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The effect of halides on emissions from circulating fluidized bed combustion of fossil fuels

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Combustion tests involved addition of chlorides and bromides while burning Highvale coal were carried out in a pilot-scale (152 mm square × 7.3 m tall) circulating fluidized bed combustor (CFBC). The halogens were added in the form of hydrochloric acid (HCl) and calcium bromide ($CaBr_2.\frac{1}{2}H_2O$) solutions (10 wt%). The thermodynamic equilibrium composition of CFBC products was calculated using the ASPEN database package. The calculations predict 12% conversion of HCl to $CaCl_2$ for an HCl feed rate of 9.78 kg h^{-1} and complete conversion of $CaBr_2$ to HBr in the vapour phase throughout the range of $CaBr_2$ solution feed rate investigated. The experimental results indicate that chloride and bromide additions increase the CO and SO_2 concentrations in the flue gases, with corresponding decreases in the NO_x level. The halides have no significant effect on N_2O emission. The CO level increased from 27 to 230 ppmv when the chloride concentration in the reactor was ~4200 ppmv (Cl/ fuel = 4.58 wt%). The effect of bromide on CO emission was more dramatic, the CO emission jumping from 56 to 480 ppmv for lower concentrations of bromide (20–400 ppmv). The experiments confirm previous work showing that halide-containing species inhibit CO oxidation through interaction with the hydrogen–oxygen radical pool. The decrease in NO concentration with chloride addition can be explained by surface modification of CaO particles due to formation of a liquid calcium chloride phase favoured by high HCl concentrations near the feed point. The formation of the liquid calcium chloride phase has the potential to make the CaO surface unavailable, thereby reducing catalytic oxidation of volatile nitrogen to NO. *Copyright © 1996 Elsevier Science Ltd.*

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Circulating fluidized bed combustion (CFBC) continues to develop as a favoured technique for burning a wide range of coals, biomass and industrial wastes. The high halogen contents of some fossil fuels and growing interest in co-firing coal with industrial wastes containing elevated halogen contents has motivated this investigation of the effect of halogens on flue gas emissions.

Chlorine, bromine and other halogens are present as components of many fossil fuels. The chlorine and bromine contents of coal usually vary in the range 50–2000 and 0.3–3550 ppmw respectively[1]. The highest reported chlorine content has been found in coals from the UK (up to 9100 ppmw) and specific sites in the USA (up to 8000 ppmw in Virginia) and Australia (up to 17 000 ppmw[2]). Canada and China have coals with the highest bromine content (up to 3550 and 1630 ppmw respectively). Further detailed information on chlorine origin and mode of occurrence can be found in the comprehensive review by Hodges *et al.*[3].

Fuel type and combustion conditions can affect the amounts of each halogen released. There is a significant database on this for pulverized coal combustion. However, less is known about the more recent and lower-temperature fluid bed combustion systems regarding both net release of halogens in the gas phase and the effect of halogens on the combustion process.

According to data cited by Sloss[4], 94–99% of the chlorine in coal is volatilized and emitted as gaseous HCl during pulverized firing. For fluid bed firing in the presence of sorbent, a typical equilibrium partial pressure of hydrogen chloride over calcium oxide is ~ 4000 ppmv. Hence, significant capture of HCl on limestone at fluid bed temperatures can occur only in systems with high chlorine concentrations. However, as the flue gas coals in the convection section and baghouse, HCl capture is favoured at the lower temperatures, and this can result in effective HCl removal. Experimental results presented by Gibb[5], again for pulverized firing, confirm that 90–100% of the evolved chlorine could be accounted for as HCl. The amount of HCl in the flue gas is ~80 ppmv for each 0.1 wt% chlorine in the coal. The HCl emission rates measured in the USA for boilers burning coals of different rank vary from boiler to boiler. It is believed that in some boilers with less complete combustion than others, chlorine can be retained in the

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*Current address: AECL, Chalk River Laboratories, Chemical Engineering Branch, Chalk River, Ontario, Canada KOJ 1JO ash[5]. Typical emissions of HCl per tonne of coal for utility and industrial boilers burning different coals in the USA are 0.5 kg for anthracite, 1.0 kg for bituminous coal and 0.01 kg for lignite[6].

The water-soluble portion of the chlorine, lightly bonded to the coal structure, is released very quickly to the gas phase during combustion. The remainder, bonded to the organic fraction of the coal, is released as the carbon burns[7]. Almost all the chlorine volatilized is present in the combustion products as HCl. During pulverized coal combustion, elemental chlorine, usually in very low concentration, can be formed by oxidation in the presence of metal oxides in the fly ash and the boiler deposits, which act as catalysts. Although other chlorine-containing species, mainly NaCl and KCl, are produced at high temperatures[8], virtually all the chlorine is present as HCl when the flue gases cool. A possible mechanism of sodium chloride decomposition with the evolution of hydrogen chloride in the presence of water has been described by Hodges *et al.*[3].

It has been established that halogenated species are good flame inhibitors[9]. Thus, when coal is burnt in a fluidized bed in the presence of small quantities of chloride, bromide or iodide ions, the concentration of CO and of other products of incomplete combustion in the flue gas might be expected to rise. This has been confirmed to some degree by experimental results obtained using a small scale bubbling bed combustor[10]. The batch introduction of an inorganic halide (NaF, NaCl, NaBr or NaI) into the combustor under steady conditions caused an immediate increase in the CO concentration from ~1000 to >30 000 ppmv with corresponding changes in O_2 and CO_2 concentrations. The effect was more dramatic for a coke, low in volatiles, than for a coal. A slight decrease in bed temperature, probably associated with lower CO-to-CO_2 conversion, was also observed. The order of effectiveness of the inorganic halides in inhibiting oxidation was $NaF \ll NaCl \ll NaBr \ll NaI$.

Liang *et al.*[11] studied chlorine and bromine capture in pilot-scale bubbling and circulating fluidized bed combustors. It was found that the CO concentrations doubled (in comparison with a baseline) for both bubbling and circulating FBC when chlorine was added continuously in the form of solid calcium chloride ($CaCl_2 \cdot 2H_2O$). Similar results were obtained for PVC addition.

Bloomer and Miller[12] carried out tests using methyl chloride–propane combustion in a small-scale bubbling FBC. They observed trends in CO, CO_2 and O_2 concentrations similar to those reported by Bulewicz *et al.*[10]. Introduction of chlorine into the combustor caused an increase in the CO concentration in the flue gases by up to 3% and in consequence a significant decrease (5–20%) in combustion efficiency. A 25–50°C drop in bed temperature was also observed.

From the above observations it can be concluded that there is reasonably widespread agreement that halogens present in such forms as HCl and HBr tend to inhibit overall CO oxidation. This conclusion is also supported by theoretical considerations presented below. The consensus is that inhibition proceeds through interaction with the hydrogen–oxygen radical pool[13,14]. However, there is no broad set of data for CFB combustion systems, and it is not clear to what extent the differences in gas mixing and contacting patterns between circulating and bubbling beds may alter or alleviate the reduction in oxidation rates associated with radical inhibition. In addition, the effects of chlorine and bromine addition on other reactions, such as those leading to NO_x formation, are poorly characterized. To address these questions, a brief experimental test programme was focused on measurement of CO and NO_x emissions as a function of chloride and bromide addition in the UBC (University of British Columbia) circulating fluidized bed combustor.

EXPERIMENTAL

A full description of the experimental pilot-scale CFBC system has been presented by Brereton *et al.*[15], so only a brief description is given here.

A schematic diagram of the pilot plant as used for the tests appears in *Figure 1*. The reactor shaft or riser consists of a refractory-lined combustion chamber of 152 mm square cross-section with an overall height of 7.32 m. Primary air is introduced to the bottom of the reactor through a multi-orifice distributor at the base. Secondary air is fed to the reactor through two opposing ports 3.4 m above the base. The primary and secondary air are metered and controlled separately so that their flow ratio can be varied at a fixed total air flow.

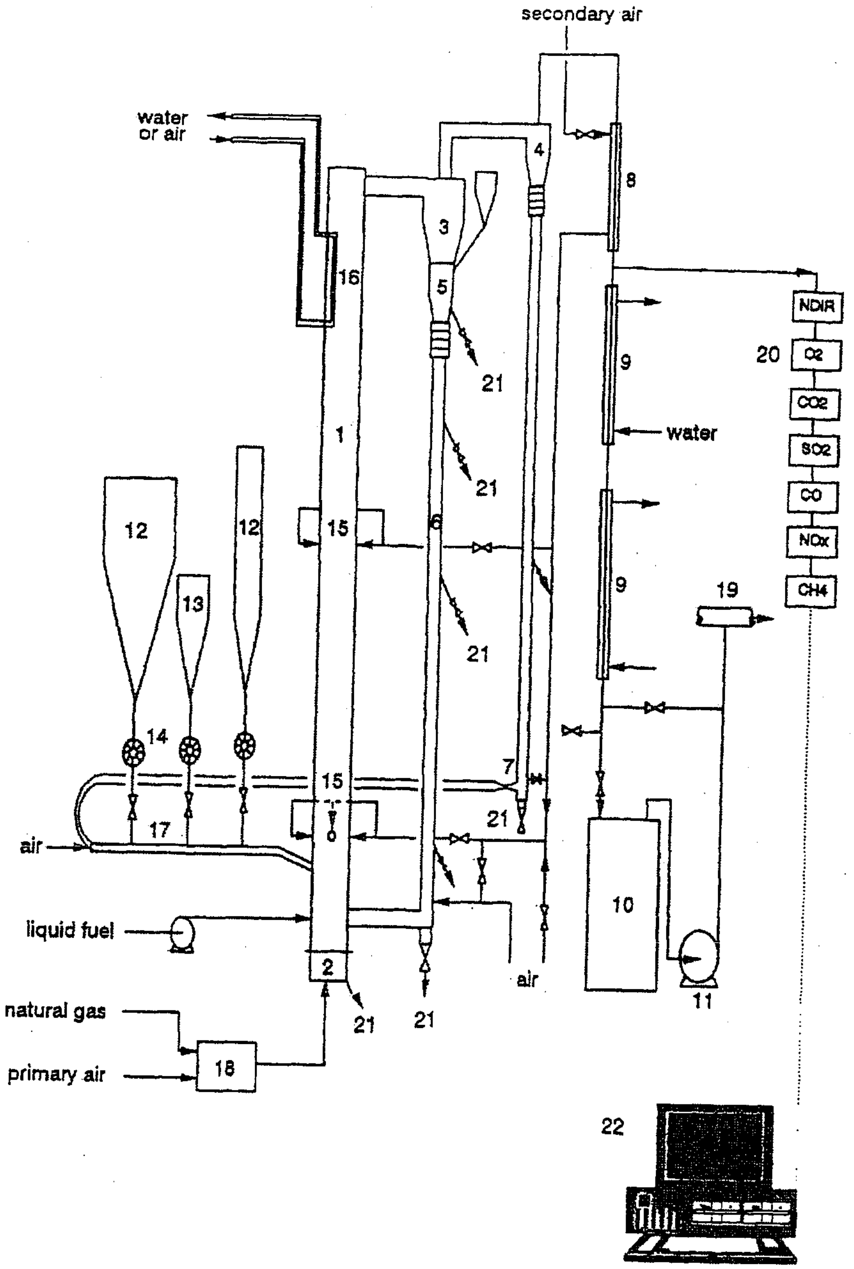
The gas leaving the top of the riser is heavily loaded with particles. These entrained solids are separated from the gas in a refractory-lined medium-efficiency primary cyclone of i.d. 305 mm. From the bottom of the primary cyclone, the solids descend as a moving packed bed, or in fully fluidized flow, through a 102 mm i.d. × 4.72 m long externally insulated stainless steel standpipe which forms the vertical leg of an L-valve. Solids are then returned to the base of the riser via the horizontal section of the L-valve to complete the primary solids loop. The circulation rate of solids is controlled by the flow rate of a small amount of aeration air supplied to the L-valve at a single point just above the corner. Coarse solids are drained from L-valve as required to prevent buildup within the system.

Gas and entrained solids leaving the primary cyclone pass to a 203 mm i.d. high-efficiency secondary cyclone. Some of the solids captured in the secondary cyclone are returned to the riser by means of an eductor, while the remainder are drained at a rate of $\sim 3\,kg\,h^{-1}$. Gas leaving the secondary cyclone is cooled before entering a baghouse where final particulate removal is accomplished.

Gas samples from the flue gas are monitored continuously to determine concentrations of O_2, CO_2, CO, SO_2, NO_x and THC (total hydrocarbons measured as methane). Periodic measurements of N_2O and NO_2 are also made using FT-i.r. spectrometry.

Highvale coal was used to study the effect of halides (chloride and bromide) on flue gas emissions because of its low inherent halogen content and because of a broad operating base established with this fuel in previous work. Proximate and ultimate analyses of the coal are presented in *Table 1*, and analyses of fuel ash and silica sand used as inert start-up material appear in *Table 2*. Chloride was chosen because it is the most abundant halide found in fossil fuels; bromide was studied for comparison and because of the specific focus of this work on radical inhibition, since bromide is known to be a more powerful radical inhibitor.

Throughout the tests to ensure a consistent feed rate at low concentrations of halide, the halogens were added as dilute aqueous solutions of an appropriate inorganic halide. The halide solutions were injected by a peristaltic



1.Reactor, 2.Windbox, 3.Primary cyclone, 4.Secondary cyclone, 5.Recycle hopper, 6.Standpipe, 7.Educator, 8.Secondary air preheater, 9.Flue gas cooler, 10.Baghouse, 11.Induced draught fan, 12.Fuel hopper, 13.Sorbent hopper, 14.Rotary valve, 15.Secondary air ports, 16.Membrane wall, 17.Pneumatic feed line, 18.External burner, 19.Ventilation, 20.NDIR and FTIR analysers, 21.Solids sampling ports, 22.Data acquisition system

Figure 1 Simplified schematic diagram of the UBC circulating fluidized bed combustion facility

Table 1 Proximate and ultimate analyses of Highvale coal (wt%)

Proximate analysis	
Volatile matter	30.5
Fixed carbon	42.1
Ash	12.2
Moisture	15.2
Ultimate analysis (db)	
C	62.4
H	3.6
N	0.8
Total S	0.2
O (by difference)	18.7
Ash	14.3
Higher heating value (MJ kg^{-1}db)	24.0

Table 2 Analyses of coal ash and sand (wt% as oxides)

	Coal ash	F70 Silica sand
CaO	15.6	0.01
SiO_2	45.7	99.7
MgO	1.0	0.01
Fe_2O_3	4.8	0.026
Al_2O_3	26.6	0.051
Na_2O	2.5	0.00
K_2O	0.35	0.00
TiO_2	0.7	0.025
P_2O_5	0.0	0.0
SO_3	1.7	0.0

Table 3 Summary of steady-state run conditions for Highvale coal and effect of chloride on flue gas emissions (series 1)

Test no.	1.1	1.2	1.3	1.4
Primary zone gas velocity ($m\,s^{-1}$)	4.9	5.1	5.3	5.0
Secondary zone gas velocity ($m\,s^{-1}$)	7.5	7.8	8.1	7.6
Primary-to-secondary air ratio	1.9	1.9	1.9	1.9
Fuel feed rate ($kg\,h^{-1}$)				
Calculated	24.0	23.5	23.9	24.7
Measured	22.7	22.6	23.1	23.5
Limestone feed rate ($kg\,h^{-1}$)	0	0	0	0
Ca:S molar ratio (inherent)	6.4	6.4	6.4	6.4
HCl (10 wt%) feed rate ($kg\,h^{-1}$)	0	4.57	9.78	0
Cl/fuel (wt% db)	0	2.21	4.58	0
Average suspension density ($kg\,h^{-3}$)	111	117	118	117
Temperature (°C)				
at base of reactor	845	852	850	862
at top of reactor	850	853	851	859
in L-valve return	858	855	854	863
in primary cyclone	855	852	852	860
in secondary cyclone	823	824	819	825
Flue gas composition (db)[a]				
O_2 (vol.%)	3.1	3.4	3.1	2.9
CO (ppmv)	27	135	233	32
SO_2 (ppmv)	109	236	260	107
CH_4 (vol.%)	0.0010	0.0026	0.0029	0.0012
NO (ppmv)	158	123	113	141
NO_2 (ppmv)	15	12	4	11
N_2O (ppmv)	32	42	38	37
Chloride (ppmv)[b]	0	2000	4200	0

[a] Values for CO, SO_2, CH_4 and N oxides corrected to 3 vol.% O_2 in flue gas

[b] Based on mass balance calculation

pump into the riser 1.3 m above the distributor through a 6.3 mm tube penetrating to the centreline of the combustor. Flow rates were monitored both by precalibration of the peristaltic pump and by measuring the loss in volume of the liquid in the aqueous halide solution reservoir.

The chloride was added as a 10 wt% solution of hydrochloric acid, diluted from commercially available. Anachemia practical grade 36.5–38% HCl. This should be immediately vaporized when injected into the riser. Because of the hazard in handling hydrogen bromide solutions, the bromide was injected as a solution of 10 wt% calcium bromide (American Chemical $CaBr_2 \cdot \frac{1}{2}H_2O$). Free energy calculations suggest that complete decomposition of $CaBr_2$ to HBr and CaO in the presence of water vapour is favoured over the full range of temperatures in the CFBC.

RESULTS AND DISCUSSION

The experimental work in the halide study consisted of three test series, each with a different objective. Series 1 studied the effect of chloride injection, and the flue gas emissions were measured as a function of the chloride-to-fuel ratio. Chloride flows in the range from 2.21 to 4.58 wt% of the fuel flow were tested. This is equivalent to a molar atomic-chlorine concentration of 2000–4200 ppm in the air stream (primary + secondary air). The chlorine concentration of 4.58 wt% corresponds to the upper limit found in some hospital and municipal solid wastes. In tests 1.1 to 1.4, beginning with zero chloride addition, the chloride feed was raised in two steps. After each step increase, emissions were allowed to stabilize. To determine any hysteresis effects, in test 1.4 the chloride flow was terminated to establish how long it would take for emissions to return to baseline levels. Operating conditions were typical for combustion of Highvale coal in the pilot plant, and were unchanged throughout the experiment except for the level of chloride addition. Results are shown in *Table 3*.

Tests series 2 and 3 were structured to study the effect on emissions of bromide addition. Series 2, which should be treated as exploratory, consisted of four steady-state periods with high bromide feed rates. Test series 3 was structured to study lower bromide additions. Bromide was fed at rates from 0.53 to 1.70 $kg\,h^{-1}$ to give a molar bromide concentration in the total air input of 85 to 275 ppm. As in the chloride addition runs, operating conditions other than the bromide feed level were maintained constant. Results for series 2 and 3 are shown in *Tables 4* and *5* respectively.

To be able to understand the influence of halide addition, it is critical to have some understanding of the underlying coal combustion. Highvale coal is a high-quality subbituminous coal from Alberta with properties shown in *Table 1*. It contains 0.27 wt% sulfur and ~12 wt% ash containing significant amounts of alkali and alkaline earth metals. Combustion of Highvale coal in the absence of any sorbent should produce ~500 ppmv of SO_2 at 3 vol.% O_2 in the flue gas. However, typical measured SO_2 emissions in the absence of any sorbent vary from as low as 20 to as high as 150 ppmv, depending on the combustion temperature and the mineral matter content of the fuel. Hence, irrespective of the conditions, there is significant inherent sulfur capture by the fuel ash ranging from 60 to 95%.

The results of chloride addition are shown in *Figures 2–4*, illustrating the effects on steady-state emissions of CO and SO_2 respectively. The influence of chloride

Table 4 Summary of steady-state run conditions for Highvale coal and effect of bromide on flue gas emissions (series 2)

Test no.	2.1	2.2	2.3	2.4
Primary zone gas velocity (m s^{-1})	4.9	4.8	5.0	4.8
Secondary zone gas velocity (m s^{-1})	7.6	7.4	7.6	7.5
Primary-to-secondary air ratio	1.9	1.9	1.9	1.9
Fuel feed rate (kg h^{-1})				
Calculated	23.0	23.4	23.1	22.6
Measured	21.5	21.8	21.4	21.1
Limestone feed rate (kg h^{-1})	0	0	0	0
$CaBr_2$ (10 wt%) feed rate (kg h^{-1})	0	2.25	1.70	0
Br/fuel (wt% db)	0	1.00	0.70	0
Average suspension density (kg h^{-3})	126	125	128	130
Temperature (°C)				
at base of reactor	844	843	840	835
at top of reactor	850	852	850	845
in L-valve return	845	843	845	839
in primary cyclone	847	850	846	843
in secondary cyclone	807	816	815	811
Flue gas composition (db)[a]				
O_2 (vol.%)	3.7	3.5	3.4	3.5
CO (ppmv)	51	1680	318	60
SO_2 (ppmv)	37	56	65	35
CH_4 (vol.%)	nm[c]	nm	nm	nm
NO (ppmv)	151	116	144	152
NO_2 (ppmv)	9	tr[d]	tr	tr
N_2O (ppmv)	34	28	33	36
Bromide (ppmv)[b]	0	365	205	0

[a] Values for CO, SO_2, CH_4 and N oxides corrected to 3 vol.% O_2 in flue gas
[b] Based on mass balance calculation
[c] Not measured
[d] Trace

Table 5 Summary of steady-state run conditions for Highvale coal and effect of bromide on flue gas emissions (series 3)

Test no.	3.1	3.2	3.3	3.4	3.5	3.6	3.7
Primary zone gas velocity (m s^{-1})	4.9	5.0	5.0	4.9	4.9	4.9	4.9
Secondary zone gas velocity (m s^{-1})	7.5	7.4	7.4	7.5	7.5	7.4	7.6
Primary-to-secondary air ratio	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Fuel feed rate (kg h^{-1})							
Calculated	22.3	21.8	21.8	21.4	21.3	21.3	21.5
Measured	21.2	20.9	20.5	20.8	20.5	20.6	20.5
Limestone feed rate (kg h^{-1})	0	0	0	0	0	0	0
$CaBr_2$ (10 wt%) feed rate (kg h^{-1})	0	1.52	0	0.53	1.09	1.70	0
Br/fuel (wt% db)	0	0.65	0	0.23	0.48	0.75	0
Average suspension density (kg h^{-3})	122	123	134	130	116	113	143
Temperature (°C)							
at base of reactor	859	855	856	856	856	850	863
at top of reactor	851	848	850	848	848	838	869
in L-valve return	840	839	838	839	841	833	850
in primary cyclone	845	843	846	840	845	836	861
in secondary cyclone	813	820	817	812	820	809	827
Flue gas composition (db)[a]							
O_2 (vol.%)	4.1	4.5	4.5	4.8	4.9	4.9	4.8
CO (ppmv)	47	384	54	117	280	482	56
SO_2 (ppmv)	nm[c]	34	12	17	30	43	nm
CH_4 (vol.%)	nm	nm	nm	nm	nm	nm	nm
NO (ppmv)	170	163	168	175	172	160	172
NO_2 (ppmv)	7	6	8	7	7	6	12
N_2O (ppmv)	30	35	31	33	33	37	25
Bromide (ppmv)[b]	0	206	0	85	176	275	0

[a] Values for CO, SO_2, CH_4 and N oxides corrected to 3 vol.% O_2 in flue gas
[b] Based on mass balance calculation
[c] Not measured

addition on CO emission is very important. As shown in *Figure 2*, the CO emission increases by one order a magnitude when the chloride-to-fuel ratio increased from 0 to 4.58 wt%. The CO emission increases almost linearly with the chloride concentration in the fuel. A similar trend was obtained in a study[16] carried out by CANMET using iodine addition in a 400 mm diameter CFB. It is clear that SO_2 emission also responds

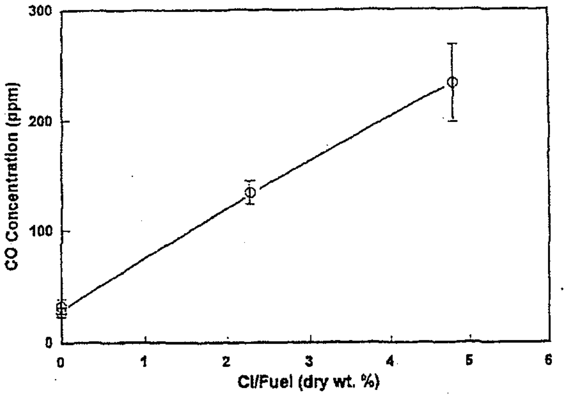


Figure 2 Effect of chloride-to-fuel ratio on CO emission. Conditions are given in *Table 3*

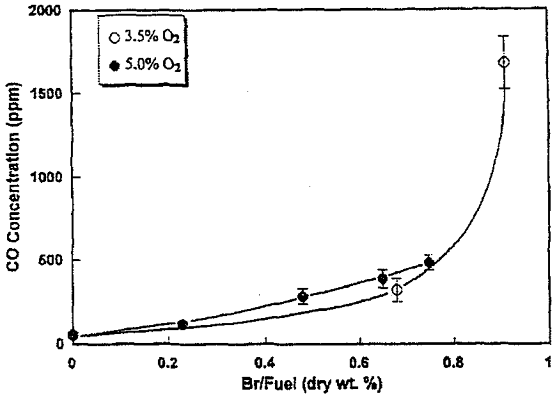


Figure 5 Effect of bromide-to-fuel ratio on CO emission. Conditions are given in *Tables 4* and *5*

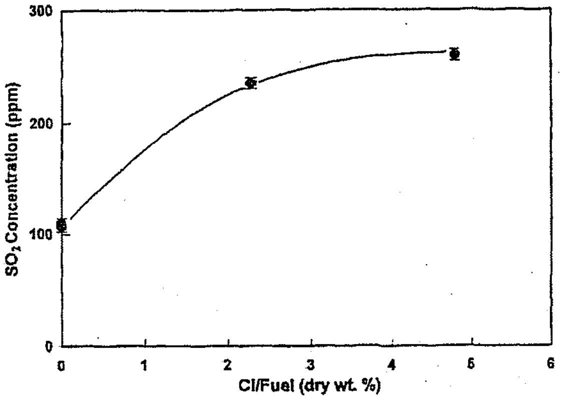


Figure 3 Effect of chloride-to-fuel ratio on SO_2 emission. Conditions are given in *Table 3*

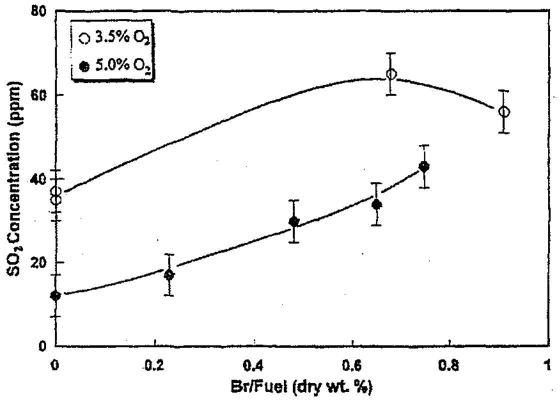


Figure 6 Effect of bromide-to-fuel ratio on SO_2 emission. Conditions are given in *Tables 4* and *5*

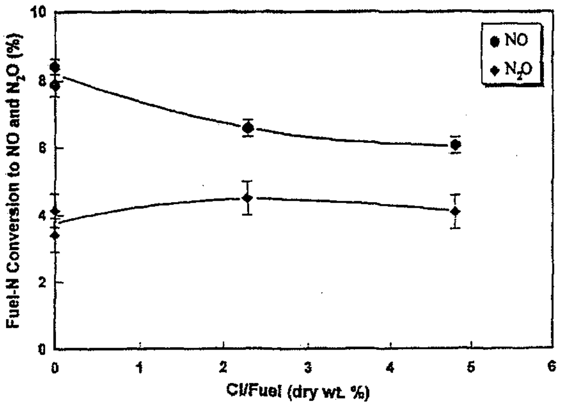


Figure 4 Effect of chloride-to-fuel ratio on fuel-nitrogen conversion to NO and N_2O. Conditions are given in *Table 3*

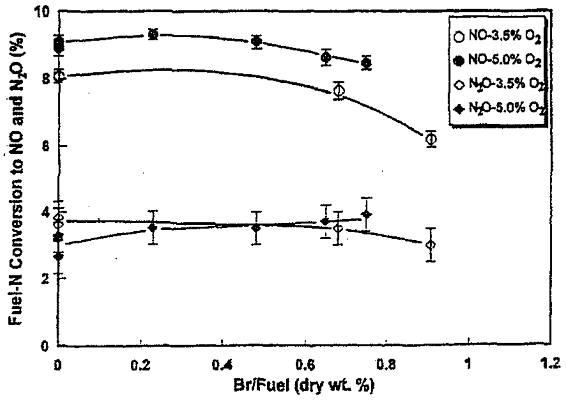


Figure 7 Effect of bromide-to-fuel ratio on fuel-nitrogen conversion to NO and N_2. Conditions are given in *Tables 4* and *5*

dramatically to the chloride addition (*Figure 3*): it almost triples as the chloride concentration relative to the fuel increases. *Figure 4* shows the effect of chloride addition on the fuel-nitrogen conversion to NO and N_2O at steady state. From these results it appears that chloride addition has little influence on NO; increasing the chloride-to-fuel ratio from 0 to 4.58 wt% produces only ~20% decrease in fuel-nitrogen conversion to NO. No distinct trend in the steady-state fuel-nitrogen conversion to N_2O is observed in *Figure 4*. Given the various uncertainties in the analytical and sampling techniques, it is not clear that the N_2O results are statistically significant. Becker *et al.*[17] studied the effect of halide addition on N_2O in a bubbling bed combustor and found a decrease in N_2O emission with chloride addition. They could not reach any conclusions as to the mechanism.

The results obtained with bromine addition are summarized in *Figures 5–7*, illustrating the effects on steady-state emissions of CO, NO and SO_2 respectively. The trends are entirely consistent with those obtained with chloride. However, the effect of bromide addition on CO emission is more dramatic, the emission jumping from 56 to 1680 ppmv for a modest change in the concentration of bromide (20–365 ppmv). The effect of bromide on suppression of CO oxidation is significantly greater than the effect of chloride, with both effects presumably attributable to the role of chloride and bromide in inhibiting free radical propagation. La Nauze[18] notes that carbon monoxide is the primary product of carbon oxidation in an FBC environment, and that it is subsequently oxidized in the gas phase by the radical reaction[19]

$$CO + OH \rightarrow CO_2 + H \qquad (1)$$

The oxidation process described by reaction (1) depends on the generation of OH free radicals during the combustion of the volatiles. It is believed that inhibition by halides results from participation in the competition between the chain branching reaction and catalysed radical recombination[20]. The chain branching reaction, responsible for the desirable production of the OH radical, is:

$$H + O_2 \rightarrow OH + O \qquad (2)$$

When halides (X: Cl, Br) are present at much higher concentrations than OH and H radicals, the sequence of reactions promoting catalysed radical recombination, and removal of H and OH radicals, can be described[10] by:

$$X + H + M \rightarrow HX + M \qquad (3)$$

where M is any stable molecule, followed by:

$$HX + H(OH) \rightarrow H_2(H_2O) + X \qquad (4)$$

Reactions (3) and (4) form a catalytic cycle, since they add up to:

$$H + H(OH) \rightarrow H_2(H_2O) \qquad (5)$$

The net result is a lowering of all active free radical concentrations in the gas phase. As expected, and in accordance with previous results of other authors discussed above, bromide is considerably more effective than chloride as a free radical inhibitor with CO levels of the order of 10^3 ppmv obtained, where corresponding molar feed rates of chloride would give CO concentrations at the 10^2 ppmv level.

The magnitude of the emission increase was considerably less than observed by Bulewicz *et al.*[10], however, the extent of the increase is expected to be a strong function of the specific geometry of the unit, since the inhibition of CO oxidation by halides is a kinetic phenomenon. It is expected that with a maximum CO discharge of ~300 ppmv from the pilot plant, CO emission should not be of major industrial concern. Larger commercial units have much longer gas residence times, which tend to result in considerably better CO burnout. However, in small transportable units, similar in size to the pilot plant, e.g. for hazardous waste incineration, CO emissions may be problematic. Such units can be subject to low permit CO emission levels, e.g. 50 ppmv in some jurisdictions. It is worthy of note that CO is the only carbonaceous species that appears to be significantly affected by the chlorine addition; total hydrocarbon concentrations (THC) as measured by i.r. do not appear to be strongly affected in these tests. Unfortunately, no measurements were made of other products of incomplete combustion (PICs) which might be of interest in hazardous waste application. Such products are organic compounds that are present in the original fuel feed stream but are generated by burning of organic materials in the feed.

The effect of the chloride addition on SO_2 emissions was to some degree unexpected. Thermodynamic calculations using the ASPEN (Advanced System for Process Engineering) package indicate that the decomposition partial pressure of calcium chloride in the presence of an H_2O partial pressure of 15 kPa at 850°C is 0.42 kPa of HCl; i.e. when the reaction:

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \qquad (6)$$

is considered, no calcium chloride (a liquid phase at these temperatures) should form unless a concentration of 4200 ppmv HCl is exceeded. At this concentration, the partial pressure should remain at 0.42 kPa until the supply of calcium oxide is exhausted. This calculation cannot take into account such complexities as alteration of $CaCl_2$ activity by solid solutions or dissolution of other solids into a liquid calcium chloride phase, but it should provide a reasonable first approximation to equilibrium conditions.

The ASPEN calculations predict that the chlorine appears entirely as gaseous HCl at HCl feed rate of 4.57 $kg\,h^{-1}$ and complete conversion of $CaBr_2$ to HBr in the vapour phase at all the $CaBr_2$ solution feed rates investigated. At an HCl feed rate of 9.78 $kg\,h^{-1}$, the results showed a theoretical 12% conversion of HCl to $CaCl_2$. The theoretical concentrations of HCl in the flue gases varied between 1950 and 4200 ppmv which correspond to HCl (10 wt%) feed rates of 4.57 and 9.78 $kg\,h^{-1}$ respectively. The theoretical concentrations of HBr in the flue gas were much lower, varying between 0 and 365 ppmv with $CaBr_2$ solution feed rate increasing from 0 to 2.25 $kg\,h^{-1}$. In view of the fact that only a small amount of $CaCl_2$ phase was anticipated from the chloride and CaO from the decomposition of $CaBr_2$ within the reactor, no significant effect on capture was expected. However, the experiments showed a marked decrease in inherent sulfur capture, especially in the case of chloride injection.

A possible explanation for this phenomenon, consistent with NO_x trends discussed below, is found by examining the local rather than global conditions within the riser. Around the halogen feed point, HCl concentrations must be $\gg$ 4000 ppmv, leading to transient formation of a liquid $CaCl_2$ phase on calcium oxide particles passing through the halogen feed zone. This phase should subsequently decompose as the HCl concentration becomes more uniform further up the riser. The formation of the liquid calcium chloride phase has the potential to:

(i) prevent sulfur capture by making the CaO surface unavailable;
(ii) decompose $CaSO_4$ formed during prior sulfur capture reactions.

Although free energy calculations are needed to establish the possibility of the second reaction, the first is clearly possible and has the potential to increase the observed SO_2 emission.

Johnsson[2] used a very similar argument, again related to surface modification due to formation of a liquid calcium chloride phase, to explain a slight increase in sulfur capture in some of his work. He suggested that this formation, followed by decomposition of the calcium chloride, reactivates the surface, providing a more open structure. It is possible that a liquid $CaCl_2$ layer could cause either an increase or a decrease in SO_2 emission, depending on the specific reactor and injection geometry.

Morphological change in CaO particles reacting with HCl was observed by Gullett *et al.*[22] SEM analyses showed that the granular sorbent particles coalesced and formed more highly ordered, crystalline structures as the formation of $CaCl_2$ increased. The coalescence of sorbent grains increased drastically the grain size and decreased the surface area of the CaO particles. A decrease in the surface area of CaO particles present in ash has the potential to decrease the sulfur capture. These results are consistent with the observed SO_2 emissions.

It would be expected that the extent of capture and release would depend greatly on the form of the halide. In these tests where the chloride was introduced as HCl, the formation of gas phase effectively instantaneous, creating the highest possible HCl partial pressure around the feed point. If the halide had been introduced in solid form, its release as HCl would have occurred more uniformly over the combustor, creating a different local reaction environment.

The location of the halogen feed may also be significant. In the experiments conducted here, while most of the reactor volume and the gas residence time lie above the halide feed point, the bulk of the solids inventory, where gas–solid reactions such as sulfur capture occur, lies below in the dense primary region. Reactors differ vastly in this regard, presenting different contacting patterns for halogen and sulfur species.

The decrease in NO_x formation associated with increased chloride feed has not, to the authors' knowledge, been reported previously. Liang *et al.*[11] observed an increase in NO_x in tests in a CFB during addition of chloride, consistent with the prior observations on bubbling beds. However, as discussed previously, the mechanism ascribed to NO_x increases in bubbling beds is not applicable to CFB studies.

NO_x formation and destruction cannot easily be tied directly to radical inhibition in the manner of CO. It is generally accepted that NO_x emission results from a series of complex competing heterogeneous and homogeneous reactions, in which both char and calcium oxide participate[23]. The overall pattern of these reactions is such as to cause net NO_x formation at the base of the reactor, followed by gradual destruction higher up. Two major reactions are:

(i) oxidation (to some extent catalysed by CaO) of volatile nitrogen to NO at the base of the reactor;
(ii) reduction of NO by CO throughout the reactor, again catalysed by CaO.

Hence CaO can either increase or decrease the overall NO_x emission, depending on the specific circumstances. In general, CaO addition may decrease NO_x emission for low-volatile fuels but increase it for high-volatile fuels, because of the different competition between the two reactions for different fuels[24]. Highvale coal can be considered a high-volatile fuel in this context.

In the current work, formation of a $CaCl_2$ liquid phase in the region of the chloride feedpoint probably reduced the amount of available CaO low in the reactor, where there was a high concentration of volatiles emanating from the fuel feed point not far below the chloride feed point. In this region CaO would otherwise be an effective catalyst for volatile-nitrogen oxidation. This proposed explanation is consistent with the findings on sulfur release.

The effect of bromide on SO_2 emissions and fuel-nitrogen conversion to NO is less clear. Since calcium bromide has a considerably higher decomposition partial pressure than calcium chloride, it should be much less prone to formation, even in the bromide-rich feed zone. As a result, the impact of bromide addition on NO_x and sulfur capture, according to the mechanism proposed above, should be less than for chloride addition. With the exception of a single point, corresponding to test 2.2, this is borne out by the experimental data, which indicate a small decrease in NO_x and some increase in SO_2, these changes being less dramatic than for the chloride. In comparing these values it is important to think in terms of the corresponding molar halide feed rates rather than their mass feed rates. The molar ratio of chlorine to bromine feed is approximately twice the corresponding mass feed rate ratio.

CONCLUSIONS

The results of chloride and bromide additions to a CFB combustor burning a subbituminous coal confirm that halogens inhibit free radical CO oxidation. As anticipated, chloride provides less inhibition than bromide. The picture with respect to sulfur capture and the effect of the halides on NO_x emissions are less clear. SO_2 emissions were found to increase with addition of halides, while NO_x levels decreased somewhat. The results presented are not always in agreement with the trends obtained by other authors, but they can be rationalized in terms of specific reactor contacting patterns. There is a strong possibility that such effects depend upon halide form, fuel type and reactor geometry. Further studies are required to clarify these effects.

These findings, together with the limited knowledge of halide effects on commercial units, suggest that elevated CO emissions in themselves are not an issue for large commercial units, where reduced CO oxidation rates are compensated by long residence times.

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