly. It may be because the reaction is almost saturated after this point in the curve, and the removal of Hg\(^0\) is less subject to the initial concentration of Fe(VI) after the absorbent reaches saturation. The time-dependence of the removal rate of Hg\(^0\) \((C_{Hg}/C_{Hg0})\) at the initial Fe(VI) concentration of 0.35 mM is presented in the inset of Fig. 2. The experiment results show the reaction between Fe(VI) and Hg\(^0\) occurred very rapidly. The outlet concentration of Hg\(^0\) decreases sharply at the beginning of the removal process, and then reaches a plateau after nearly 10 min; afterwards, the removal rates of Hg\(^0\) \((C_{Hg}/C_{Hg0})\) remain constant, which shows the stable removal capability of Hg\(^0\) by Fe(VI).
3.1.2. Initial pH

The pH of the reaction solution strongly affects the stability and oxidation potential of Fe(VI) in aqueous conditions [29], and has a significant effect on the removal efficiency of Hg⁰. The factorial experimental results demonstrate the close relationship between pH and removal efficiency of Hg⁰, as provided in Fig. 3. The removal efficiencies of Hg⁰ are low in the pH range from 4 to 6, which can be attributed to the aqueous decomposition rate of Fe(VI) under acidic conditions. Subsequently, the removal efficiency of Hg⁰ increases noticeably with pH. The most effective pH range is from 7 to 9, indicating that neutral and weak alkaline condition is favorable for Hg⁰ removal. The highest removal efficiency of Hg⁰ (82.13%) was observed at pH 8.5; then the removal efficiency of Hg⁰ drops continuously but the change is relatively flat, reflecting the decrease in oxidation potential of Fe(VI) with pH in this range. The stark shifting trends of curve in the wide range of pH (4.3–12.7) reveal that the pH value of the reaction solution is an important determinant in removal of Hg⁰.

3.1.3. Reaction temperature

Hg⁰ removal with Fe(VI) is a heterogeneous reaction process, in which temperature plays an important role in both Hg⁰ diffusion and Hg binding on the metals [30]. Fig. 4 indicates the dependence of the removal efficiencies of Hg⁰ on reaction temperature. The removal efficiencies of Hg⁰ vary considerably from between room temperature and 75 °C. At first, the removal efficiencies of Hg⁰ increase gradually with temperature; then, the removal efficiencies of Hg⁰ decrease. The highest removal efficiency of Hg⁰ was obtained at 45–50 °C, which is close to the inside temperature of flue gas desulfurization (FGD) equipment in coal-fired power plants [31]. Although there exits some optimal points, the variation of removal efficiency of Hg⁰ with the temperature is still very gentle and the effect of temperature is not as sharp as that of pH presented in Fig. 3.

3.1.4. Synergistic effects

Synergistic effect is usually taken to mean an effect arising between two or more factors that produce an effect greater than the sum of their individual effects. It is important to check the significance of the synergized effects of variables on the removal of Hg⁰, but it is difficult to obtain the integrated rules with conventional factor experimental methods. In this work, based on the central composite experimental design, the regression coefficients of synergized effect were calculated using Multiple Linear Regression (MLR) method and the probabilities indexes of multi-factor interactions, also known as P-values, were obtained by the analysis of variance (ANOVA). The statistical calculation process in detail is shown in SI-1 part of the supplementary data. P-value less than 0.05 was taken as a significant interaction effect [27]. The ANOVA statistical calculated results show that the quadratic interactions between the initial pH of reaction solution and reaction temperature have the strongest effect (P-value is 0.0039) on the removal of Hg⁰, while both the integrated effect between initial concentration of Fe(VI) and pH (P-value is 0.6311) and between the initial concentrations of Fe(VI) and the reaction temperature (P-value is 0.3269) are inferior than the former. Fig. 5 presents the three-dimensional (3D) response surface experimental result and two-dimensional (2D) contour plots of the integrated effect of the initial pH of solution and reaction temperature on the Hg⁰ removal process. The response surface has a clear peak, suggesting that optimum conditions for maximum Hg⁰ removals are within the design boundary. The oxidation potential and decomposition rate of Fe(VI) significantly depend on the initial pH of the reaction solution, while the synergistic effect of pH and reaction temperature is considerable.

3.2. RSM model and optimization of the Hg⁰ removal

The model of surface response corresponding to CCD takes into account all the major factors and their interactions. The quality of the RSM model and its power of prediction were checked by some statistical values (i.e., F-value, P-value, R², and adjusted-R²). The
response surface model was validated statistically for adequacy with ANOVA, which also demonstrated the significance of various factors. The calculated ANOVA results (Tables S3 and S4) show that the importance-decreasing order of the individual factors affecting the Hg⁰ removal with Fe(VI) is initial pH of the reaction solution (pH), initial Fe(VI) (C⁰_{Fe(VI)}) concentration and reaction temperature (T), which is consistent with the factor-effect experimental results in the above section. The Hg⁰ removal process is also significantly affected by quadratic interaction between the initial pH of the reaction solution and the reaction temperature (pH • T). In addition, several interrelated variables including two factor interactions (pH², C²_{Fe(VI),0} • T), cubic interactions (C_{Fe(VI),0} • pH², C²_{Fe(VI),0} • pH), and four-dimensional interactions (C³_{Fe(VI),0} • pH²) have some influence. Thus, the RSM model obtained with the twenty Hg⁰ removal tests is

\[ \eta_{Hg} = -3.3 \times 10^2 + 1.3 \times 10^3 C_{Fe(VI),0} + 74.8 \text{pH} + 1.4T - 3.9 \times 10^{-2} \text{pH} \cdot T - 2.2 \times 10^2 C_{Fe(VI),0}^2 - 3.7 \text{pH}^2 - 7.2T^2 + 4.4 \times 10^2 C_{Fe(VI),0} \cdot \text{pH} + 12.8 C_{Fe(VI),0} \cdot \text{pH}^2 - 22.8 C_{Fe(VI),0} \cdot \text{pH}^2. \]  

(E2)

The RSM model is not confined for the significance analysis of various factors in this work, but also be used for the prediction of the removal efficiency of Hg⁰ by Fe(VI) as the operational conditions change in the industrial process. Based on the above built RSM model (E2), the optimal conditions were determined by a Monte Carlo simulation method combined with Design-Expert 8.0.5b software, and the theoretical results were presented in Table 1. To confirm the prediction ability of the response model and ensure the experimental stability, further parallel experiments for removal of Hg⁰ using Fe(VI) were conducted under the established optimal conditions. The experimental values against the predicted responses for the removal of Hg⁰ were compared as presented in Table 1 and Fig. 6. The realized Hg⁰ removal efficiency was 82.75% under the initial reaction conditions of 0.35 mM Fe(VI), pH 8.50 and 50 °C, as shown in Table 1. It appears that the theoretical Hg⁰ removal efficiency, 84.84%, predicted with the modified RSM model, was achieved when the initial concentration of Fe(VI), pH and reaction temperature are 0.42 mM, 8.71 and 44.96 °C, respectively. It should be noted that higher than both the theoretical efficiency (84.84%) and experimental value (82.75%) would have been achieved if different condition such as higher Fe(VI) dosages had been used. In addition, it is clearly shown in Fig. 7 that the modified response model is a good predictor of the experimental data and high statistical significances. Table 1 also validates that the experimental results correlate well with the data predicted by the modified RSM model since the derived high determination coefficient (R²) is 0.9985 and the relative standard deviation value is 0.12%. Consequently, the modified RSM model can serve as a prediction tool for removal efficiency of Hg⁰ with Fe(VI), and it could be utilized to design and optimize the large-scale Fe(VI)-based Hg⁰ removal.

3.3. Reaction species and removal mechanism

The reduction potential of Fe(VI) and the associated electron transfer number change with pH, leading to the significant differences in the reaction pathways and products when Fe(VI) and Hg⁰ interact. These factors directly affect the removal efficiencies of Hg⁰. Generally speaking, Fe(VI) can exist in the forms of H₃FeO₄, H₂FeO₄, HFeO₄, and FeO₄²⁻ within aqueous environment [23,32].

\[ \text{HFeO}_4^{-} \rightarrow \text{H}^{+} + \text{H}_2\text{FeO}_4^{-} \quad K_1 = 10^{-1.6} \]  

(R1)

\[ \text{H}_2\text{FeO}_4^{-} \rightarrow \text{H}^{+} + \text{HFeO}_4^{-} \quad K_2 = 10^{-3.5} \]  

(R2)

\[ \text{HFeO}_4^{-} \rightarrow \text{H}^{+} + \text{FeO}_4^{2-} \quad K_3 = 10^{-7.3} \]  

(R3)

where Ki (i = 1, 2, 3) is the corresponding equilibrium constant. The fractions of the different Fe(VI) species as a function of pH are revealed in Fig. 7(a). Within the strong acidic environment (pH < 4), there are three protonated forms of Fe(VI) (H₃FeO₄, H₂FeO₄, and HFeO₄), while in the weak acidic environment (4 < pH < 7), HFeO₄ dominates. When the pH is in the range of 7–12, the existing species of Fe(VI) are HFeO₄ and FeO₄²⁻, in which FeO₄²⁻ dominates. Strong alkaline environment (pH > 12) leads to the disappearance of HFeO₄.

Mercury species can be in the forms of Hg⁰, Hg²⁺, Hg³⁺, HgOH⁻, Hg(OH)₂⁻, Hg(OH)₃⁻, HgO, Hg₂(OH)₂, and Hg₂O. The interactions of different mercury species in aqueous solution and their equilibrium constants are listed below [25,26]

\[ \text{Hg}^0(l) + \text{Hg}^{2+} \rightarrow \text{Hg}^{2+} \quad K_4 = 10^{2.06} \]  

(R4)

\[ \text{Hg}^{2+} + \text{H}_2\text{O} \rightarrow \text{HgOH}^{+} + \text{H}^{+} \quad K_5 = 10^{-3.40} \]  

(R5)

\[ 2\text{Hg}^{2+} + \text{H}_2\text{O} \rightarrow \text{HgOH}^{+} + \text{H}^{+} \quad K_6 = 10^{-2.08} \]  

(R6)

\[ \text{HgOH}^{+} + \text{H}_2\text{O} \leftrightarrow \text{Hg(OH)}_2(s) + \text{H}^{+} \quad K_7 = 10^{-2.60} \]  

(R7)
Hg(OH)$_2$ + H$_2$O → Hg(OH)$_3^+$ + H$^+$ $K_a = 10^{-14.7}$ (R8)
Hg(OH)$_2$ ↔ HgO(s) + H$_2$O $K_9 = 10^{3.70}$ (R9)
Hg$_{\text{II}}^{2+}$ + 2OH$^-$ → Hg(OH)$_2$(s) $K_{10} = 10^{-23.7}$ (R10)
Hg$_{\text{II}}$(OH)$_{2+}$(s) → HgO(s) + H$_2$O $K_{11} = 10^{-24.8}$ (R11)

where $K_i$ (i = 4, 5, ..., 11) represents the corresponding equilibrium constants. The changes in the fractions of different ionized mercury species (Hg$^{2+}$, Hg$_{\text{II}}^{2+}$, HgO, Hg$_{\text{II}}^{2+}$, Hg(OH)$_2$), determined by the pH of a given solution, are presented in Fig. 7(b). The Hg(OH)$_2^+$ concentration declines with pH in the pH = 6 range; the fraction of Hg$_{\text{II}}^{2+}$ reaches its maximum value at pH 3. The fraction of HgO$^-$ is higher in the wide pH range of 2–11; the fraction of Hg(OH)$_2^+$ increases with pH at pH > 6 while that of Hg$_{\text{II}}^{2+}$ is much lower in the whole pH scale. Under weak alkaline conditions, the fractions of Hg$_{\text{II}}^{2+}$ and Hg$^0$ are practically zero and the main existing mercury species are Hg(OH)$_2$ and HgO$^-$. According to the experimental results as shown in Fig. 3, very low or high pH conditions are not favorable to removal of Hg$^0$ and the optimal Hg$^0$ removal was achieved in the moderately alkaline solutions. Thus the following discussion will only focus on the moderately acid and alkaline conditions.

In the moderately alkaline environment, the stable Fe(VI) and Hg species in this pH range are FeO$_4^{2-}$, Hg(OH)$_2$ and HgO, respectively. There are two possible reaction pathways associated with Hg$^0$ oxidation by Fe(VI). The first one can be expressed as [33,35]

2FeO$_4^{2-}$ + 3Hg$^0$ + 8H$_2$O → 2Fe(OH)$_3$ + 3Hg(OH)$_2$ + OH$^-$ (R12)
Hg(OH)$_2$ → HgO + H$_2$O (R14)

and the second one is [34,35]

2FeO$_4^{2-}$ + 3Hg$^0$ + 8H$_2$O → 2Fe(OH)$_3$ + 3HgOH$^+$ + 7OH$^-$ (R15)
HgOH$^+$ → Hg(OH)$_2$ (R16)
Hg(OH)$_2$ → HgO + H$_2$O (R17)

The overall reaction of both pathways is

2FeO$_4^{2-}$ + 3Hg$^0$ + 5H$_2$O → 2Fe(OH)$_3$ + 3HgO + 4OH$^-$ (R18)

Based on the stoichiometric coefficients of the reactants and products in R18, the Gibbs free energy change ($\Delta G$, kJ/mol) of R18 can be calculated with

$$\Delta G = -120.03 + \frac{2.303RT}{1.0 \times 10^5} \ln \left[ \frac{[\text{OH}^-]^4}{[\text{FeO}_4^{2-}]^2} \right]$$

(E3)

where $R$ is the universal gas constant, 8.314 J K$^{-1}$mol$^{-1}$, $T(K)$ is the absolute temperature of the reaction; and [OH$^-]$ and [FeO$_4^{2-}$] are the concentrations (M) of OH$^-$ and FeO$_4^{2-}$, respectively. E3 reveals two facts: Firstly, R18 is spontaneous due to its negative $\Delta G$ ($-120.03$ kJ/mol), which was confirmed with the success of this research in the removal of Hg$^0$ with Fe(VI) in the pH range. Moreover, at a given temperature, $\Delta G$ or the equilibrium constant $K$ of R18 is determined by concentrations of both OH$^-$ and FeO$_4^{2-}$. More negative $\Delta G$ leads to higher $K$ and thus higher $n_{\text{Hg}}$. It is obvious that $n_{\text{Hg}}$ increases with the concentration of FeO$_4^{2-}$ as predicted by E3 and confirmed with the results in Fig. 2. However, the overall effect of pH in Hg$^0$ removal in E3 should be considered from two aspects. On one hand, $n_{\text{Hg}}$ decreases with the increase in [OH$^-$] according to E3. On the other hand, [FeO$_4^{2-}$] varies with [OH$^-$]. Higher [OH$^-$] makes FeO$_4^{2-}$ more stable. The overall effect of OH$^-$ on $n_{\text{Hg}}$ depends on which one of these two roles dominates. In the pH 7–8.5 range, the role of OH$^-$ in stabilizing FeO$_4^{2-}$ governs, which leads to the $n_{\text{Hg}}$ increase with pH. When pH is higher 8.5, the situation becomes different. In other words, the highest $n_{\text{Hg}}$ was achieved at pH 8.5.

In contrast, under the mild acid to neutral pH conditions, Fe(VI) mainly exists in forms of HFeO$_4^-$ and FeO$_4^{2-}$, while the stable Hg species is HgOH$^-$. HFeO$_4^-$ is the dominant Fe(VI) species in this pH range [Fig. 7(a)]. Density function study indicates that protonated HFeO$_4^-$ has a larger spin density on the oxo ligands than deprotonated FeO$_4^{2-}$ [36], which is beneficial to increase the oxidation ability of Fe(VI) [37]. The possible pathway for the interaction between Hg$^0$ and Fe(VI) in the pH range is

2HFeO$_4^-$ + 3Hg$^0$ + 11H$^+$ → 2Fe$^{3+}$ + 3HgOH$^+$ + 5H$_2$O (R19)
HgOH$^+$ + H$^+$ → Hg$^{2+}$ + H$_2$O (R20)

or

2HFeO$_4^-$ + 3Hg$^0$ + 14H$^+$ → 2Fe$^{3+}$ + 3Hg$^{2+}$ + 8H$_2$O. (R21)

The Gibbs free energy change ($\Delta G$, kJ/mol) of R21 can be calculated with

$$\Delta G = -235.42 + \frac{2.303RT}{1.0 \times 10^5} \ln \left[ \frac{[\text{Hg}^{2+}]^3}{[\text{Fe}^{3+}]^2} \right]$$

(H$^+$)

(E4)

where [H$^+$], [Fe$^{3+}$], [HFeO$_4^-$] and [H$^+$] are the concentrations of the corresponding ions. The negative $\Delta G$ ($-235.42$ kJ/mol) in E4 means that the Fe(VI) based Hg$^0$ oxidation can also take place spontaneously, as confirmed with the results in Fig. 3. It should be noted that the power of [H$^+$] in E4 is much higher than those for other ions. Consequently, [H$^+$] plays an important role in the oxidation of Hg$^0$ by Fe(VI), which is consistent with the prediction of modified RSM model and experimental results.

3.4. Other effects and industrial feasibility prospect

In an industrial application, the removal efficiency of Hg$^0$ will be affected by the factors already mentioned as well as several that were not, such as flue gas flow rate, the ratio of liquid and gas, residence time, the limestone quality, the type of coal, and so on. These operation parameters will be involved in a large-scale reactor, and they will be discussed in the upcoming pilot-scale results. Here, only the effects of the components of flue gas were considered to make a simple analysis. There are many components, such as CO$_2$, N$_2$, SO$_2$, NO, O$_2$ and so on, exit in real flue gas. Generally speaking, fly ash would need to be removed by electrostatic precipitators (ESP) or fabric filters (FF) prior to the FGD, and N$_2$ seldom reacts with other matter. Our recent experimental studies [24] show that an amount of SO$_2$ in flue gas is to the benefit of removing Hg$^0$. The promoting action of SO$_2$ on Hg$^0$ removal may be attributed to the complex of HgS(IV). The lower concentration of NO also has a promoting effect on Hg$^0$ removal. This may be because in the absence of buffer solution, with an increase of NO concentration, the solution pH raised due to the release of OH$^-$ during oxidation of NO by Fe(VI), which helped increase the Fe(VI) absorbent stability and promoted the removal efficiency. Additionally, the produced Hg$^{2+}$ seemed to slightly catalyze Hg$^0$ absorption in the presence of HNO$_3$ resulting from the oxidation of NO. The effects of CO$_2$ and O$_2$ were preliminarily investigated in this work. CO$_2$ might affect the acidity of the removal environment, thereby influencing the removal of Hg$^0$ by Fe(VI). Indeed, a non-significant trend of the effect of CO$_2$ on the removal efficiency was observed. Conversely, the content of O$_2$ was found to affect the removal of Hg$^0$. The removal efficiency of Hg$^0$ rises gently with the increase of the content of O$_2$. This may be because the presence of O$_2$ can promote the oxidation of Hg$^0$. In addition, the previous study [38] shows that too low O$_2$ content in flue gas might make the Hg$^0$ reemission rates increase.

Hg$^{2+}$ + HSO$_3^-$ + H$_2$O → SO$_4^{2-}$ + Hg$^0$ + 3H$^+$ (E5)
However, the adoption of Fe(VI) absorbent can avoid this undesirable feature, because SO\(_2\) is oxidized by Fe(VI) completely, and the products are dominated by sulfate radicals and rare sulfite species [24]. In addition, sulfate ions could be contributing to the formation of a small amount of mercury sulfate which then precipitates with the gypsum particles or decomposes in HgO(s).

In terms of the industrial implementation, Fe(VI) absorbent can be directly applied in the conventional wet FGD or semi FGD system without any additional Hg removal equipment or equipment retrofit. Considering the case of a jet bubbling absorption tower for example, the Fe(VI) absorbent can be directly fed into the slurry (mainly limestone or lime) of the wet scrubber. Untreated flue gas expelled from the boiler first passes through the gas gas heater (GGH) and then can be cooled by a heat exchanger. During this period, the fresh water and the slurry containing Fe(VI) absorbent are sprayed into the absorption tower. The cooled flue gas enters a closed entrance cabin of the absorption tower, and then is pushed into the absorption bubbling zone by the jet pipes installed on the bottom of the entrance cabin. In the bubbling zone, the concurrent chemical reactions occur, namely, limestone or lime dissolution, the flue gas oxidation and absorption, neutralization, gypsum precipitation, and gypsum crystal growth.

Taking account of economics, the estimated capital cost of Fe(VI) is hopefully more economical than traditional activated carbon injection. It has lower energy consumption than activated carbon injection, because it neither requires the installation of the additional Hg control unit nor an equipment retrofit, and the facility cost would be significantly reduced.

As far as environment benefits are concerned, Fe(VI) is considered an environmentally benign chemical. There is no potential secondary pollution issues in wet FGD wastewater, and the remaining Fe(VI) in the absorption solution will not produce any harmful byproducts [39]. In addition, the reduced ions could be recycled to use as raw materials for Fe(VI) production. The gypsum byproducts can be used in construction [23].

4. Conclusions

Ferrate(VI), a green and multifunctional material, promises to be a new technology for Hg\(^0\) control, the most challenging task for implementation of the overall mercury emission regulation in the near future. Multiple factors synergistically affect the performance of Fe(VI) on the Hg\(^0\) removal. High Hg\(^0\) removal is achievable with Fe(VI) after optimizing the operation parameters by response surface methodology. Industrial feasibility analysis indicates that Fe(VI) could be a promising alternative to conventional activated carbon-based mercury removal methods, as it is more easily implemented and has lower capital costs, more energy conservation, smaller occupy area and long-term environmental benefits.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2014.09.072.

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