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Chemical kinetics simulation of semi-dry dechlorination in coal-fired flue gas*

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Abstract: HCl in coal-fired flue gas has adverse impact on the environment, equipment, and the flue gas desulfurization (FGD) system. The existence of HCl also increases the difficulty of the treatment of desulfurization waste water. Semi-dry dechlorination technology is put forward to attach chlorine to fly ash by spraying in alkaline solution. Simultaneously, desulphurization waste water is used as the solvent of alkali, and this could help realize the target of near-zero emission of desulfurization waste water. CHEMKIN is used to build a chemical kinetics model, which is based on the measured components of flue gas in a coal-fired power plant. NaOH is set as the alkali absorbent in the model. Both the competitive relationship of SO_2 and HCl and the effects of different factors on HCl reaction efficiency are analyzed. SO_2 with high concentration would compete for more NaOH, but when Na/Cl (ratio in mole) is 1, the reaction efficiency of HCl achieves 22.28%, and it is positively correlated with Na/Cl. When Na/Cl surpasses 5, the reaction efficiency of HCl increases to beyond 70%. As Na/Cl continues to increase, there is a slower growth of HCl reaction efficiency and it finally achieves 100% when Na/Cl reaches 12. With a fixed value of Na/Cl, a change of 1000 mg/m^3 in SO_2 concentration would change the reaction efficiency of HCl about 13%. The effect of flue temperature on HCl reaction efficiency is not significant. Acid gases in flue gas react with NaOH completely in 0.1 s and come to equilibrium after about 1 s.

Key words: Coal-fired flue gas; Semi-dry dechlorination; Chemical kinetics; Competition relationship; Na/Cl; CHEMKIN
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1 Introduction

In the process of electricity generation in coal-fired power plants, not only SO_2 and NO_x are produced as gaseous pollutants, but also others such as HCl, HF, and SO_3. Although at a low level, HCl in the flue gas still has huge harmful effects on the environment, plants, and animals. Beyond that, the boiler, gas flue, and flue gas desulfurization (FGD) system will also suffer from corrosion (Takeda et al., 2006).

China is the largest producer and consumer of coal in the world. Although the content of chlorine in Chinese coal is low—averagely at 197 mg/kg (Xu et al., 2002), research showed that the impact of an element occurrence state sometimes is much more important than concentration as the former plays a role in deciding toxicity and the difficulty of releasing (Finkelman et al., 1999). Because of the structural complexity of coal, there is still no unified conclusion of the occurrence state of chlorine. Poskrobko et al. (2012) thought that chlorine in coal mainly exists in

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ORCID: Chang LIU, https://orcid.org/0000-0001-5906-6037; Jian-guo YANG, https://orcid.org/0000-0002-3070-5111 the forms of sodium chloride, potassium chloride, and other inorganic chlorides in pore water and maceral adsorption of chloride. Shao et al. (1994) found that chlorine is combined with nitrogen functional groups in the form of a covalent bond. Through analyzing Spanish coal, Jimenez et al. (2000) concluded that the content of chlorine in coal is related to organic matter and mostly exists in the lattice of coal.

Takeda et al. (2006) showed that in the process of coal pyrolysis, combustion, and gasification, chlorine is released mainly in the form of HCl. Further research from Poskrobko et al. (2010) showed that Cl_2 generated by oxidation of HCl is the main cause of corrosion. Deng et al. (2014) indicated that the FGD system could absorb 93% to 98% of HCl. After HCl is absorbed into FGD slurry, corrosion of equipment and pipelines would occur (Hu et al. 2015). In addition, HCl would not only produce adverse effects on the FGD system, but also be discharged with FGD waste water in the form of Cl^-. In recent years, with the government strengthening its supervision of pollutant emission continuously, the project of near-zero emission of FGD waste water in coal-fired power plants is on the agenda. However, Cl^- is removed usually by an evaporation crystallization process, which is difficult to implement and entails huge operational cost (Hu et al., 2015).

At present, HCl is always removed in FGD together with SO_2. A method for HCl removal in coal-fired power plant flue gas is still unimplemented. On the other hand, the existence of Cl^- would cause an increase of the quantity of waste water in a desulphurization system. Therefore, semi-dry dechlorination is put forward in this study as a technology to remove HCl in coal-fired power plants. CHEMKIN is used to analyze the chemical kinetics mechanism of the reaction process. Both the competitive relationship between SO_2 and HCl and effects of different factors such as Na/Cl ratio, SO_2 concentration, temperature, and reaction time on HCl reaction efficiency are analyzed by simulation.

2 Methods

2.1 Idea of the dechlorination system

As shown in Fig. 1, through spraying alkaline solution into flue gas after the air preheater (APH), HCl can be removed by neutralization reactions, and the final products would be attached to fly ash and finally be discharged in the electrostatic precipitator (ESP). Compared to gas and liquid pollutants, solid pollutants are generally easier to handle. At the same time, in the removal process of HCl, other acid gases such as SO_3 and HF could also be removed synchronously. Since SO_3 and HF have been removed from flue gas, corrosion (Zhang et al., 2011) and poisoning of desulfurization slurry (Mori et al., 1981; Farmer et al., 1989) would be alleviated. As waste water of FGD is generally discharged according to the concentration of Cl^- in the desulfurization slurry (Hu et al., 2015), when HCl is largely removed, the quantity of waste water would be greatly reduced per unit time. At the same time, the significantly reduced waste water would be used as solvent of alkali circularly sprayed in the flue to achieve near-zero emission of FGD waste water, and water consumption in the process of desulphurization would be reduced. Both environmental and economic interests would profit from this simple process.

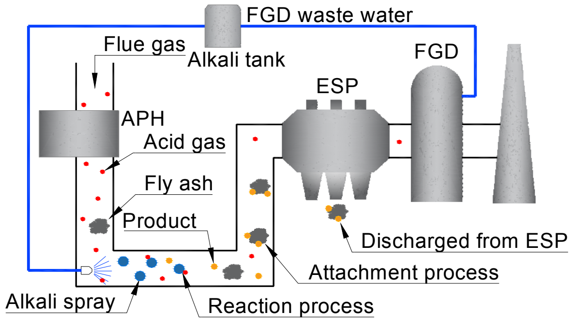

Fig. 1 Schematic of semi-dry dechlorination system

2.2 Reaction process of the dechlorination

Semi-dry dechlorination has similarities with semi-dry desulphurization. Both are gas-liquid-solid reactions among three phases which include heat and mass transfer and chemical reactions. As shown in Fig. 2, first, acid gas molecules dissolve into the liquid membrane of an alkaline solution droplet; next, ionization would occur and the dissociated ion transfers to the reaction interface; then, a neutralization reaction occurs between the dissociated acid ion and alkali ion (Gao et al., 2008).

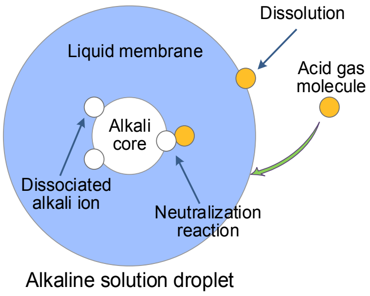

Fig. 2 Reaction process of gas-liquid-solid three phases

2.3 Mechanism model

The flue gas contains many kinds of acid gases, mainly including CO_2, SO_2, HCl, HF, and SO_3. Semi-dry dechlorination technology could theoretically remove all the acid gases from the flue gas, but taking cost into consideration, in the case of alkali matter, limited and complex competitive relationships which exist among acid gases should be considered (Liu et al., 2002; Stein et al., 2002).

Relative to HCl and SO_3, although the solubility of SO_2 is small, but with a much higher concentration, SO_2 probably interferes with semi-dry dechlorination. At present, there is still a lack of detailed chemical kinetics mechanisms for reactions between acid gases and alkali. And there is even less research of reactions between NaOH and acid gases in coal-fired boiler flue gas. Glarborg and Marshall (2005) built a formation model of gaseous alkali sulfates. Xie et al. (2008) studied the removal process of HCl and SO_2 in waste incineration power plants by building a computational fluid dynamics model.

As shown in Table 1, HCl and SO_3 are both strong acid. In addition, the medium acid gas SO_2 would also have certain interference effects on the target reaction due to its high concentration. The concentration of CO_2 is much higher, but as the products of its reactions with NaOH, $NaHCO_3$ and Na_2CO_3 can still be used as alkali matter to react with HCl further (Hartman et al., 2014). Thus, we speculate that CO_2 does not have much influence on the removal process of HCl.

The concentration of HF in flue gas is close to that of HCl. However, there is a big difference in their chemical properties. Reaction mechanisms between HF and alkali are still unavailable. In the process of semi-dry dechlorination, HF would dissolve into the sprayed liquid which would produce a low concentration of acid. Due to hydrogen bondings between HF molecules and H-F key bond which is difficult to disintegrate, the low concentration of HF solution is a very weak acid (Ayotte et al., 2005). Thus, we put forward a reasonable assumption that the existence of HF would not significantly affect the removal process of HCl, and HF is not considered in the model.

Table 1 Properties of acid gases in flue gas

Gas	Acidity	Concentration	Water solubility
SO_2	Medium	High	Low
SO_3	Strong	Low	High
HCl	Strong	Low	High
HF	Week	Low	High
CO_2	Week	High	Low

It is assumed that all reactions are in gas phase. Based on the composition in coal-fired power plant flue gas, with NaOH as alkali, the reaction processes and degree among NaOH and HCl, SO_2, SO_3 were simulated by building a perfectly stirred reactor (PSR) model. The model contains 24 elementary reactions (Appendix A). The 4th and 5th elementary reactions were chosen from Glarborg and Marshall (2005)'s model, and the remaining kinetics data were all taken from the National Institute of Standards and Technology (NIST, USA) database. The elementary reaction coefficients follow the Arrhenius formula.

2.4 Parameter setting

The flue gas composition of a 660 MW coal-fired unit at rated load after the air preheater was measured. Coal quality is shown in Table 2, and the composition of flue gas used in the model is shown in Table 3. The reactor in the model is at a state of micro negative pressure which is set at 9.93×10^4 Pa.

3 Analysis of sensitivity and competition relationship

The sprayed amount of NaOH is controlled insufficiently to study the competitive relationships among HCl, SO_2, and SO_3. Ratio of moles of NaOH

Table 2 Proximate analysis and ultimate analysis of coal

Content (%)										Caloric value, $Q_{\mathrm{net,ar}}$ (MJ/kg)
Proximate analysis				Ultimate analysis					Cl_{ar}	
M_t	V_{ar}	A_{ar}	FC_{ar}	C_{ar}	H_{ar}	N_{ar}	O_{ar}	S_t		
10.80	25.96	18.37	44.87	57.56	3.55	1.01	7.97	0.74	0.038	21.84

M: moisture; V: volatile; A: ash; FC: fixed carbon; Q_{net}: net calorific value; t: total; ar: as received basis

Table 3 Composition in flue gas

Component	Concentration
CO_2	14.00% (in volume)
H_2O	7.50% (in volume)
O_2	3.00% (in volume)
SO_2	2285.71 mg/m^3
SO_3	32.14 mg/m^3
HCl	54.59 mg/m^3
HF	25.36 mg/m^3
N_2	75.46% (in volume)

and HCl is 1, namely Na/Cl=1. Temperature of flue gas is set at 393.15 K, and the reaction time is 1 s. Gas components are shown in Table 3.

3.1 Reaction path and rate analysis

Figs. 3 and 4 are reaction paths of HCl, SO_2, and NaOH after the calculating of the PSR model, in which the thickness of the arrows qualitatively describes the absolute rates of chain branches. Figs. 5–7 represent the absolute rates of particular production at 1 s. Figs. 3 and 5 show that most HCl that participates in reacting is transformed into NaCl and H_2O by NaOH. In the reaction system of HCl, NaOH, Na_2SO_4, and H can all promote the consumption of HCl. On the other hand, Cl and OH can produce HCl continually. However, the reaction described in Eq. (1) plays an absolutely dominant role. It is shown in Fig. 3 that SO_2 reacts with NaOH in two ways: (i) SO_2 directly reacts with NaOH and produces $NaSO_2$ and (ii) SO_2 is oxidized by O to SO_3 first and then reacts with NaOH which produces $NaHSO_4$. As shown in Fig. 6, the vast majority of SO_2 reacts directly with NaOH.

$$NaOH+HCl=NaCl+H_2O. \tag{1}$$

Fig. 7 shows that there are many components reacting with NaOH, such as SO_2, HCl, SO_3, and H which eventually transform NaOH into $NaSO_2$,

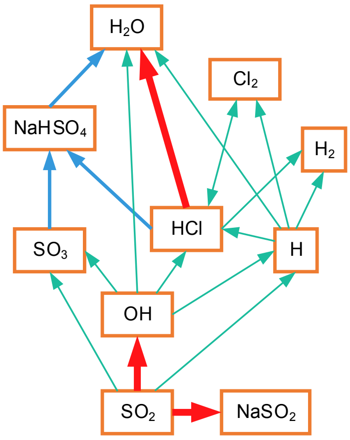

Fig. 3 Reaction paths of HCl and SO_2

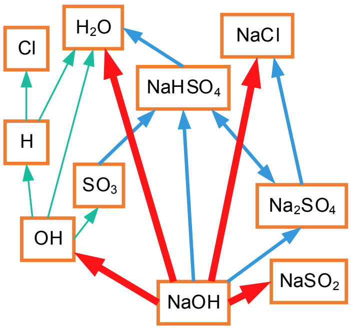

Fig. 4 Reaction paths of NaOH

NaCl, $NaHSO_4$, and Na_2SO_4. However, as shown in Fig. 7, the main three components are listed as SO_2, HCl, and SO_3 with reaction rate decreasing.

3.2 Sensitivity analysis

Sensitivity analysis was used to study the sensitivity of parameters' changes in particular reactions. When the sensitivity coefficient is positive, this means that the reaction would result in a rise of concentration of the relevant substance. On the other hand, a negative sensitivity coefficient means the reaction would reduce the concentration. Sensitivity analysis can examine different roles of different elementary reactions played in the process of generation or consumption of a certain substance (Hall et al., 1991). The stronger the absolute value of the sensitivity coefficient is, the greater the influence of the reaction is.

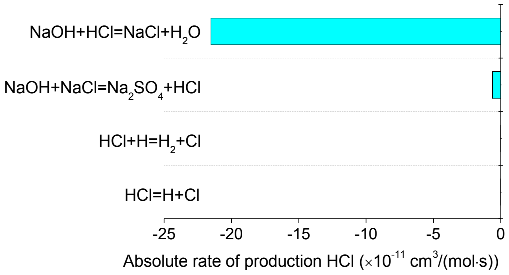

Fig. 5 Absolute rate of production HCl

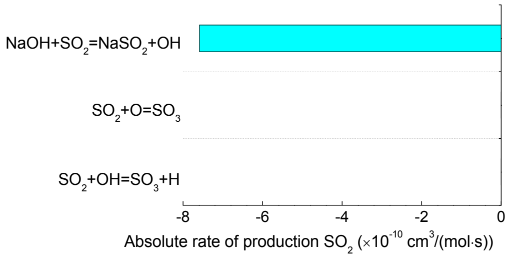

Fig. 6 Absolute rate of production SO_2

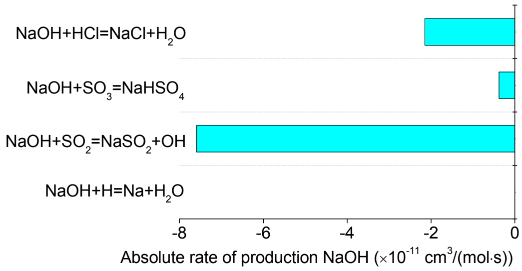

Fig. 7 Absolute rate of production NaOH

Sensitivity coefficients of NaOH, HCl, and SO_2 in 1 s are shown in Figs. 8–10. Reactions with sensitivity coefficients above 0.0001 are listed. Fig. 8 shows that NaOH is consumed mostly by SO_2. Fig. 9 shows that SO_2 plays a main role in competing with HCl. However, as shown in Fig. 10, HCl still has large effect on reactions between SO_2 and NaOH even though it is at a low concentration. At the same time, when considering engineering practice, reactions happen among the gas-liquid-solid three phases. The process of gas dissolving into liquid droplets of the sprayed alkaline solution is an extremely important step. The solubility would greatly influence the amount of gas involved in the reactions in such a limited period before evaporation. As HCl has much stronger solubility than SO_2, it is assumed that the competition of SO_2 is smaller than the simulation result when it comes to practical engineering of the semi-dry dechlorination process.

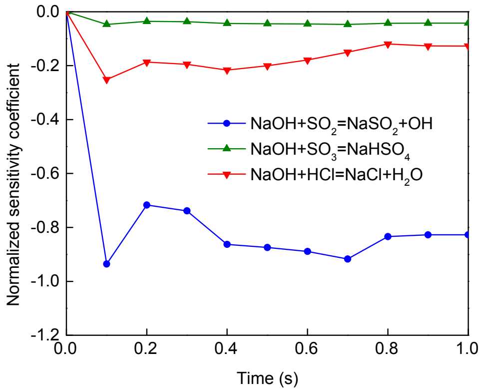

Fig. 8 Sensitivity analysis of NaOH

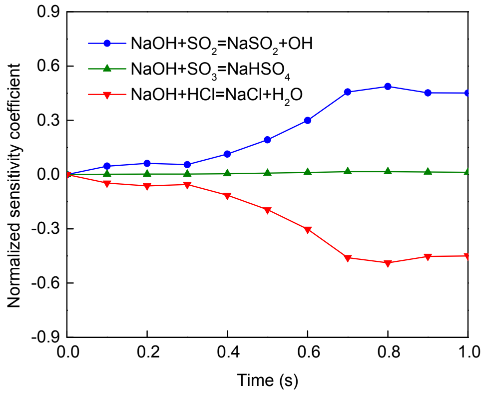

Fig. 9 Sensitivity analysis of HCl

3.3 Reaction efficiency analysis

When experimental conditions remain unchanged, Fig. 11 shows the reaction efficiencies of HCl, SO_2, and SO_3 in 1 s. It is revealed that the three reactions have basically finished within 0.1 s and then remain stable. The reaction efficiencies of HCl, SO_2, and SO_3 at 1 s are respectively 22.28%, 3.10%, and 14.03%. NaOH is nearly fully reacted. It is expressed intuitively in Fig. 12 that NaOH's consumption ratios by HCl, SO_2, and SO_3 are respectively 22.3%, 73.9%, and 3.8%.

A high concentration of SO_2 in flue gas would compete for NaOH and has a certain negative influence on the removal of HCl. However, reactions between HCl and NaOH still occurred. Even in the case when only a small amount of NaOH has been sprayed in, the reaction efficiency of HCl is still considerable. Therefore, the conclusion might be safely drawn that semi-dry dechlorination technology is feasible in theory.

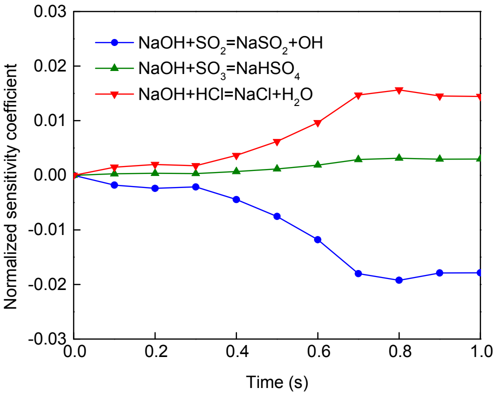

Fig. 10 Sensitivity analysis of SO_2

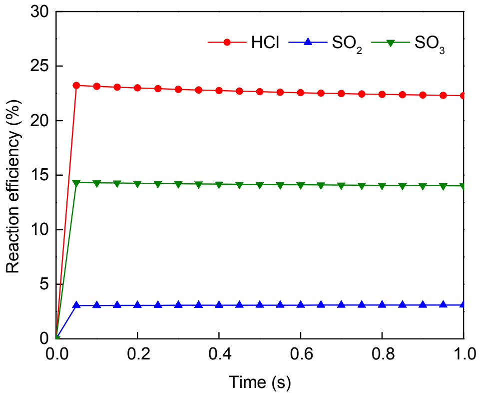

Fig. 11 Changes of reaction efficiencies over time

4 Influence factors analysis

4.1 Influence of Na/Cl on reaction efficiency of HCl

When the concentration of HCl in flue gas is relatively stable, Na/Cl virtually reflects the actual sprayed quantity of NaOH, which directly determines the reacted quantity of acid gases. If Na/Cl is too small, reactions would not happen completely, so that the reaction efficiencies could not be high. On the contrary, if the sprayed quantity is too high, although high reaction efficiencies can be guaranteed, the cost is enormous. Thus, the choice of an appropriate Na/Cl is of great significance in practice. Reaction efficiencies of HCl, SO_2, and SO_3 corresponding to different Na/Cl are calculated and the result is shown in Fig. 13.

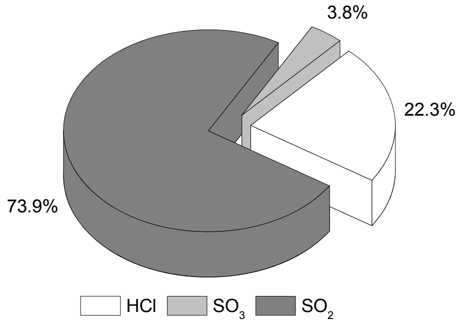

Fig. 12 Consumption distribution of NaOH

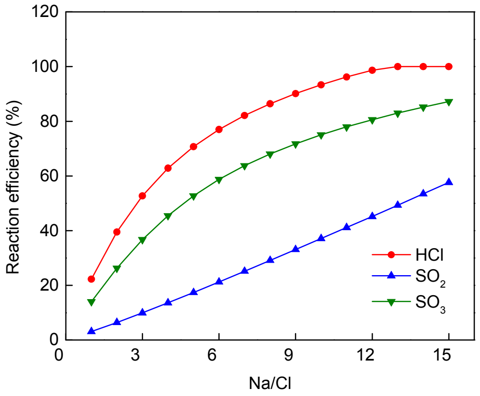

Fig. 13 Effects of Na/Cl on reaction efficiencies

Experimental conditions: temperature is 393.15 K; reaction time is 1 s; gas components are shown in Table 3

Reaction efficiencies of HCl, SO_2, and SO_3 are positively correlated with Na/Cl. As Na/Cl increases from 1 to 15, the reaction efficiency of SO_2 increases nearly linearly from 3.10% to 57.64%. The reaction efficiencies of HCl and SO_3 have similar trends. With the increase of Na/Cl, the ascensional range of reaction efficiencies is gradually decreased. Reaction efficiency of HCl increases from 22.28% to 100% as Na/Cl increases from 1 to 12. Combined with the analysis of Fig. 10, initial concentrations of HCl and SO_3 are far below SO_2 at the beginning, and with the reacting ongoing, their concentration ratio with SO_2 continues to decrease. As a result, the competitiveness of HCl and SO_3 declines and thus causes the gradual decrease of the rising range of reaction efficiencies of HCl and SO_3.

Based on the condition of gas composition in Table 3, when Na/Cl is 5, the HCl reaction efficiency has reached 70.71%. Considering both of the cost of NaOH and the reaction efficiency of HCl, it is appropriate to set Na/Cl as 5 in this situation.

4.2 Influence of SO_2 concentration on reaction efficiency of HCl

The concentration of SO_2 in Chinese coal-fired power plants flue gas is usually dozens of times that of HCl. SO_2 concentration is commonly between 400–3500 mg/m^3 (Xu et al., 2012), and the concentration of HCl is usually a few dozen μL/L. As SO_2 has a great negative influence on the removal process of HCl, as summarized in the above calculations, the effect of different concentrations of SO_2 is further analyzed. The result is shown in Fig. 14.

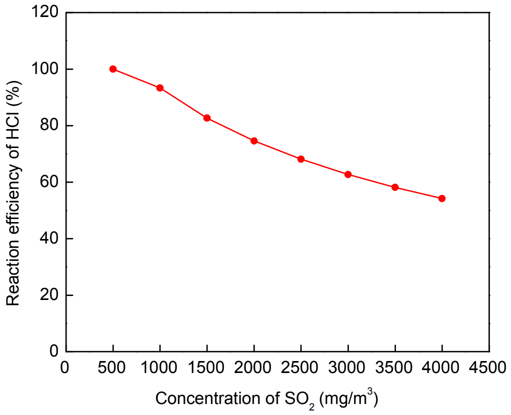

Fig. 14 Effects of concentration of SO_2 on reaction efficiency

Experimental conditions: Na/Cl=5; temperature is 393.15 K; reaction time is 1 s; gas components are shown in Table 3

As the SO_2 concentration increases from 500 mg/m^3 to 4000 mg/m^3, the reaction efficiency of HCl falls from 100% to 54.2%. When SO_2 concentration changes 1000 mg/m^3, the reaction efficiency of HCl changes about 13%. It is visible that when the concentration of SO_2 changes in large measure, the reaction efficiency of HCl is greatly affected. However, for a specific boiler, the burning coal is usually relatively stable so that the concentration of SO_2 in flue gas only fluctuates to a small amount with load changes, and this means that the reaction efficiency of HCl would not be greatly affected.

4.3 Influence of flue temperature on the reaction efficiency of HCl

Temperature is one of the important factors influencing the degree of reaction. After air preheater, the flue temperature commonly fluctuates between 100 °C and 140 °C with the change of load and environmental temperature. To study the effect of different temperatures on HCl reaction efficiency, a calculation is carried out with temperature as the single variable.

It is shown in Fig. 15 that as the flue temperature rises from 373.15 K to 413.15 K, the efficiency of HCl basically remains unchanged. It means that the reaction efficiency of HCl is not sensitive to the flue temperature. However, in practice, the flue temperature may significantly affect the persistence of liquid drops, and this would affect the process of semi-dry dechlorination. Thus, the effect of flue temperature on HCl reaction efficiency still needs further study.

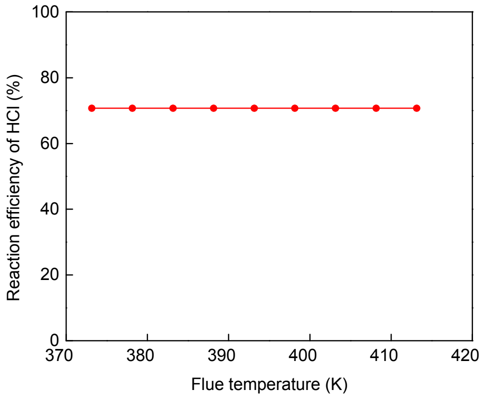

Fig. 15 Effects of flue temperature on reaction efficiency

Experimental conditions: Na/Cl=5; reaction time is 1 s; gas components are shown in Table 3

4.4 Influence of reaction time on the reaction efficiency of HCl

After air preheater, the velocity of flue gas is about 7–10 m/s, and the contact time of reactants is usually 1–3 s (Pang, 1998) of semi-dry dechlorination. Time is one of the important influencing factors on reaction. Fig. 16 shows the change of reaction efficiency of HCl with time.

As shown in Fig. 16, the reactions among acid gases in flue gas with NaOH mainly finish within 0.1 s and reach equilibrium after 1 s. The reaction efficiency of SO_2 has a very slight rise at the early stage, while the reaction efficiencies of HCl and SO_3 appear to show slight downward trends which reduce by 11.28% and 6.98%, respectively. Thus, it is not the longer the time, the higher the reaction efficiency, especially for gases in low concentration. When it comes to the later period, it is more difficult for gases of low concentrations to compete with gases of high concentrations. Therefore, it is important in practice to select an appropriate position to spray alkali solution after air preheater to control reaction time.

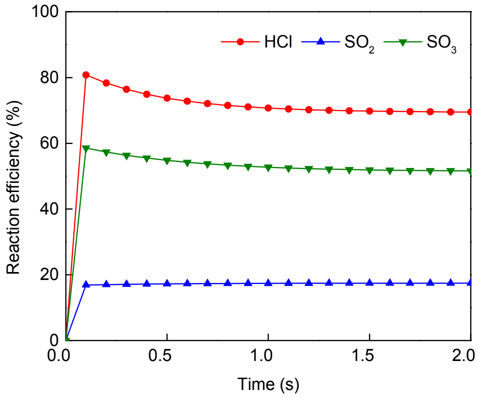

Fig. 16 Effects of reacting time on reaction efficiency
Experimental conditions: Na/Cl=5; temperature is 393.15 K; gas components are shown in Table 3

5 Conclusions

The existence of HCl increases the difficulty of the treatment of desulfurization waste water. Semi-dry dechlorination technology is put forward to attach chlorine to fly ash by alkaline matter. The significantly reduced desulfurization waste water would be used as a solvent of alkali to realize the near-zero emission of desulfurization waste water. A chemical kinetics model was built to study the reaction mechanism of semi-dry dechlorination based on the measured components of flue gas in a coal-fired power plant, and the following conclusions can be drawn:

1. The high concentration of SO_2 in flue gas has great influence on the semi-dry dechlorination process. NaOH would be partly robbed by SO_2. However, even if Na/Cl is only 1, the reaction efficiency of HCl could still reach 22.28%.

2. The reaction efficiency of HCl is positively correlated with Na/Cl. It increases from 22.28% to 100% as Na/Cl increases from 1 to 12. However, the ascensional range decreases gradually. When Na/Cl surpasses 5, the reaction efficiency of HCl reaches 70.71%. Considering the cost of NaOH and the reaction efficiency of HCl, it is appropriate to set Na/Cl at 5.

3. With a fixed value of Na/Cl, a change of 1000 mg/m^3 in SO_2 concentration would change the reaction efficiency of HCl by about 13%. For a particular boiler, a slight variation of SO_2 concentration would not affect the reaction efficiency of HCl significantly.

4. Flue gas temperature hardly affects the reaction efficiency of HCl in simulation. However, if in practice, the effect of temperature on the evaporation process of alkali solution droplets probably could not be ignored.

5. The reactions among acid gases in flue gas with NaOH can mainly finish within 0.1 s and reach equilibrium after 1 s.

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中文概要

题　目：燃煤烟气半干法脱氯的化学动力学模拟

目　的： 燃煤锅炉烟气中的 HCl 对环境、设备及脱硫系统有不利的影响，也是脱硫废水处理的难点。本文提出半干法脱氯技术，探讨其技术合理性，并研究不同因素对反应效率的影响，为进一步工程应用提供理论依据，实现燃煤烟气中 HCl 的脱除及脱硫废水零排放。

创新点： 1. 提出半干法脱氯技术，将氯离子固化到飞灰中；2. 脱氯后脱硫废水大幅减少，将脱硫废水作为碱基溶剂回喷到烟道中，实现脱硫废水零排放；3. 建立良搅拌反应器（PSR）模型，探讨半干法脱氯过程的化学动力学反应机理与关键参数。

方　法： 1. 通过 CHEMKIN 构建 PSR 模型，模拟实际燃煤烟气组分下的半干法脱氯过程；2. 通过敏感性分析，探讨 SO_2 与 HCl 之间的竞争关系（图 8~10）；3. 通过单变量模拟，研究不同因素对反应效率的影响（图 13~16）。

结　论： 1. 烟气中的 SO_2 对 HCl 的脱除存在较大竞争关系，但即使 Na/Cl（摩尔比）为 1 时，HCl 的反应效率依然可观。2. HCl 的反应效率与 Na/Cl 呈正相关；综合考虑反应效率和运行成本，设置 Na/Cl 为 5 较为合理。3. SO_2 浓度的小范围变化不会对 HCl 的反应效率造成显著影响。4. 仅通过化学动力学模拟，烟气温度对 HCl 的反应效率影响不明显。5. 烟气中酸性气体与 NaOH 在 0.1 s 内即可完成反应，在 1 s 左右达到平衡。

关键词： 燃煤烟气；半干法脱氯；化学动力学；竞争机理；钠氯比；CHEMKIN

Appendix A Elementary reactions of perfectly stirred reactor model

Table A1 Elementary reactions of PSR model

No.	Reaction	*A*	*n*	*E*
1	O_2+H=OH+O	1.20×10^{15}	0	1.78×10^{4}
2	O_2=O+O	6.08×10^{15}	−1	1.18×10^{5}
3	OH+O_2=HO_2+O	2.23×10^{13}	0	5.27×10^{4}
4	NaOH+SO_2=$NaSO_2$+OH	2×10^{13}	0	0
5	NaOH+SO_3=$NaHSO_4$	1×10^{14}	0	0
6	$NaHSO_4$+NaOH=Na_2SO_4+H_2O	1×10^{14}	0	0
7	$NaHSO_4$+NaCl=Na_2SO_4+HCl	1×10^{14}	0	0
8	SO_2+OH=SO_3+H	4.90×10^{2}	2.69	2.38×10^{4}
9	SO_2+O=SO_3	3.67×10^{11}	0	1.69×10^{3}
10	SO_3+O=SO_2+O_2	1.40×10^{8}	0	9.68×10^{2}
11	HCl=H+Cl	6.61×10^{12}	0	6.99×10^{4}
12	HCl+O=OH+Cl	1.51×10^{12}	0	5.90×10^{3}
13	HCl+Cl=Cl_2+H	7.08×10^{13}	0	4.81×10^{4}
14	HCl+H=H_2+Cl	1.21×10^{13}	0	3.56×10^{3}
15	Cl+ClO=Cl_2+O	1.05×10^{12}	0	9.12×10^{3}
16	Cl+HO_2=OH+ClO	2.47×10^{13}	0	8.94×10^{2}
17	Cl+HO_2=HCl+O_2	1.08×10^{13}	0	-3.38×10^{2}
18	Cl+O_2=ClO+O	8.77×10^{14}	0	5.50×10^{4}
19	H+OH=H_2O	4.46×10^{20}	−1.18	6.16×10^{2}
20	Cl+Cl=Cl_2	5.79×10^{14}	0	-1.60×10^{3}
21	HCl+Cl=HCl+Cl	1.72×10^{12}	0	4.81×10^{3}
22	NaOH+HCl=NaCl+H_2O	1.69×10^{14}	0	0
23	NaOH+H=Na+H_2O	2.41×10^{12}	0	0
24	NaOH=Na+OH	1.51×10^{12}	−1	7.83×10^{4}

A is pre-exponential factor; *n* is temperature correction index; *E* is apparent activation energy (units are based on cal, mol, and K)