Fate of the Chlorine in Coal in the Heating Process

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Pyrolysis of 29 coals with carbon contents of 71–92 mass% on a dry, ash-free basis (daf) has been performed mainly in a temperature-programmed mode at 10°C/min up to 800°C with a flow-type fixed bed quartz reactor, and some factors controlling HCl formation have been examined. The rate profiles of HCl formation exhibit at least three distinct peaks at around 260–360, 470–510 and 580–630°C, and the lowest temperature peak is present for 8 coals alone, whereas the middle and highest temperature peaks are common with almost all of the coals. The HCl profile is also affected by the size of coal particles and the height of coal particles in the fixed bed. Yields of HCl and char-Cl at 800°C for 28 coals except an American bituminous coal are 44–95 and 4–54%, respectively, and tar-Cl is as low as ≤ 7% in all cases. The chlorine distribution is almost independent of the heating rate in the range of 2.5–400°C/min and has no distinct relationship with carbon or chlorine content in coal, but HCl tends to increase with increasing amount of (Na + 2Ca) in coal with a corresponding decrease in char-Cl. When an Indonesian sub-bituminous coal is injected into an O₂-blown entrained bed gasifier under pressure, there is an almost 1:1 relationship between carbon and nitrogen conversions, whereas the sulfur and chlorine are enriched in the remaining char, and the degree of the enrichment is higher with chlorine. The method of evaluating coal-Cl forms quantitatively using model chlorine compounds is proposed.

KEY WORDS: coal; pyrolysis; gasification; chlorine distribution; HCl formation; chlorine enrichment.

1. Introduction

Chlorine contained in coal—denoted as coal-Cl—is transformed into hydrogen chloride (HCl) via coal conversion processes, such as pyrolysis, combustion and gasification. This is feared to pose harmful consequences for a number of technologies currently under development, including integrated gasification combined cycle (IGCC) and integrated gasification fuel cell (IGFC) systems. Moreover, it is believed that HCl arising from chlorine contained in coke may cause corrosion of furnace installations.1) These problems arising from chlorine—while relatively new compared to long-studied phenomena arising from nitrogen or sulfur in coal—pose unavoidable challenges for the development of coal-utilization technologies that seek to achieve zero-emission operation.

The chlorine content of coal typically measures 2 000 µg/g-dry or below, and in many cases lies around 1 000 µg/g-dry. However, some coal produced in the U.K. or the U.S. contains high concentrations of chlorine in the vicinity of 10 000 µg/g-dry.2) By way of contrast, in Japan—where environmental regulations are stringent—the coal used for electric power production is said to have a chlorine content of 500 µg/g-dry or below, and the chlorine content of the caking coal imported by Japan for coke has been determined to be in the range of 100–1 500 µg/g-dry.3) When coal is heated during combustion or gasification, pyrolysis occurs first, and the volatile portion is released; it has been reported that coal-Cl separates in the form of HCl during this process.1–3) According to Herod et al.,3) when 6 types of U.K.-produced coal containing high concentrations of chlorine in the range of 4 000–9 000 µg/g-dry were heated at a rate of 2°C/min to 300°C, then maintained at that temperature for 24 hours, some 40–60% of the chlorine was converted to HCl; this was confirmed via mass analysis. In addition, Fourier-transform infrared spectroscopy was used to demonstrate that HCl and NH₃ are produced in nearly the same temperature region, somewhere in the vicinity of 450°C.3) Thus, we see that reports of HCl formation during coal pyrolysis have appeared in various places to date; however, there have been essentially no systematic studies involving multiple types of coal.4) Elucidation of the nature of HCl formation during pyrolysis would be of significant interest in conjunction with the formation of HCl in subsequent combustion or gasification steps. Moreover, HCl reacts easily with chemical species, such as alkali metals and mercury, and thus affects the evolution of these substances,3,8) and for this reason is thought to be closely related to the behavior of trace quantities of harmful metals in coal, a focus of current interest. Previous studies5,9) have reported that (a) the oxidation of elemental mercury during
pulverized coal combustion proceeds via heterogeneous reactions involving HCl and unburnt carbon in an electrostatic precipitator (90–300°C), and (b) when attempting to eliminate mercury from the gas produced by coal gasification using activated coal, the yield at 80°C is significantly improved in the presence of HCl.

For these reasons, in this study we subject 29 varieties of coal, of significantly different carbon and chlorine content, to temperature-programmed pyrolysis. In addition to conducting a detailed study of the effect of types of coal and reaction conditions on the chlorine distribution and the temperature dependence of the rate of HCl formation, we focus on the fate of nitrogen, sulfur, and chlorine during pressurized O²-blown coal gasification. Our primary objective is to clarify differences in the behavior of the distributions of these substances at high temperature and pressure. We also apply curve-fitting techniques to profiles of HCl formation during pyrolysis in an attempt to identify and quantify sources of HCl by their chemical form.

2. Experimental

2.1. Coal Samples

We used 29 varieties of coal as samples, ranging from lignite to anthracite. In most cases, upon obtaining coarse particles of a given sample, we air-dried the particles, then ground and sieved them to yield particles of size 150–250 μm. Finally, we dried the particles for 1 h in N₂ at 108°C before using the sample in our experiments. Table 1 lists results of elemental analysis and proximate analysis for.

Table 1. Analyses of coals used.

| Coal | Country | Elemental analysis (mass%-daf) | Proximate analysis (mass%-dry) |
|------|---------|-------------------------------|-------------------------------|
|      |         | C    | H    | N    | S    | O    | Cl   | Ash | VM  | FC   |
| BFT  | CAN     | 69.2 | 4.4  | 1.3  | 0.61 | 24.5 | 150  | 16.5| 37.4| 46.1 |
| WMG  | USA     | 69.8 | 4.9  | 1.1  | 0.49 | 23.6 | 250  | 5.4 | 45.0| 49.6 |
| BRU  | IDN     | 71.1 | 5.1  | 1.6  | 0.61 | 21.6 | 230  | 3.1 | 45.6| 51.3 |
| BZP  | USA     | 71.3 | 5.8  | 0.71 | 0.76 | 21.4 | 220  | 9.6 | 44.9| 45.5 |
| PSR  | IDN     | 72.1 | 5.2  | 1.4  | 0.27 | 21.0 | 160  | 4.1 | 45.2| 50.7 |
| OBM  | CAN     | 72.5 | 5.0  | 1.7  | 0.63 | 20.2 | 300  | 12.6| 40.7| 46.7 |
| MBW  | USA     | 73.4 | 5.2  | 1.6  | 0.43 | 19.4 | 420  | 4.3 | 38.0| 57.7 |
| WAN  | USA     | 73.7 | 5.4  | 0.76 | 0.63 | 19.5 | 190  | 8.8 | 44.7| 46.5 |
| THY  | JPN     | 74.8 | 6.0  | 1.3  | 0.25 | 17.6 | 440  | 11.3| 42.6| 46.1 |
| BCN  | USA     | 76.1 | 5.4  | 1.3  | 0.65 | 16.5 | 300  | 4.7 | 45.8| 49.5 |
| ILL  | USA     | 76.9 | 5.3  | 1.3  | 0.55 | 0.10 | 810  | 14.3| 40.1| 45.6 |
| BON  | IDN     | 77.2 | 5.4  | 1.8  | 0.58 | 0.50 | 340  | 5.7 | 43.4| 50.9 |
| PRM  | IDN     | 77.7 | 5.4  | 1.9  | 0.57 | 1.44 | 280  | 4.1 | 41.7| 54.2 |
| DTN  | CHI     | 78.8 | 4.8  | 0.87 | 0.91 | 1.46 | 240  | 8.1 | 27.6| 64.3 |
| DRT  | AUS     | 79.7 | 5.3  | 1.9  | 0.13 | 1.18 | 260  | 12.4| 32.8| 54.8 |
| TGH  | AUS     | 79.7 | 5.4  | 2.0  | 0.64 | 2.12 | 260  | 10.9| 35.9| 53.2 |
| FSL  | CHI     | 80.0 | 6.0  | 1.2  | 0.56 | 2.12 | 640  | 12.6| 35.2| 52.2 |
| EML  | SAF     | 80.1 | 5.3  | 1.9  | 0.13 | 1.16 | 230  | 12.9| 29.7| 57.4 |
| LDL  | AUS     | 81.1 | 5.4  | 2.1  | 0.57 | 1.08 | 470  | 8.3 | 33.9| 57.8 |
| LSN  | USA     | 81.3 | 5.3  | 1.5  | 0.89 | 1.10 | 580  | 19.4| 30.2| 50.4 |
| ENM  | AUS     | 82.3 | 5.1  | 1.9  | 0.06 | 9.7  | 240  | 11.2| 25.4| 63.4 |
| PIT  | USA     | 82.4 | 5.4  | 1.6  | 0.32 | 8.2  | 840  | 9.0 | 37.8| 53.2 |
| MUR  | AUS     | 83.7 | 5.5  | 1.8  | 0.75 | 8.2  | 370  | 12.0| 28.0| 60.0 |
| UFT  | USA     | 85.8 | 5.2  | 1.5  | 2.7  | 4.8  | 1600 | 13.0| 27.5| 59.5 |
| CNZ  | CHI     | 88.4 | 4.1  | 1.7  | 0.44 | 5.4  | 380  | 15.0| 9.4 | 75.6 |
| YRB  | AUS     | 89.5 | 3.7  | 2.0  | 0.78 | 4.0  | 1300 | 9.8 | 7.3 | 82.9 |
| JET  | AUS     | 89.7 | 4.5  | 2.1  | 0.56 | 3.1  | 750  | 7.4 | 13.6| 79.0 |
| POC  | USA     | 90.8 | 4.8  | 1.2  | 0.77 | 2.4  | 1500 | 4.6 | 18.6| 76.8 |
| HGI  | VIE     | 91.5 | 3.4  | 1.3  | 0.55 | 3.2  | 190  | 10.2| 4.7 | 85.1 |

a CAN, Canada; USA, United States of America; IDN, Indonesia; JPN, Japan; CHI, China; AUS, Australia; SAF, South Africa; VIE, Vietnam.
b Volatile matter.
c Fixed carbon.
the coal samples used. The concentrations of carbon, chlorine, and ash varied respectively over the ranges of 71–92 mass%-daf, 160–1 600 µg/g-dry and 3.1–19 mass%-dry. For this study, we selected only coal samples within or near the van Krevelen coal band.

2.2. Pyrolysis Experiments and Analysis of Products

For pyrolysis, we used a flow-type fixed-bed quartz reactor.15,16 In our experiments, a quartz cell filled with 2.5 g of coal was held in a quartz holder; after evacuation, ultra-high purity (>99.99995%) He was introduced into the system and a high-speed micro gas chromatograph (Agilent Technologies) was used to analyze the gas at the reactor outlet, with the system left untouched until the N₂ and H₂O concentrations fell to 20 ppm or below. Then, the gas flow was switched to ultra-high purity (99.9995%) N₂ and the heating of the sample was initiated. The temperature was controlled via K- or R-type thermocouples in contact with the bottom of the cell; the cell was heated to 800℃ primarily at a rate of 10℃/min.

The HCl evolved by the pyrolysis process was analyzed online at 1-min intervals using an IR analyzer (Thermo Environmental Instruments).13,14,19 The correlation coefficient for the calibration curves—constructed for HCl diluted by ultra-high purity N₂ to 20, 50, 100, 200 ppm—was 0.99986. The gas resulting from O₂ bomb combustion was captured in an aqueous solution of (NH₄)₂CO₃ and an absorption spectrophotometer (Hitachi) was used to measure quantities of coal-Cl and of chlorine contained in tar (tar-Cl) and char (char-Cl).13,15,17–19 The reproducibilities of our chlorine-content analyses were ±5, ±7 and ±4% respectively for HCl, tar-Cl and char-Cl.

Using the results of these analyses, we express the yields of HCl, tar-Cl and char-Cl as fractions of the total content of chlorine present in the coal supplied. As discussed in more detail below, the total of these pyrolysis yields fell within the range of 90–108% for the 29 types of coal we considered, indicating that the chlorine balance was roughly appropriate. All gases at the reactor outlet were collected in a gas bag and investigated with a gas-detection tube in an effort to detect the presence of Cl₂. No Cl₂ was detected (levels below 0.5 ppm) for any of the 29 types of coal we tested.

2.3. Elemental Analysis of Char after Gasification under Pressure

To investigate the behavior of coal-Cl under gasification following pyrolysis, we conducted an elemental analysis of a sample of high-pressure-gasified char (from BON raw coal) supplied by Babcock Hitachi, and then calculated the carbon conversion and the chlorine conversion. For comparison, we also determined the nitrogen conversion and sulfur conversion. Gasification was conducted at pressures of 0.9–2.6 MPa using an entrained bed gasification system with O₂/coal ratios in the range 0.66–0.83 kg/kg.15 Gasification temperatures varied slightly depending on the experimental conditions; the average temperature at an O₂/coal ratio of 0.83 kg/kg and 2.6 MPa was 1 400℃.

2.4. Mineral Composition Analysis

To measure the mineral composition of our coal samples, high-temperature ash obtained by combustion at 815℃ in air was fully dissolved in a blended aqueous solution of HF and aqua regia, and metal ions were measured using an inductively coupled plasma emission spectrometer (ICP-ES) (Perkin Elmer).20 In our ICP-ES analysis we measured 8 elements: Na, Mg, Al, Si, K, Ca, Fe and Ti. We assumed the chemical form of these metals would be oxides (with the exception of Ca in high-sulfur-content coal, which forms sulfate). Calculated values of ash contents fell in the range of 94–110% of the experimental ash-content values determined by proximate analysis (Table 1).

2.5. Solid-State Nuclear Magnetic Resonance Measurements

In previous research, the presence of NaCl hydrate has been noted among the chemical forms of coal-Cl,21,22 and it has even been reported that the majority of coal-Cl forms hydrated NaCl.13,23 Thus, to test for the presence of NaCl, we used a Fourier-transform nuclear magnetic resonance spectrometer (Chemiagnetics) to conduct solid-state ²³Na-NMR measurements of YRB coal.24 We used the method of single-pulse excitation with magic-angle spinning (SPERMAS) with a rotation rate of 15 kHz and a ²³Na resonance frequency of 79.4 MHz at 25℃ and with the number of iterations in the range of 130 000–170 000. As an external reference, we used 1 N NaCl aqueous solution and set the chemical shift of the ²³Na obtained to 0 ppm.

3. Results and Discussion

3.1. Temperature Dependence of HCl Formation

Figure 1 shows the temperature dependence of the rate of HCl formation in the process of temperature-programmed pyrolysis of WMG, DRT and HGI coals. For WMG coal, HCl evolution starts near 200℃; the formation rate exhibits a slight peak at 260℃ and a major peak at 490℃, as well as a shoulder that appears in the range of 580–630℃. In contrast, for DRT coal the formation of HCl occurs at higher temperatures than for WMG coal; here the formation rate attains its maximum at 470℃, with a peak also visible near 580℃. For HGI coal, we observe just a single peak at 580℃.

Fig. 1. Rate profiles for HCl formation in the temperature-programmed pyrolysis of WMG, DRT and HGI coals.
Figure 2 shows results for JET and MBW coals. As is clear from comparison to Fig. 1, MBW coal exhibits an HCl formation profile similar to that seen for DRT coal. In contrast, for JET coal we see two peaks in the vicinity of 360°C and 510°C, as well as a shoulder in the range of 580–630°C.

Table 2 collects the peak temperatures of HCl formation for all of the coals studied. From this table the following findings are evident:

1. A low-temperature HCl peak in the range of 260–360°C is present only for BFT, WMG, LDL, PIT, UFT, YRB, JET and POC coals.
2. An HCl peak in the range of 470–510°C is observed for all types of coal with the exception of CNZ, YRB and HGI coals.
3. The high-temperature HCl peak at 580–630°C is common to all types of coal.

Thus, we see that peaks in HCl formation may be broadly divided into three temperature regions: 260–360°C, 470–510°C and 580–630°C; the presence of peaks in the various regions depends on the type of coal.

3.2. Chlorine Distribution and Coal Type

Table 2 also lists the HCl yield at 800°C for all coals used. For all types of coal, Cl2 was not detected (concentration, <0.5 ppm). Previous studies of pyrolysis also did not report formation of Cl2.3,4,23) As we see from Table 2, the HCl yield depends strongly on the type of coal; yield values vary over the range of 23–95%, with discrepancies as large as over fourfold depending on the type of coal. We may summarize the results by saying that, with the exception of POC coal, more than half of the coal-Cl is converted to the gas phase. Yields of tar-Cl are smaller, in the range of 0–7%. This suggests that tar-Cl is converted to HCl via secondary reactions in the pyrolysis process. Yields for char-Cl vary from 4 to 72%, differing significantly for different coal types, as is true for the case of HCl. Total yields (HCl + tar-Cl + char-Cl) were reasonable, in the range of 90–108%.

For char-Cl, multiple scenarios may be considered: perhaps the coal-Cl originally present in the coal remains unchanged, or with some partial change of form, in char; or perhaps a portion of the HCl evolved reacts with char (minerals or carbon substances) and is incorporated into the solid phase. For example, calcium contained in coal exists in various forms—including limestone, dolomite, gypsum and ion-exchange Ca—while iron exists in the forms of pyrite, carbonate, ferric oxide and ion-exchange Fe and undergoes reduction reactions during pyrolysis. The reactions of HCl with CaCO3 and FeO are expressed by Eqs. (1) and (2), respectively.

\[
\text{HCl} + 0.5\text{CaCO}_3 \rightarrow 0.5\text{CaCl}_2 + 0.5\text{CO}_2 + 0.5\text{H}_2\text{O} \quad (1)
\]
\[
\text{HCl} + 0.5\text{FeO} \rightarrow 0.5\text{FeCl}_2 + 0.5\text{H}_2\text{O} \quad (2)
\]

At 200–800°C, the change in standard Gibbs free energy is calculated to be in the range of –10 to –7.3 kcal/mol for Eq. (1) and in the range of –8.7 to –0.72 kcal/mol for Eq. (2). Thus, the formation of CaCl2 or FeCl2 is thermodynamically favored. The results of mineral composition analysis (section 2.4) indicate that, among all alkali metals and alkaline-earth metals present in our 29 coal samples, the

| Coal | Peak temperature observed in HCl profile (°C) | HCl yield at 800°C (%) |
|------|--------------------------------------------|------------------------|
| BFT  | ○ ○ ○                                    | 91 |
| WMG  | ○ ○ ○                                    | 86 |
| BRU  | ○ ○                                       | 47 |
| BZP  | ○ ○                                       | 81 |
| PSR  | ○ ○                                       | 75 |
| OBM  | ○ ○                                       | 71 |
| MBW  | ○ ○                                       | 86 |
| WAN  | ○ ○                                       | 70 |
| THY  | ○ ○                                       | 95 |
| BON  | ○ ○                                       | 45 |
| PRM  | ○ ○                                       | 55 |
| DTM  | ○ ○                                       | 56 |
| DRT  | ○ ○                                       | 80 |
| TGH  | ○ ○                                       | 69 |
| FSL  | ○ ○                                       | 69 |
| EML  | ○ ○                                       | 77 |
| LDL  | ○ ○                                       | 66 |
| LSN  | ○ ○                                       | 63 |
| ENM  | ○ ○                                       | 60 |
| PIT  | ○ ○                                       | 57 |
| MUR  | ○ ○                                       | 56 |
| UFT  | ○ ○                                       | 74 |
| CNZ  | ○ ○                                       | 61 |
| YRB  | ○ ○                                       | 89 |
| JET  | ○ ○ ○                                    | 82 |
| POC  | ○ ○ ○                                    | 23 |
| HGI  | ○ ○                                       | 69 |
abundance of Ca is greatest (0.011–1.4 mass%-dry) for most types of coal, while the Fe content (0.23–2.2 mass%-dry) is also fairly significant. Reactions between HCl and surface OH groups in silicate or aluminosilicate may also occur. For non-minerals, we may also consider scenarios in which reactions of surface active sites of carbon in char with HCl proceed and the resulting chlorine is observed as char-Cl.

3.3. Effects of Coal and Mineral Compositions on Chlorine Distribution

Figure 3 shows the effect of the carbon content of coal (C%) on the yield of HCl, tar-Cl and char-Cl. We see no clear relationship between HCl yield and C%; for example, although the C% values of THY and ILL coals are nearly equal (75 and 77 mass%-daf, respectively), their HCl yields differ by nearly 50%. We find similar behavior for tar-Cl and char-Cl. We also investigated the relationship between chlorine distribution and chlorine content (Cl%), but again found no clear correlation. We conclude that the yields of HCl, tar-Cl and char-Cl produced under the pyrolysis conditions of this study do not depend on the C% or Cl% of the feed coal.

As noted above, the majority of coal-Cl is thought to exist in the form of NaCl hydrate,\textsuperscript{1,4,23} and Cl-XANES measurements indicating the presence of NaCl·H\textsubscript{2}O, CaCl\textsubscript{2}·6H\textsubscript{2}O and organic hydrochlorides have been reported.\textsuperscript{21,22} Thus, assuming that Na and Ca are present in the form of NaCl and CaCl\textsubscript{2}, we investigated the relationship between chlorine distribution and the quantity (Na + 2Ca) in coal. The results are shown in Fig. 4. Although exceptions exist, the general trend is that, as the value of (Na + 2Ca) increases, HCl increases and char-Cl decreases. We also attempted to plot the data with only Na or Ca on the horizontal axis, but found no clear trend of the sort visible in Fig. 4. Thus, it seems that the fate of coal-Cl during pyrolysis is best characterized in terms of the quantity (Na + 2Ca) in coal.

Several possible explanations for the fluctuations in the data of Fig. 4 may be considered. One explanation derives from the fact, noted above, that calcium in coal exists in the form of carbonate and hydrosulfate. The results of our mineral composition analysis (section 2.4) revealed that atomic Ca/Cl ratio was greater than 1 for almost all of the 29 coal samples used; thus, chlorides are relatively scarce, and limestone, dolomite and gypsum are the principal components. In contrast, atomic Na/Cl ratio was less than 1 in many cases, and thus chlorides may mainly constitute Na-containing compounds. The coal-Cl concentration has been reported to increase with increasing quantities of Na in coal.\textsuperscript{23} For these reasons, we performed solid-state \textsuperscript{23}Na-NMR measurements of YRB coal, and the results are shown in Fig. 5. As expected, an Na\textsuperscript{+} chemical shift appears at −5 ppm, confirming the presence of NaCl. Another possible explanation for the fluctuations in the data of Fig. 4 is the presence of Cl species other than inorganic chlorides, such as organic hydrochlorides.\textsuperscript{21,22}

In the pyrolysis of 15 types of caking coal for coke (10°C/min, 900°C), char-Cl was reported to increase as the Ca content of the coal increased.\textsuperscript{1} However, we observed no such trend in this study. A possible reason for the increase

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig3.png}
\caption{Effect of carbon content in coal on chlorine distribution at 800°C.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig4.png}
\caption{Relationship between the amount of (Na + 2Ca) in coal and yield of HCl, tar-Cl or char-Cl at 800°C.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig5.png}
\caption{Solid-state \textsuperscript{23}Na-NMR spectrum for YRB coal.}
\end{figure}
in char-Cl is the formation of CaCl₂ due to the progress of secondary reactions between HCl once-evolved and CaCO₃ (Eq. (1)) or CaO. However, if the coal contains sulfur in abundance, secondary reactions between H₂S and CaCO₃ or CaO occur with greater frequency, creating conditions unfavorable for the formation of CaCl₂. The S content of the caking coal for coke remains unclear, but is probably considerably smaller than the values used in this study for the quantity of S in coal (Table 1). Thermodynamic considerations suggest that the driving force for Eq. (1) is larger at a higher temperature; thus, even under the conditions of our experiments this could take place at high temperatures. In either case, there can be no doubt that the chemical form of coal-Cl is one important factor governing the HCl formation profile and the chlorine distribution.

3.4. Effect of Coal Sample State on HCl Formation

As is well known, the ash content and mineral composition of coal may vary depending on particle size. Since coal-Cl consists primarily of inorganic chlorides, the content of coal-Cl may also be affected by the coal particle size. For this reason, we used the method described in section 2.1 to prepare JET coal particles of size 55–75 μm and subjected these to elemental analysis. The results indicated a Cl content of 930 μg/g-dry, which is somewhat increased from the value of 750 μg/g-dry observed for particles of size 150–250 μm. This particle-size dependence merits a detailed future investigation.

Figure 6 shows the effect of particle size on the temperature dependence of the HCl formation rate. The HCl peak observed near 360°C for the original sample sizes (150–250 μm) is reduced by a factor of more than 4 for particle sizes of 55–75 μm; however, above 450°C the two rates do not differ significantly. The reason for this is presently unknown; however, it means that, if HCl in the vicinity of 360°C arises from a specific chloride compound, its content varies with coal particle size. Clarifying this point is a topic for future work; however, the results of Fig. 6 already suffice to indicate at the very least that particle size must be held constant for experiments testing HCl formation in pyrolysis.

3.5. HCl Formation and Coal-Sample Heating Rate

To investigate the impact of heating rate on HCl formation, we measured the temperature dependence of the HCl yield in pyrolysis of DRT coal with heating rates reduced from the original rate of 10°C/min to 2.5°C/min and 5°C/min. The results are shown in Fig. 8. As the heating rate

Figure 7 shows the effect of sample layer height on HCl formation from DRT coal. Here we have fixed the particle size in the range of 150–250 μm and reduced the layer height to 1.5 mm from its original value of 8 mm. In other words, we have reduced the sample volume to decrease the layer height to approximately 1/5 of its original value. Comparing results for the two sample heights, we see that the rate of HCl formation does not differ much at 500°C or below, but is greater for the higher-height layer above this temperature, particularly in the vicinity of 580°C. Thicker sample layers facilitate more secondary reactions among initial products, so the results of Fig. 7 suggest that secondary reactions promoting HCl formation proceed near 580°C.
decreases, the HCl yield in the low-temperature region increases; however, at 800°C the yield is essentially independent of heating rate.

Based on the results of these temperature-programmed pyrolysis tests, we calculated the apparent activation energy of HCl formation, obtaining a value of 20 kcal/mol for HCl yields in the range of 10–40% and 25–30 kcal/mol for HCl yields in the range of 50–70%. Herod et al.3) heated at 2°C/min and performed pyrolysis at 300°C, concluding that the rate-controlling step of HCl formation corresponded to diffusion within micro-pores; thus, it is possible that the rate-determining step of HCl formation from bituminous coal involves diffusion in pores at low temperature region but crosses over to chemical reactions at higher temperatures of 450°C or above.

Figure 9 shows the chlorine distributions resulting from pyrolysis of CNZ, YRB and JET coals at a heating rate of 400°C/min. When the heating rate is increased from the original value of 10°C/min to this higher rate, the HCl yields for all types of coal decrease slightly. On the other hand, the char-Cl yield at the higher heating rate increased 6% for CNZ coal and 13% for JET coal, but did not increase at all for YRB coal. Tar-Cl was not detected for any of the three coal types. As shown in Figs. 1 and 2, HCl formation increases with increasing temperature; however, the HCl yield at 800°C does not depend much on heating rate within the range of 2.5–400°C/min. When coal is injected into a pulverized coal combustion furnace or a gasification furnace, it is heated rapidly at a heating rate of 10⁴–10⁵°C/s to induce pyrolysis; future work is likely needed to study the fate of coal-Cl under these types of heating conditions.

3.6. Behavior of Chlorine in High-Temperature and -Pressure Gasification

As noted in section 3.2 above, although exceptions exist, in general at least 50% of coal-Cl is evolved in the form of HCl in pyrolysis up to temperatures of 800°C, with the majority of the non-HCl portion remaining in char. If all of this char-Cl were converted to HCl in the processes of combustion or gasification, the majority of coal-Cl would be converted to the gas phase. According to previous research,26) in an entrained bed gasification test of THY coal using Coal Partial Combustor (CPC) techniques (1 600°C, 2.0 MPa), approximately 90% of coal-Cl was converted to gas phase, although chlorine remaining in slag or char was also observed. In the pyrolysis of the THY coal used in this study, 95% of coal-Cl was released as HCl (Table 2); applying this value to gasification suggests that chlorine remaining in slag or char is produced by secondary reactions of HCl.

Thus, to investigate the behavior of coal-Cl in high-temperature, high-pressure gasification processes, we conducted elemental analysis of char obtained by the pressurized O₂-blown coal gasification (section 2.3) and studied the relationship between the carbon and chlorine conversions. The results are shown in Fig. 10. For comparison, the figure also shows conversion for nitrogen and sulfur. The values plotted here, which are the quantities of carbon, chlorine, nitrogen and sulfur relative to the corresponding quantity of each substance in the char after pyrolysis under ambient pressure, represent conversion for the process of char gasification after volatile matters have been released. As can be seen from Fig. 10, whereas nitrogen in char gasifies to approximately the same extent as carbon, sulfur and chlorine are more resistant than carbon to gasification. The conversion for chlorine is particularly low: whereas some 80% of carbon is converted, 70–80% of char-Cl remains in char. Another way of saying this is that, compared to nitrogen and sulfur, chlorine is an easily condensed heteroelement. Results of this type strongly suggest secondary reactions between HCl once-evolved and alkali-metal compounds or carbon active sites, and corroborate reports that some portion of coal-Cl transitions to slag or char.26)

3.7. Quantifying Differences in the Chemical Forms of the Substances Responsible for HCl Formation

In this section we perform a curve-fitting analysis of profiles plotting HCl formation rate versus temperature during temperature-programmed pyrolysis (Fig. 1, etc.), attempting to quantify the HCl sources for various different forms.

![Fig. 9. Effect of heating rate on chlorine distribution at 800°C.](image_url)

![Fig. 10. Relationship between carbon conversion and chlorine, nitrogen or sulfur conversion during O₂-blown entrained bed gasification under pressure.](image_url)
For curve-fitting in the low-temperature region of 450°C or below, we used temperature and peak-width (full width at half maximum) data for previously-reported HCl formation peaks for chlorine model compounds.\(^6,13\) As fitting parameters for HCl peaks in the range of 470–510 and 580–630°C, we computed the mean values of the peak temperature and peak width for all types of coal that exhibited the respective peaks (Table 2). The resulting values were: for the range of 470–510°C, a peak temperature of 490 ± 30°C and a peak width of 60 ± 10°C; for the range of 580–630°C, a peak temperature of 590 ± 10°C and a peak width of 200 ± 10°C. The reproducibility of the present curve-fitting method was ±3%.

Figures 11 and 12 show curve-fitting results for YRB and JET coals, which exhibited characteristic HCl peaks in the low-temperature region. For both of these coals, the particle size was 150–250 μm. For YRB coal, we estimate values of 25% for organic hydrochlorides, 35% for CaCl\(_2\)-6H\(_2\)O, 31% for NaCl-nH\(_2\)O and 9% for the remainder (labeled in the figure as Cl-containing carbon species: C(Cl) or C(HCl)). In our previous studies,\(^6,13\) HCl formation rates for YRB coal at temperatures of 210–280°C decreased significantly with water washing before pyrolysis; however, a peak at 360°C remained, and ultimately 28% of coal-Cl eluted in water. If the curve-fitting results of Fig. 11 are applicable in their current form, this indicates the partial elimination of organic hydrochlorides and CaCl\(_2\) hydrate. The peak in the range of 580–630°C may be attributed to Cl-containing carbon species formed by secondary reactions between carbon active sites in char and HCl evolved. If 100 ppm HCl/N\(_2\) gas is exposed over lignite char at 500°C, the HCl reacts easily with carbon active sites, transforming into organic C–Cl bonds and/or carbon species containing HCl; in subsequent temperature-programmed desorption runs, an HCl-formation peak was reported in the range of 550–620°C.\(^6\) As shown in Fig. 12, for JET coal with particle sizes of 150–250 μm, estimated values were 53% for NaCl-nH\(_2\)O and 47% for the remainder [total for 470–510°C (unidentified chlorine compounds) and 580–630°C]. For JET coal with particle sizes of 55–75 μm we estimated a value of 13% for NaCl hydrates. After water washing of the latter sample, the peak at 360°C disappeared entirely\(^6\) and approximately 15% of coal-Cl was removed,\(^6\) indicating that all NaCl elutes in water.

If this argument is correct, it implies that the elimination extent for NaCl hydrate should depend on the type of coal; this may signify differences in the structure or distribution of pores in which NaCl is present.\(^3\)

It remains unclear why the HCl peak at 260–360°C appears only for BFT, WMG, LDL, PIT, UFT, YRB, JET and POC coals (Table 2). As noted above, if the source of this HCl is attributed to organic hydrochlorides and inorganic chlorides CaCl\(_2\)-6H\(_2\)O and NaCl-nH\(_2\)O, our findings perhaps suggest that these chloride species are present only in the 8 types of coal listed above. Alternatively, it may be the case that, although organic hydrochlorides and inorganic chlorides are also present in other types of coal, all HCl molecules evolved in this temperature region are recaptured by mineral matters and/or carbon active sites in those types of coal.

Needless to say, the methods used in this section to quantify separately the sources of the HCl evolved in the pyrolysis are insufficient. Future studies are needed to corroborate the accuracy of the present curve-fitting analysis through a combination of measurements of Ca or Na ions in the filtrate remaining after water washing, investigations of changes in solid-state \(^{23}\)Na-NMR spectra before and after washing and chemical state analysis of coal-Cl using solid-state \(^{35}\)Cl-NMR.

4. Conclusions

Using 29 types of coal with carbon content in the range of 71–92 mass%-daf and chlorine content in the range of 160–1 600 μg/g-dry, we studied the temperature dependence of the rate of HCl formation during temperature-programmed pyrolysis and the effects of coal type and reaction conditions on chlorine distribution, and obtained the following conclusions.

(1) HCl formation peaks may be roughly separated into three temperature ranges: 260–360°C, 470–510°C and 580–630°C. Although instances of HCl formation at low temperatures were rare, HCl formation at intermediate temperatures was observed for essentially all types of coal.

(2) The yields of HCl and char-Cl at 800°C fell respec-
tively in the ranges of 23–95% and 4–72%. On the other hand, for tar-Cl the yield never exceeded 7%. Thus, 90% or more of coal-Cl was transformed into HCl and char-Cl.

(3) As the quantity $(Na + 2Ca)$ in coal increased, the HCl yield increased, while the char-Cl yield decreased.

(4) Although profiles plotting HCl formation rate versus temperature were affected by the size of coal particles and the height of coal particles in the fixed bed, the HCl yield at 800°C was essentially independent of heating rate over the range of $2.5–400°C/min$.

(5) When an Indonesian sub-bituminous coal was injected into an O$_2$-blown entrained bed gasifier under pressure, nitrogen and carbon contained in char gasified to the same extent, but sulfur and chlorine did not gasify, instead remaining in the char. In particular, we found that chlorine was the most easily condensed in char.

(6) We also showed that curve-fitting methods based on results for model chlorine compounds may be successfully applied to profiles of HCl formation during temperature-programmed pyrolysis to quantify different chemical forms of the chlorine present in coal.

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