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Interactions of CO, HCl, and SO_x in pulverised coal flames

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Abstract

The effect of HCl and SO_2 on CO oxidation in pulverised coal flames was investigated experimentally and kinetically in an entrained flow combustion reactor. Two bituminous coals (German 'Goettelborn' and a Polish coal) were used as fuels with a feeding rate of 1 or 1.5 kg/h. HCl or SO_2 is introduced into the reactor premixed with the primary air. Experimental results indicate that HCl addition may inhibit CO oxidation in coal flames and increases CO emission. Reducing temperature in the reactor will enhance the inhibitory effect of HCl on CO oxidation. The measured CO profiles along the reactor height clearly show that the addition of HCl may inhibit CO oxidation. In the experimental range of SO_2 addition, the inhibiting effect of SO_2 on CO oxidation is less significant than HCl. A detailed kinetic mechanism is used to model the reactions, and the controlling reactions are analysed.
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Keywords: Pulverised coal flame; CO oxidation; Interactions of CO, HCl and SO_x

1. Introduction

Chlorine and sulfur are commonly present as impurities in several fuels used in industrial furnaces, such as coals, wastes, biomass, and even some natural gases and petroleum fuels. During combustion HCl and SO_x are released into the flue gas as pollutants. It is known that HCl and SO_x may affect the ratio and compositions of the radicals O, H, OH, and HO_2 in the flame [1,2]. Therefore, complex interactions of HCl, SO_x, CO, NO_x, and H_2O, etc. may occur at higher temperature combustion, which will influence the flame characteristics and pollutant chemistry.

The interactions of CO, NO_x, and H_2O have been previously investigated [3–6]. Results showed that the concentration of H_2O has a strong effect on the postcombustion CO oxidation. Depending on the concentration, an increase of H_2O may act to enhance or inhibit the CO oxidation rate through affecting the OH concentration.

The effect of NO on CO oxidation is complex, as it depends on both, the NO concentration and the amount of water present [5]. Under coal combustion conditions with high H_2O and NO concentrations, NO may promote the CO oxidation via $NO + HO_2 = NO_2 + OH$ in the postcombustion gases [5].

At excess air combustion the sulfur is oxidized almost completely to sulfur dioxide (SO_2), with minor amounts of sulfur trioxide (SO_3) also formed. SO_2 is known to catalyze the recombination of radicals in the flame and thus to inhibit CO oxidation [7–11]. SO_x may also affect the formation of NO_x from fuel-bound nitrogen. The interactions via the radical pool as well as direct interactions between sulfur and nitrogen species appear to explain the effects of SO_x on NO_x [12,13]. The combustion kinetics of sulfur compounds and potential interactions with fuel oxidation processes have been established based on previous studies and QRRK calculations [2,14]. Results showed that the inhibition of SO_2 is most pronounced at high O atom levels and addition of NO significantly reduces the effect of SO_2 [2]. Under the conditions of CFBC or pulverised coal combustion, adding SO_2 with combustion air leads to a decrease in NO emissions and an increase in CO and N_2O emissions [15,16].

During combustion or gasification, chlorine is released as HCl. The kinetic interactions that occur between CO, NO_x, and HCl in the postflame have been previously studied

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[1,17–19]. HCl is known to act as inhibitors by catalyzing the recombination of radicals and thus decreasing the radical pool [20,21]. This effect is sensitive to the concentration of H_2O and NO_x [17]. Under FBC or CFBC conditions, adding HCl or other halides leads to an increase in CO emissions [22,23].

Although some studies have been carried out about the influence of SO_x or HCl on CO emissions during combustion, the interactions involving all these pollutants in pulverised coal combustion are still not well understood because the reaction mechanisms are found very sensitive to the air/fuel ratio, temperature, and concentrations of H_2O, NO_x, HCl, and SO_x. The objective of this work was to perform an experimental and theoretical study of the interactions of CO, SO_x, and HCl under pulverised coal combustion conditions. The influence of HCl and SO_2 on NO formation in coal flames can be found in a recent paper [24]. Experiments were performed in a flow reactor in the wall temperature range from 1223 to 1523 K. The added SO_2 or HCl concentrations were varied between 0 and 600 ppmv. A detailed kinetic mechanism was used to model the reactor under various operating conditions. The controlling reactions for homogeneous reactions during combustion were analysed.

2. Experimental facility

The trials were conducted in an entrained flow combustion reactor (EFCR) and the detailed description of this reactor may be found in the other paper [24]. The electrically heated reactor has five regulated heating zones with a maximum temperature of 1673 K. The combustion air can be preheated up to approximately

Table 1
The properties of coals

Chemical analysis	Bituminous Polish coal	Bituminous Goettelborn coal
Moisture (raw)[a]	1.57	1.69
Proximate analysis (wt%, dry basis)		
Volatile	30.46	31.94
Fixed carbon	62.87	57.32
Ash	6.67	10.74
Ultimate analysis (wt%, dry basis)		
Carbon	78.90	74.16
Hydrogen	4.86	4.42
Nitrogen	1.25	1.18
Sulfur	0.57	1.12
Chlorine	0.14	0.22
Oxygen (by diff.)	7.61	8.16
LHV (MJ/kg dry basis)	31.19	30.89

[a] 'Raw' analysis stands for 'as fed to the furnace', i.e. milled and sampled from the dosing system.

Table 2
The operating conditions

Flame	Coal	Coal rate (kg/h)	Wall temp. (°C)	Added HCl (ppmv)	Added SO$_2$ (ppmv)
1	Polish	1	1250	0–567	0–603
2	Goettelborn	1	1250	0–610	0–649
3	Polish	1	[a]	0–567	0–603
4	Polish	1.5	1150	0–378	
5	Polish	1	1050	0–567	0, 362, 603
6	Polish	1	950	0–567	0–603

[a] Flame 3 with various wall temperatures in 5 heating zones: $T_1 = 1150\,°C$, $T_2 = 1100\,°C$, $T_3 = 1030\,°C$, $T_4 = 960\,°C$, $T_5 = 900\,°C$.

673 K. The carrying air with pulverised coal enters the burner centre, surrounded by the primary air and the secondary air. A gravimetric screw conveyor supplies a constant coal-feeding rate between 0.5 and 5 kg/h. The furnace (ceramic tube) has a length of 2.5 m and an internal diameter of 200 mm. The flue gas composition (NO, NO_2, CO, CO_2, O_2, SO_2, and HCl) in the different combustion zones is measured on-line using standard instrumentation (paramagnetic O_2; NDIR CO, CO_2; chemiluminescent NO_x; infrared photometer HCl, SO_2).

Two bituminous coals, the German 'Goettelborn' and a Polish coal, were used as fuels with a feeding rate of 1 or 1.5 kg/h. The coal analyses are given in Table 1. The air-to-fuel equivalence ratio (λ) was 1.15, corresponding to 3% oxygen in the flue gas at the exit. The reactor wall temperature was adjusted automatically for the five heating zones and changed from 1223 to 1523 K for various operating conditions (Table 2).

HCl and SO_2 were added to the primary air. The sample gases HCl and SO_2, diluted with nitrogen, had concentrations of 1.87 and 1.99%, respectively. The in-furnace concentrations of added SO_2 or HCl were changed between 0 and 649 or 610 ppmv, respectively.

3. Kinetic model

The GRI 3.0-mechanism with 325 elementary reactions and 53 species [25] was used as the base reaction mechanism for the C/H/O/N system. Sulfur chemistry was taken from the work of Glarborg et al. [2]. This submechanism consists of 67 elementary reactions involving 14 sulfur-containing species. Chlorine chemistry was taken from the mechanism of Roesler et al. [1]. This submechanism consists of 29 elementary reactions to describe the reactions between HCl and the species of the CO/H_2O/O_2 system. Seven chlorine-containing species were included in this mechanism. Thermodynamic data were taken from the database of Burcat [26].

The SENKIN code was used to calculate the reactions of N/Cl/S system and to analyse the effect of HCl and SO_2 on CO oxidation [27,28]. A sensitivity analysis was also performed.
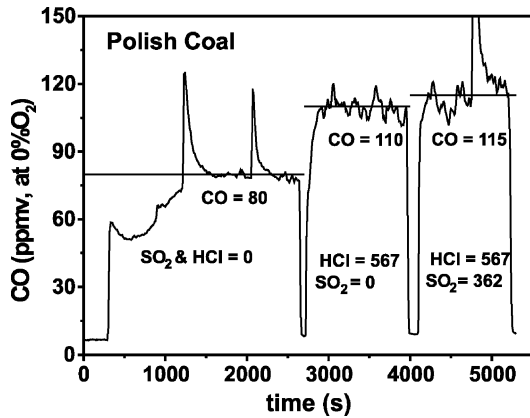
Fig. 1. Responses of CO emissions on the addition of HCl and SO₂.

4. Experimental results

In order to consider the effect of HCl or SO_2 released from the coals on CO emissions, the baselines of HCl and SO_2 concentrations were measured for some operating conditions [24]. For various operating conditions, the base emission of HCl at the reactor exit varied in the range of 29–83 ppmv for Polish coal, and 30–95 ppmv for Goettelborn coal. The base emission of SO_2 in the flue gas exit varied in the range of 465–518 ppmv for Polish coal, and 901–923 ppmv for Goettelborn coal.

The typical responses of CO emissions on the addition of HCl and SO_2 are shown in Fig. 1 for flame 5. The baseline CO emission is about 80 ppmv, with two peak values due to strong fluctuations of the operating conditions. They might be caused by the variation of fuel feeding rate. Except the peaks, the maximum variation of CO under each condition is likely to attain ± 20 ppmv. When 567 ppmv HCl is added into the reactor, CO emission increases, attaining up to 110 ppmv. When 362 ppmv SO_2 is also added, CO emission further increases slightly.

Fig. 2 indicates CO emissions in the flue gas for various HCl additions for flames 1–6. With increasing reactor temperature, CO emissions decrease. The effect of HCl on CO emissions is different for various conditions. At higher temperatures, i.e. for flames 1–4, CO emissions are lower
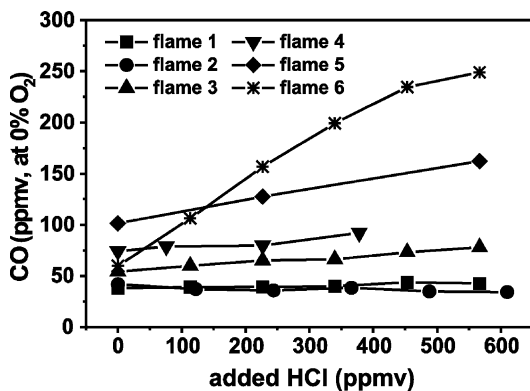

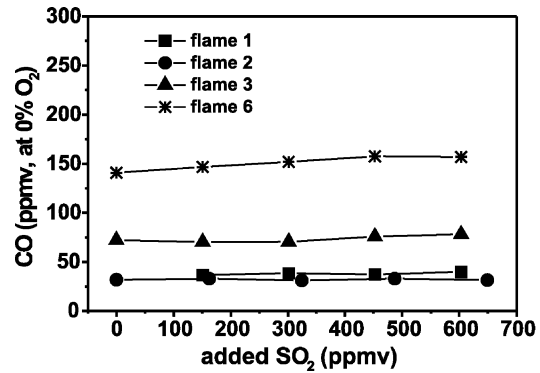Fig. 2. CO emissions in the flue gas for various HCl additions.

Fig. 3. CO emissions in the flue gas for various SO₂ additions.

than 100 ppmv and the added HCl has very limited influence. However, at lower temperatures, i.e. for flames 5 and 6, CO emissions significantly increase with increasing HCl addition.

CO emissions in the flue gas for various SO_2 additions for flames 1, 2, 3, and 6 are shown in Fig. 3. Compared to the effect of HCl, SO_2 has only a slight influence on CO emissions, even for flame 6 with low temperatures.

The effect of SO_2 addition on CO emission is less pronounced than that of HCl addition. This might be explained by the different base amounts of HCl and SO_2 released from the coal. In the experiments, the base concentrations of HCl and SO_2 in the flue gas were 40 and 400 ppmv, respectively, and the maximum amount of HCl or SO_2 added is approximately 600 ppmv. Therefore, the relative amount of HCl added is significantly higher than SO_2. In the experiments of Anthony et al. in a fluidized bed [15], the maximum amount of SO_2 added was up to 9000 ppmv in the flue gas, resulting in a more significant effect of SO_2 on CO emissions.

Fig. 4 indicates CO emissions with increasing HCl and various SO_2 additions for flames 3 and 6. At higher temperature (flame 3), HCl and SO_2 have little influence on CO emissions. At lower temperature (flame 6), CO emissions significantly increase with increasing HCl
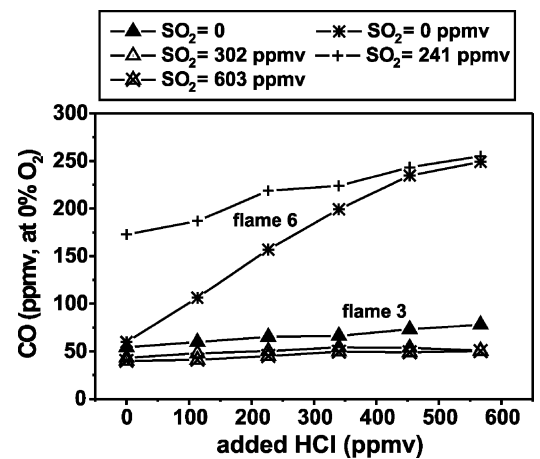

Fig. 4. CO emissions in the flue gas with increasing HCl and various SO₂ additions.
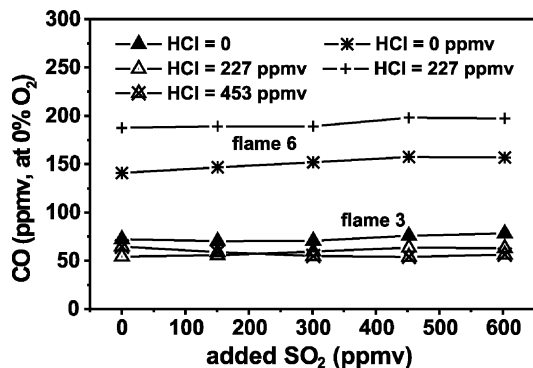
Fig. 5. CO emissions in the flue gas with increasing SO_2 and various HCl additions.

additions. In this case, SO_2 addition may inhibit CO oxidation and impair the effect of HCl.

Fig. 5 shows CO emissions with increasing SO_2 and various HCl additions for flames 3 and 6. It is found that increasing SO_2 addition only has little influence on CO emissions because the base concentration of SO_2 in the flue gas is comparable with the concentration of added SO_2. The effect of various HCl addition on CO emissions is more significant for flame 6 with a lower reactor temperature.

The measured CO profiles along the reactor axis with HCl addition are shown in Fig. 6 for flames 1, 2, 4, and 5. Results show that HCl has a significant influence on the CO concentration in coal flames. In the first stage of the combustion process, CO rapidly forms in the near-burner zone and attains a maximum value, followed by gradually decreasing CO concentrations along the reactor height. HCl addition leads to an increase of CO concentrations in the near-burner zone, and this influence continues up to the flue gas exit. The influence on CO concentrations for flames 4 and 5 is more obvious than for flames 1 and 2 because of the lower temperature of flames 4 and 5. In order to evaluate the differences of CO concentrations with and without HCl or SO_2 additions, the average CO decreasing value is calculated for the different flames. For flame 1, 2, 4, and 5
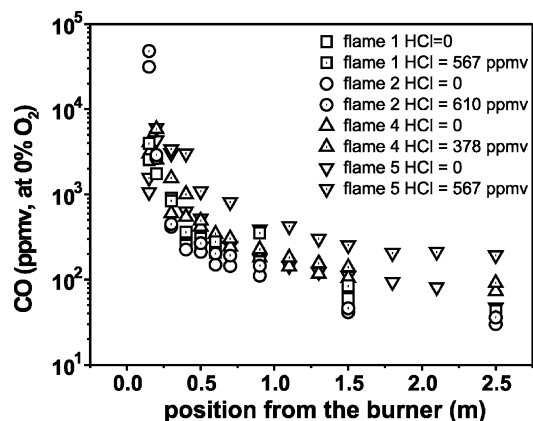

Fig. 6. Measured CO profiles with HCl addition along the reactor axis for flames 1, 2, 4, and 5.
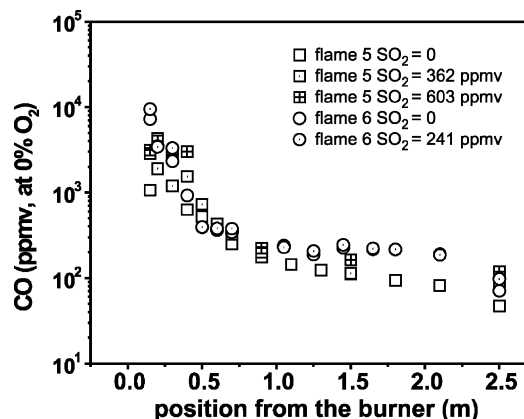

Fig. 7. Measured CO profiles with SO_2 addition along the reactor axis for flames 5 and 6.

with HCl addition, the relative change rate of CO concentration may attain 41, 25, 51, and 153%, respectively.

Fig. 7 shows the measured CO profiles along the reactor axis with SO_2 addition for flames 5 and 6. Although SO_2 addition also results in an increase of CO concentration, this effect is less pronounced than the effect of HCl addition in Fig. 6. The relative change rate of CO concentration is 42% for flame 5 with 362 ppmv SO_2 addition and 11% for flame 6 with 241 ppmv SO_2 addition.

5. Kinetic modeling and discussion

The influence of HCl or SO_2 on CO oxidation in coal flames is directly connected with combustion temperature, the stoichiometric ratio, the gas composition of the released volatiles, and CO formation from char combustion. In the following, the $CO/H_2O/NO/HCl/SO_2$ reaction system is modeled with a detailed mechanism to explain the experimental results.

Fig. 8 shows the effect of HCl addition on CO oxidation under fuel-lean conditions ($\lambda = 2.0$). The calculations are performed for a mixture with an initial composition of 4% CO, 16% CO_2, 4.35% O_2 (corresponding to $\lambda = 2.0$), 0.1% HCN, various HCl concentrations (0, 0.025, 0.05, 0.1, and
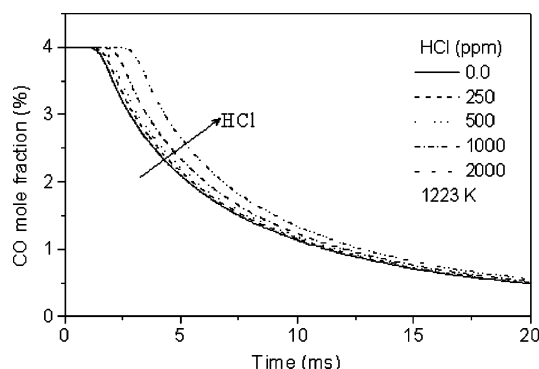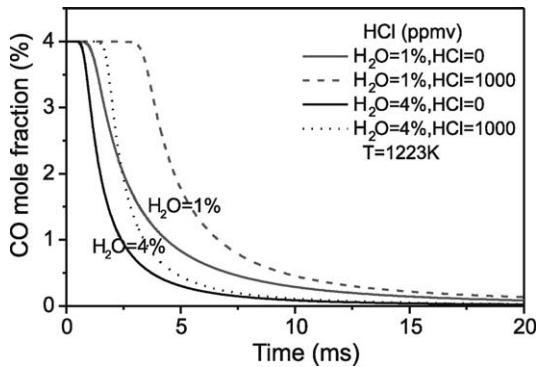

Fig. 8. The effect of HCl addition on CO oxidation.

Fig. 9. The effect of HCl and H_2O on CO oxidation.

Fig. 11. The effect of SO_2 and H_2O on CO oxidation.

0.2%), and a balance of N_2 at 1 atm and 1223 K. In Fig. 8, HCl delays CO oxidation (approximately 2.5 ms) for 0.2% HCl addition. The inhibition of HCl on CO oxidation may be attributed to the effect of HCl on the CO consuming reactions. At postflame combustion (near 1000 K), 95% of the CO is consumed by the reaction $CO + OH \rightleftharpoons CO_2 + H$ [1]. In addition, according to our calculations, the reaction $O_2 + CO \rightleftharpoons O + CO_2$ may also become important to consume CO at higher temperatures (e.g. 1223 K). Because HCl may act as inhibitors by catalyzing the recombination of radicals (e.g. H, O, and OH, etc.) in the flame, the reaction $CO + OH \rightleftharpoons CO_2 + H$ represents the major pathway influenced by HCl. The H radicals react with O_2 via $H + O_2 \rightleftharpoons OH + O$ to form OH radicals and O radicals is consumed by $O + H_2O \rightleftharpoons OH + OH$ to form more OH radicals.

Fig. 9 shows the effect of HCl addition on CO oxidation for two different H_2O concentrations (1 and 4% H_2O). For lower H_2O concentrations, the inhibition of HCl is more significant compared to higher H_2O concentrations. H_2O may enhance CO oxidation via the reaction $O + H_2O \rightleftharpoons OH + OH$. But at lower temperatures (i.e. 1023 K) and higher H_2O concentrations, H_2O may inhibit CO oxidation via the H recombination reaction $H + O_2 + H_2O \rightleftharpoons HO_2 + H_2O$ [17].

Fig. 10 shows the effect of HCN and HCl addition on CO oxidation. According to the calculated results, 70% HCN will be oxidized to NO in about 4 ms and others reduced to N_2. In Fig. 10, it seems the presence of NO may enhance CO
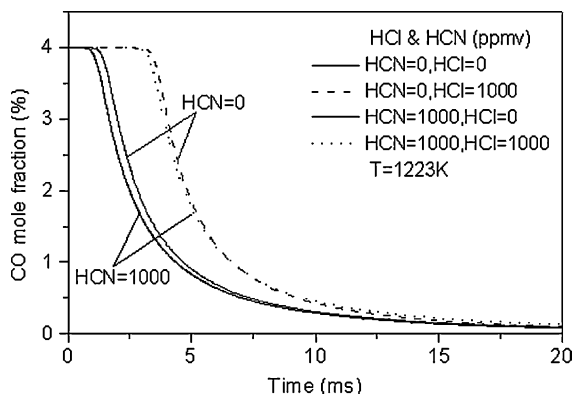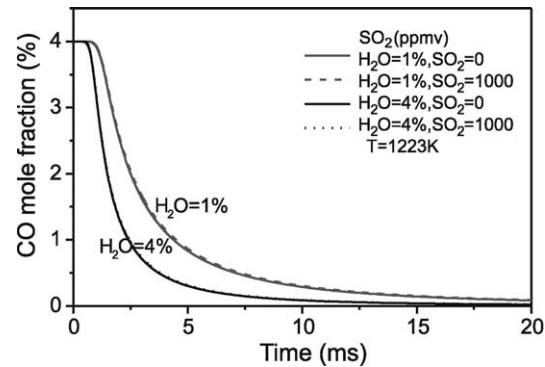

Fig. 10. The effect of HCl and HCN on CO oxidation.

oxidation. This may be explained by the reaction $NO + HO_2 \rightleftharpoons NO_2 + OH$ to form more OH radicals [5].

Fig. 11 shows the effect of SO_2 addition on CO oxidation for various H_2O concentrations (1 and 4% H_2O) at fuel-lean conditions ($\lambda = 2.0$). Obviously, under the present conditions, SO_2 only has a limited inhibitory effect on CO oxidation.

Table 3 shows the sensitivity coefficients of Cl-reactions with respect to CO under fuel-lean conditions ($\lambda = 2.0$). The relative sensitivity coefficient $S_{i,\text{rel}}$ is defined as: $S_{i,\text{rel}} = S_i/\max(S_i)$. S_i is the sensitivity coefficient of the ith reaction with respect to the species CO.

From Table 3, the reactions controlling the interaction between CO and HCl were identified for fuel-lean conditions. In the order of importance, the reactions inhibiting CO oxidation with HCl addition are summarized as follows

$$HCl + H = Cl + H_2 \tag{1}$$

$$HCl + OH = Cl + H_2O \tag{3}$$

Table 3
Sensitivity coefficients of major reactions involving chlorine chemistry ($\lambda = 2.0$)

Reaction	$S_{i,\text{rel}}$	No
$HCl + H = Cl + H_2$	33.79	1
$HCl + O = Cl + OH$	−22.39	2
$HCl + OH = Cl + H_2O$	5.90	3
$Cl + HO_2 = HCl + O_2$	4.73	4
$Cl + NO + M = NOCl + M$	4.14	5
$NOCl + Cl = Cl_2 + NO$	3.13	6
$Cl + HO_2 = ClO + OH$	−2.12	7
$2Cl + M = Cl_2 + M$	2.09	8
$Cl_2 + H = Cl + HCl$	1.26	9
$Cl + HNO = HCl + NO$	0.81	10
$Cl + H + M = HCl + M$	0.69	11
$ClO + CO = Cl + CO_2$	−0.41	12
$ClO + O = Cl + O_2$	0.37	13
$ClCO + Cl = Cl_2 + CO$	0.36	14
$Cl_2 + O = ClO + Cl$	−0.13	15
$ClO + NO = Cl + NO_2$	−0.11	16
$NOCl + H = HCl + NO$	0.11	17
$H + O_2 = O + OH$	−100	

Table 4
Sensitivity coefficients of major reactions involving sulfur chemistry ($\lambda = 2.0$)

Reaction	$S_{i,\text{rel}}$	No
$SO_2 + O + M = SO_3 + M$	2.89	18
$SO_2 + H + M = HOSO + M$	1.52	19
$SO_2 + H = SO + OH$	-0.12	20
$SO_3 + O = SO_2 + O_2$	0.10	21
$OH + CO = H + CO_2$	-100	

$$Cl + HO_2 = HCl + O_2 \qquad (4)$$

$$Cl + NO + M = NOCl + M \qquad (5)$$

$$NOCl + Cl = Cl_2 + NO \qquad (6)$$

The reactions enhancing CO oxidation with HCl addition are given as follows

$$HCl + O = Cl + OH \qquad (2)$$

$$Cl + HO_2 = ClO + OH \qquad (7)$$

The competition between the above reactions inhibiting and enhancing CO oxidation will determine the effect of HCl on the final CO emission. From Table 3, it can be seen that reactions inhibiting CO oxidation are more dominant than reactions enhancing CO oxidation, and thus CO emission increases due to HCl addition. This conclusion agrees with the experimental data.

Table 4 shows sensitivity coefficients of S-reactions with respect to CO at $\lambda = 2.0$. The reactions inhibiting the oxidation of CO with SO_2 addition are summarized as follows

$$SO_2 + O + M = SO_3 + M \qquad (18)$$

$$SO_2 + H + M = HOSO + M \qquad (19)$$

$$SO_3 + O = SO_2 + O_2 \qquad (21)$$

The reaction enhancing CO oxidation with SO_2 addition is

$$SO_2 + H = SO + OH \qquad (20)$$

According to the results of the sensitivity analysis in Table 4, the reactions inhibiting CO oxidation are more important than the reactions enhancing CO oxidation, and thus CO emissions increase due to SO_2 addition. However, compared with the results in Table 3, the sensitivity data for the conditions with SO_2 addition are less significant than for the conditions with HCl addition. Therefore, the effect of SO_2 on CO oxidation is less significant than for HCl.

6. Conclusions

Interactions of CO, HCl, and SO_x in pulverised coal flames were studied in an EFCR. Experimental results indicate that HCl addition may inhibit CO oxidation in coal flames and increases CO emission. Reducing temperature in the reactor will enhance the inhibitory effect of HCl on CO oxidation. The measured CO profiles along the reactor height clearly show that the addition of HCl may inhibit CO oxidation. SO_2 can also inhibit CO oxidation but it was found that the effect of SO_2 addition on CO oxidation is less pronounced than the effect of HCl addition.

The reactions inhibiting CO oxidation with HCl addition are summarized as: $HCl + H = Cl + H_2$, $HCl + OH = Cl + H_2O$ and $Cl + HO_2 = HCl + O_2$, which lead to the recombination of the radicals H, OH, and HO_2. The reactions enhancing CO oxidation with HCl addition are: $HCl + O = Cl + OH$, and $Cl + HO_2 = ClO + OH$, which produce OH radicals and promote the CO consuming reaction $CO + OH \Rightarrow CO_2 + H$. In addition, the kinetic modeling results also show that the influence of SO_2 on CO oxidation is less significant than the effect of HCl.

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