

Supporting Information for

Removal of Carbon Monoxide from Simulated Flue Gas Using Two New Fenton Systems: Mechanism and Kinetics

Yan Wang, Xuan Han and Yangxian Liu*

School of Energy and Power Engineering, Jiangsu University, Zhenjiang, 212013, China

*Corresponding authors E-mail: liuyx1984@126.com

Submitted to

Environmental Science & Technology

Number of pages (including this page): 11

Number of texts: 4

Number of figures: 3

Number of tables: 1

1. Simultaneous removal of multi-pollutants (SO₂, NO, Hg⁰, CO) from waste incineration flue gas

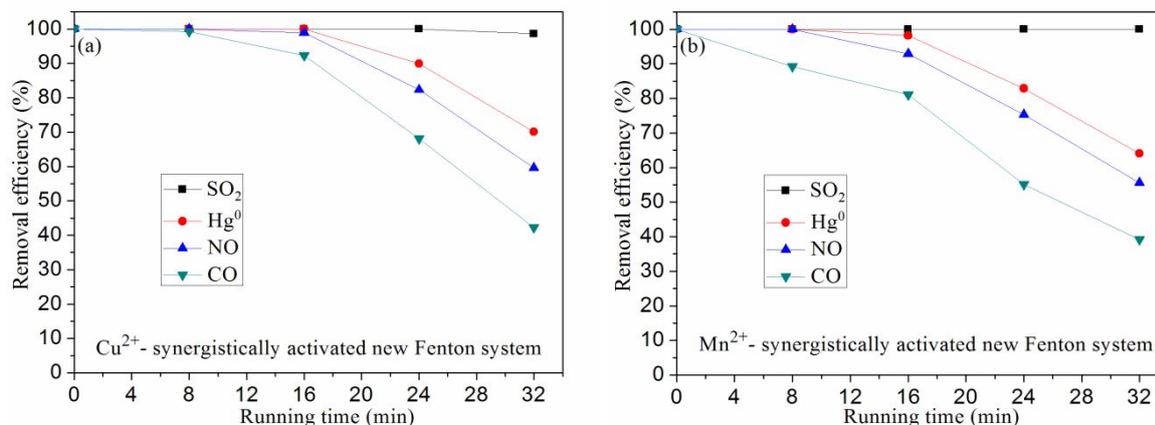


Figure S1. Simultaneous removal efficiency vs running time of multi-pollutants (SO₂, NO, Hg⁰, CO) from waste incineration flue gas (using a semi-batch operation mode): (a) Cu²⁺-based new Fenton system; (b) Mn²⁺-based new Fenton system.

2. Process flow and removal products processing strategy

During the combustion process of solid wastes, various gaseous pollutants, mainly including sulfur dioxide, nitrogen oxides, hydrogen chloride, mercury, carbon monoxide, dioxine, particulate matter, etc., are often produced. At present, some of these pollutants such as sulfur dioxide, nitrogen oxides, hydrogen chloride, mercury, particulate matter, are mainly controlled using complex combined processes (e.g, SNCR/SCR denitration + acid gases removal +activated carbon adsorption + dust removal + CO removal, etc.). This kind of independent processing strategy has very high investment and operating costs, which is not suitable for large-scale application. Many researchers have indicated that simultaneous removal processes of multi-pollutants from exhaust gas (e.g, SO₂, NO_x, HCl, CO, Hg⁰, VOCs, etc.) have more obvious advantages such as simple process and low expenses than the complex combined treating systems(e.g, SNCR/SCR denitration + acid gases removal +activated carbon adsorption + dust removal + CO removal, etc.).

In this work, two new Fenton systems have been proved to be able to achieve simultaneous removal of multi-pollutants such as SO₂, NO_x, CO, Hg⁰. The removal of VOCs such as dioxins was not carried out because

we lack sufficient experimental and measurement conditions. However, Fenton or $\cdot\text{OH}$ oxidation has been widely proved to be a very effective method for the degradation of most organic pollutants. From the theoretical point of view, VOCs degradation is also feasible by using two new Fenton systems. In addition, HCl is a very soluble gas, and thus can be easily absorbed through simple solution washing. Based on the product analysis in Table 1, we can see that HCO_3^- , SO_4^{2-} , NO_3^- and Hg^{2+} were detected. According to previous research results¹⁻⁴ and as shown in Figure S2, it can be seen that Hg^{2+} can be recycled by adding S^{2-} to produce HgS precipitate. All of acidic products such as HCO_3^- , SO_4^{2-} and NO_3^- can be recycled by adding ammonia to produce ammonium fertilizer, including ammonium sulfate, ammonium nitrate and ammonium bicarbonate.

The aqueous ammonium fertilizer can be converted into solid-state ammonium fertilizer by evaporation and crystalline of liquid products using waste heat of flue gas. Transition metal ions such as Fe^{3+} , Cu^{2+} and Mn^{2+} can be conveniently recycled in the neutralization process of adding ammonia water. They can even be recycled gradually (independent recovery facilitates separation of ions) because the form of transition metal hydroxides precipitation is often at different pH values. Therefore, all the reaction products can be recovered and separated without any secondary pollution. The novel technique and obtained results will provide valuable guidance for emission reduction of CO and multi-pollutants from waste incineration exhaust gas, and recycling of Cu^{2+} and Mn^{2+} from containing- Cu^{2+} and Mn^{2+} industrial wastewater, which has good prospects for development. The above process can also be described more intuitively by the following Figure S2.

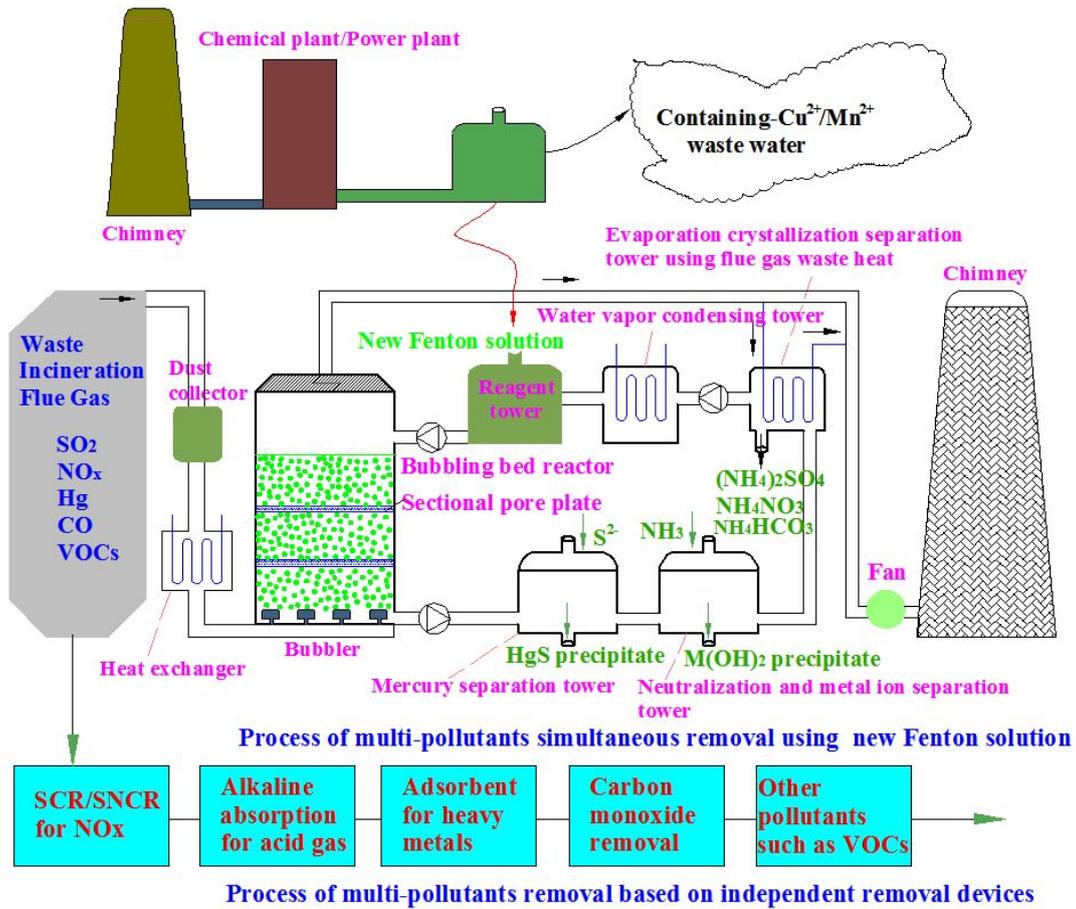


Figure S2. Simultaneous removal of multi-pollutants using new Fenton systems, and a contrast with independent systems.

3. Derivation/establishment of removal rate equation (mass transfer-reaction kinetics of CO removal)

As a heterogeneous reaction that involves gas-liquid two-phases, revealing the mass transfer-reaction kinetic law and obtaining the mass transfer and kinetic parameters (removal rate, rate constant and Hatta coefficient) are the key works for further strengthening CO removal, and optimum design and amplification of reactor. Based on the results of CO removal mechanism and products, the total reaction of CO removal can be described by the following equation (S1):¹⁻⁴



where a, b, c, d, e and f are the stoichiometric coefficients for CO, H_2O_2 , Fe^{2+} , M^{2+} (Cu^{2+} or Mn^{2+}), $\text{HCO}_3^- / \text{CO}_2$ and by-products, respectively.

The intrinsic rate equation of CO oxidation removal using two new Fenton systems can be expressed as the following equation (S2):¹⁻⁴

$$r_{CO,x} = k_{m_x, n_x, i_x, j_x} \cdot C_{CO,i,x}^{m_x} \cdot C_{H_2O_2,x}^{n_x} \cdot C_{Fe^{2+},x}^{h_x} \cdot C_{M^{2+},x}^{j_x} \quad (S2)$$

where $r_{CO,x}$ is the chemical reaction rate of CO, $mol/(L \cdot s)$; k_{m_x, n_x, h_x, j_x} is the pseudo- $(m_x+n_x+h_x+j_x)$ -order reaction rate constant for the total reaction (S2), $L^{(m_x+n_x+h_x+j_x-1)} \cdot mol^{(1-m_x-n_x-h_x-j_x)} \cdot s^{-1}$; $C_{CO,i,x}$ is CO interface concentration, mol/L ; $C_{H_2O_2,x}$ is H_2O_2 concentration, mol/L ; $C_{Fe^{2+},x}^{h_x}$ is Fe^{2+} concentration, mol/L ; $C_{M^{2+},x}^{j_x}$ is Cu^{2+} or Mn^{2+} concentration, mol/L ; m_x, n_x, h_x and j_x are the partial reaction order for CO, H_2O_2 , Fe^{2+} and M^{2+} , respectively; x is Cu^{2+} or Mn^{2+} (Cu^{2+} represents Cu^{2+} -based new Fenton system and Mn^{2+} represents Mn^{2+} -based new Fenton system).

The concentration of CO in liquid phase is the order of magnitude of 10^{-8} . The concentrations of H_2O_2 , Fe^{2+} and M^{2+} are the orders of magnitude of 10^{-1} , 10^{-2} , 10^{-3} , respectively, and thus all of them can be recognized as the constants in a short period of time.¹⁻⁴ Thus the above equation (S2) can be further reduced to the equation (S3):

$$r_{CO,x} = k_{m_x} \cdot C_{CO,i,x}^{m_x} \quad (S3)$$

where $k_{m_x} = k_{n_x, h_x, j_x} \cdot C_{H_2O_2,x}^{n_x} \cdot C_{Fe^{2+},x}^{h_x} \cdot C_{M^{2+},x}^{j_x}$ represents pseudo- m_x -order reaction rate constant for CO in two new Fenton systems, $L^{(m_x-1)} \cdot mol^{(1-m_x)} \cdot s^{-1}$.

Based on the intrinsic rate equation (S3), the double-film theory and the results of the other researchers,¹⁻⁴ for a fast reaction, the removal rate of CO in solution can be described by the following equation (S4):

$$N_{CO,x} = \left(\frac{2D_{CO,L,x} \cdot k_{m_x} \cdot C_{CO,i,x}^{m_x+1}}{m_x + 1} \right)^{1/2} \quad (S4)$$

where $N_{CO,x}$ is the CO removal rate, $mol/m^2 \cdot s$; $D_{CO,L,x}$ is the liquid phase diffusion coefficient of CO, respectively, m^2/s .

In the equation (S4), $N_{CO,x}$ can be calculated by the equation (2) in the manuscript (main document). CO interface concentration, $C_{CO,i,x}$, can be calculated by the following equation (S5):^{1,2}

$$C_{CO,i,x} = H_{CO,L,x}(p_{CO,G,x} - N_{CO,x}/k_{CO,G,x}) \quad (S5)$$

where $H_{CO,L,x}$ is the solubility coefficient of CO in solution, $mol/(L \cdot Pa)$; $p_{CO,G,x}$ is CO partial pressure in gas phase body, Pa ; $k_{CO,G,x}$ is CO gas phase mass transfer coefficient, $mol/s \cdot m^2 \cdot Pa$.

$H_{CO,L,x}$ were calculated by the methods in references;⁵⁻⁸ $D_{CO,L,x}$ were calculated using the Wilke-Chang empirical equation.¹⁻⁴ $k_{CO,L,x}$, $k_{CO,G,x}$ and $a_{CO,x}$ were determined using the classical chemical removal methods and Danckwerts plot theory.¹⁻⁴ The described calculation and measurement methods can be found in Section 3. These key parameters were summarized in Table S1.

In order to determine m_x value in the equation (S4), the following equation (S6) can be obtained by taking the logarithm on both sides of the equation (S4):

$$\log N_{CO,x} = \frac{m_x + 1}{2} \log C_{CO,i,x} + \frac{1}{2} \log \left(\frac{2D_{CO,L,x} \cdot k_{m_x}}{m_x + 1} \right) \quad (S6)$$

where $N_{CO,x}$ can be calculated by the equation (2) in the manuscript (main document), and $C_{CO,i,x}$ can be calculated by the equations (2) in the manuscript (main document) and (S5).

Based on the data of CO concentration vs CO removal efficiency in Figure 3(a), the plots of $\text{Log}(C_{CO,i,x})$ vs $\text{Log}(N_{CO,x})$ are conducted, and the results are shown in Figure S3 (a) and (b). As shown in Figure S3 (a) and (b), $\text{Log}(N_{CO,Cu})$ keeps a good linear relationship with $\text{Log}(C_{CO,i,Cu})$, and $\text{Log}(N_{CO,Mn})$ also keeps a good linear relationship with $\text{Log}(C_{NO,i,Mn})$. The slopes of the two fitted line $(m_{Cu}+1)/2= 0.97$ and $(m_{Mn}+1)/2= 0.98$. Thus $m_{Cu}= 0.94 \approx 1.0$, and also $m_{Mn}= 0.96 \approx 1.0$, suggesting that both of CO removal processes using Cu^{2+} -based new Fenton system and Mn^{2+} -based new Fenton system can be regarded as a pseudo-first-order reaction with respect to CO, respectively.

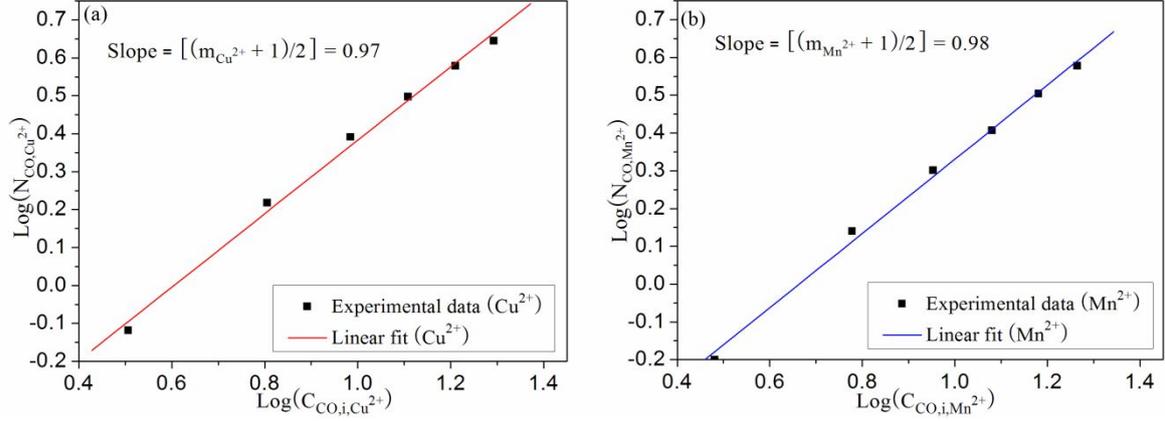


Figure S3. Log($N_{CO,Cu}$) vs Log($C_{CO,i,Cu}$) (a) and Log($N_{CO,Mn}$) vs Log($C_{CO,i,Mn}$) (b).

Thus, CO removal rate equation (S4) can be further represented as the following expressions (S7) and (S8):

$$N_{CO,Cu} = \sqrt{D_{CO,L,Cu} \cdot k_{m_{Cu}}} \cdot C_{CO,i,Cu} \quad (S7)$$

$$N_{CO,Mn} = \sqrt{D_{CO,L,Mn} \cdot k_{m_{Mn}}} \cdot C_{CO,i,Mn} \quad (S8)$$

According to the double-film theory,⁵⁻⁸ the Hatta coefficient Ha can be described by the equation (S9) as below.

$$Ha_x = \frac{\left\{ \frac{2}{m_x + 1} k_{m_x} \cdot D_{CO,L,x} \cdot C_{CO,i,x}^{m_x - 1} \right\}^{1/2}}{k_{CO,L,x}} \quad (S9)$$

where Ha is defined as the ratio of chemical reaction rate to physical removal rate. When $Ha < 0.03$, the removal process of CO in liquid phase belongs to a slow reaction; when $3.0 > Ha > 0.03$, the removal process of CO in liquid phase belongs to a moderate speed reaction; when $Ha > 3.0$, the removal process of CO in liquid phase belongs to a fast reaction, and the chemical reaction enhancement factor $E \approx Ha$.⁵⁻⁸

Ha_{Cu} and Ha_{Mn} can be obtained when m_{Cu} and m_{Mn} are brought back to the above equation (S9), and the equation (S9) is finally changed to the equations (S10) and (S11) as below:

$$Ha_{Cu} = \frac{\sqrt{k_{m_{Cu}} \cdot D_{CO,L,Cu}}}{k_{CO,L,Cu}} \quad (S10)$$

$$Ha_{Mn} = \frac{\sqrt{k_{m_{Mn}} \cdot D_{CO,L,Mn}}}{k_{CO,L,Mn}} \quad (S11)$$

Based on the above discussions, the key kinetic parameters such as k_{m_x} and Ha_x are calculated, and the

results are summarized Table 2 in the manuscript (main document). It can be seen that under all experimental conditions, $Ha_{Cu} > 3.0$ and also $Ha_{Mn} > 3.0$, indicating that both of CO removal processes using Cu^{2+} -based new Fenton system and Mn^{2+} -based new Fenton system belong to a fast reaction. It shows that the chemical reaction rate is far larger than mass transfer rate,⁵⁻⁸ and thus the mass transfer rate has been proved to be the rate control step of CO removal in two new Fenton systems. Thus, CO removal can be elevated via the rise of mass transfer. The mass transfer and kinetic data in Table 2 and Table S1 can provide an important support for amplification and design of reactor and numerical simulation of CO removal in two new Fenton systems.

4. Calculation and measurement methods of physical and mass transfer parameters

4.1. Solubility coefficients of gas

The solubility coefficients of gas in solution, $H_{gas,L}$, can be calculated using the solubility coefficients of gas in water, $H_{gas,w}$, and the following Van Krevelen and Hoftizer empirical equation (S12):⁵⁻⁸

$$\lg\left(\frac{H_{gas,w}}{H_{gas,L}}\right) = \sum hI \quad (S12)$$

where $H_{gas,w}$ and $H_{gas,L}$ are the solubility coefficients of gas in water and in salt solution, $mol/L \cdot Pa$, respectively; $H_{gas,w}$ can be obtained by consulting the References.⁵⁻⁸ h is a salting out parameter given by $h = h_+ + h_- + h_g$. h_+ and h_- are the contributions due to anions and cations of the electrolyte, respectively. h_g is the contribution of the solute gas. The values of the salting out parameters for various cations, anions, and gases can be obtained from the literatures;⁵⁻⁸ $I = \frac{1}{2} \sum_{i=1}^2 C_i \cdot z_i^2$ is the ionic strength of the solution, and where C_i and z_i are the concentrations and the valences of anions and cations in solutions, mol/L , respectively; More specific calculation methods and related parameters can be obtained by these literatures.⁵⁻⁸

4.2. Diffusion coefficients of gas in solutions

The diffusion coefficients of gas in water, $D_{gas,w}$, can be estimated by the following equation (S13):^{1,2}

$$D_{gas,w} = 7.4 \times 10^{-12} \frac{(\phi_w M_w)^{0.5} T}{V_{gas}^{0.6} u_w} \quad (S13)$$

where $D_{gas,w}$ is the diffusion coefficient of gas in water (m^2/s); ϕ_w is the association factor, which is 2.6 for H_2O ; M_w is the molecular weight of water, g/mol ; V_{gas} is the molar volume of gas, which is 23.6 and 34.0 for NO and CO_2 (cm^3/mol); T is the temperature in Kelvin (K).

The diffusion coefficient of gas in solution, $D_{gas,L}$, can be calculated by the following relationship (S14):⁵⁻⁸

$$(D_{gas,L} \cdot \mu_L)_T = (D_{gas,w} \cdot \mu_w)_T = const \quad (S14)$$

where μ_w and μ_L are the kinetic viscosities of water and solution, $Pa \cdot s$, respectively; The μ_w can be obtained by consulting the References [5-8]; μ_L can be measured by a viscometer.

4.3. Diffusion coefficients of gas in gas phase

The diffusion coefficients of gas in gas phase, $D_{A,B}$, are estimated by using the following Chapman-Enskog semi-empirical equations (S15)-(S19).¹⁻⁴

$$D_{A,B} = 0.00266 \frac{T^{1.5}}{p M_{AB}^{0.5} \sigma_{AB}^2 \Omega_D} \quad (S15)$$

$$M_{A,B} = \frac{2}{\frac{1}{M_A} + \frac{1}{M_B}} \quad (S16)$$

where M_A and M_B are the molecular weights of A, B (g/mol); p is the pressure (atm); T is the thermodynamic temperature (K); σ_{AB} is the characteristic length, which can be calculated by the following equation (S17); Ω_D is the collision integral, which can be calculated by the following equations (S18) and (S19).

$$\sigma_{A,B} = \frac{\sigma_A + \sigma_B}{2} \quad (S17)$$

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)} \quad (S18)$$

$$T^* = \frac{kT}{(\epsilon_A \epsilon_B)^{1/2}} \quad (\text{S19})$$

where the values of $\sigma_A, \sigma_B, \epsilon_A$ and ϵ_B for different gases can be obtained by consulting the References.¹⁻⁴

4.4. Mass transfer parameters

The gas-liquid mass transfer parameters of CO₂ in the reactor can be determined by using the classical chemical removal methods,¹⁻⁴ such as the removal of CO₂ in NaClO-Na₂CO₃/NaHCO₃ solution and the removal of CO₂ in NaOH solution, and the Danckwerts plot theory. The gas-liquid mass transfer parameters of CO in the same reactor can be obtained by the following relations (S20)-(S22):¹⁻⁴

$$k_{CO,L} = \left(\frac{D_{CO,L}}{D_{CO_2,L}} \right) \cdot k_{CO_2,L} \quad (\text{S20})$$

$$k_{CO,G} = \left(\frac{D_{CO,G}}{D_{CO_2,G}} \right) \cdot k_{CO_2,G} \quad (\text{S21})$$

$$a_{CO} = a_{CO_2} \quad (\text{S22})$$

where $k_{CO,L}$ and $k_{CO_2,L}$ are the liquid phase mass transfer coefficients of CO and CO₂, respectively, m/s ; $D_{CO,L}$ and $D_{CO_2,L}$ are the liquid phase diffusion coefficients of CO and CO₂, respectively, m^2/s ; $k_{CO,G}$ and $k_{CO_2,G}$ are the gas phase mass transfer coefficients of CO and CO₂, respectively, $mol/s \cdot m^2 \cdot Pa$; $D_{CO,G}$ and $D_{CO_2,G}$ are the gas phase diffusion coefficients of CO and CO₂, respectively, m^2/s ; a_{CO} and a_{CO_2} are the specific interfacial areas of CO and CO₂, respectively, m^{-1} .

Based on the above calculation and measurement methods, the related physical and mass transfer parameters for CO are summarized in Table S1.

Table S1. The diffusion coefficients, solubility coefficients and mass transfer parameters

Cu²⁺ system	$D_{CO,L,Cu} \times 10^9$	$H_{CO,L,Cu} \times 10^9$	$k_{CO,L,Cu} \times 10^4$	$k_{CO,G,Cu} \times 10^6$	$a_{CO,Cu}$
Solution temperature (K)	m^2/s	$mol/L \cdot Pa$	m/s	$mol/s \cdot m^2 \cdot Pa$	m^{-1}

298	1.58	8.60	0.49	0.81	15.8
308	2.03	7.56	0.58	0.89	13.1
318	2.53	6.84	0.66	0.95	12.3
328	3.08	6.30	0.71	1.05	11.5
338	3.69	5.98	0.77	1.16	10.3
348	4.35	5.90	0.82	1.21	9.8
Mn²⁺ system	$D_{CO,L,Mn} \times 10^9$	$H_{CO,L,Mn} \times 10^8$	$k_{CO,L,Mn} \times 10^4$	$k_{CO,G,Mn} \times 10^6$	$a_{CO,Mn}$
Solution temperature (K)	m^2 / s	$mol / L \cdot Pa$	m / s	$mol / s \cdot m^2 \cdot Pa$	m^{-1}
298	1.46	8.45	0.54	0.93	17.2
308	1.88	7.43	0.60	0.99	15.1
318	2.34	6.71	0.65	1.04	14.3
328	2.84	6.19	0.74	1.11	12.1
338	3.41	5.87	0.82	1.25	11.9
348	4.02	5.79	0.89	1.39	11.6

References

- [1] Liu, Y. X. Study on Integrated Desulfurization and Denitrification by UV/H₂O₂ Advanced Oxidation Process. *Nanjing: Southeast University*, **2010**.
- [2] Liu, Y.X.; Wang, Y. Simultaneous Removal of NO and SO₂ Using Aqueous Peroxymonosulfate with Coactivation of Cu²⁺/Fe³⁺ and High Temperature. *AIChE Journal*, **2017**, *63*, 1287–1302.
- [3] Liu Y.X.; Wang Q. Removal of Elemental Mercury from Flue Gas by Thermally Activated Ammonium Persulfate in A Bubble Column Reactor. *Environ. Sci. Technol.* **2014**, *20*, 12181–12189.
- [4] Liu Y.X.; Wang Y.; Liu Z.Y.; Wang Q. Oxidation Removal of Nitric Oxide from Flue Gas Using UV Photolysis of Aqueous Hypochlorite. *Environ. Sci. Technol.* **2017**, *51*, 11950–11959.
- [5] Feng BH. Chemical Engineering Handbook: Gas removal (Chapter 12). *Beijing: Chemical Industry Press* 1982.
- [6] Zhang, C. F. Gas-Liquid Reaction and Reactor. *Beijing: Chemical Industry Press*, **1985**.
- [7] Danckwerts, P. V. Gas-Liquid Reactions. *New York: McGraw-Hill*, **1970**.
- [8] Ye, Q. F. Gaseous Mercury Removal from Simulated Flue gas. *Hangzhou: Zhejiang university*, **2006**.