Mass Spectrometric Investigations on the Release of Inorganic Species during Gasification of Lignite

Marc Bläsing, Michael Müller*

Institute of Energy Research, IEF-2, Forschungszentrum Jülich, D-52525 Jülich

*Corresponding author: Phone: +49-2461-61-6812, E-mail: mic.mueller@fz-juelich.de

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ABSTRACT

Coal contains different minor elements, which may be released during the gasification process and may cause severe problems. In order to develop technical measures to reduce the concentration of the released species in the flue gas and because of a lack of information about the release and especially the release mechanisms an enhanced basic understanding of the release of minor species during coal gasification is needed. For this reason basic investigations have been performed with four different lignites in an atmospheric tube furnace at 1400°C under strictly reducing conditions. Qualitative and quantitative analysis of the hot product gas was carried out using Molecular Beam Mass Spectrometry (MBMS). The main effort of MBMS is determination and specification of vapour species, in particular condensable species as Na, K, Cl and S species in the hot gas. Some results of the measurements are: The main amount of HCl, NaCl, and K is released at the pyrolysis in only few seconds. SO2 is released in two steps. The first release step had a high intensity and occurred immediately after sample insertion during pyrolysis. The second step happened with low intensity, over long-term during char reactions. Highly deoxidised species, like H2S, occur under reduced oxygen content of the pyrolysis phase. The release of NaCl is dependent on the Na/Cl and Na/S ratios of the investigated lignite. High Ca/S and Na/S ratios seem to reduce the SO2 release during gasification.
1 INTRODUCTION

The greenhouse effect, the limitation of fossil fuel resources and the increase in energy consumption during the next years require an increase in the efficiency of power plants. One way to tackle this problem is the use of coal gasification in combined cycle power systems (IGCC).\textsuperscript{1,2,3} During thermo-chemical conversion of coal, elements like Na, K, Cl and S are released as gaseous species (HCl, NaCl, KCl, H\textsubscript{2}S/ SO\textsubscript{2}) or remain in the fly ash, bound in different forms (e.g. inorganic salts like oxides or alkali silicates and alkali alumosilicates). The released species can cause severe corrosion and slagging problems in the power plant. With increasing temperatures in turbine processes, problems like fouling, slagging and corrosion are expected to become more severe.\textsuperscript{4} The need for a diversification in fuel lead to the use of coal to produce a highly clean fuel for turbine processes to minimise problems like corrosion and erosion. By now it is not possible to predict the kind of alkali specie that will be released from a coal during gasification in dependence of coal composition, temperature and atmosphere. Therefore, research has been undertaken to measure the alkali species released during coal gasification under highest temperature and reducing atmosphere conditions using molecular beam mass spectrometry. The use of MBMS allow on-line, in-situ measurement of hot reaction gases, to distinguish between the different species using their mass/charge ratio and has proven worthwhile in several studies for direct measurement of coal combustion and biomass gasification.\textsuperscript{5-14} However, the direct identification of non-condensed gaseous species released during gasification was outstanding so far. The given information by MBMS will be used to determine predictive correlations between ultimate composition and release of Na, K, Cl, and S containing species. This will help to select the process conditions and develop hot-gas-cleanup methods.

2 EXPERIMENTAL

2.1 Sample preparation

Samples were taken from four different Rheinisch brown coals. The ultimate and proximate analysis of the coals under investigation is given in Table 1 and Table 2. The coals were chosen for investigation of a broad range of different fuels and because of their different ratios of K/Si, Na/Si, K/S, Ca/S, Mg/S, and Na/Cl, which are assumed to have a major influence on the release of inorganic species during gasification as had been shown for thermo-chemical conversion of coal and biomass.\textsuperscript{5-11} The coals were dried and ground in a mill to a particle size <100\textmu m. After this treatment the coals were stored under dry conditions at room temperature.
### Table 1: Chemical composition of the coal samples [mass.-%]

<table>
<thead>
<tr>
<th></th>
<th>HKN-S -</th>
<th>HKN-S +</th>
<th>HKS</th>
<th>HKT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ash (dry)</strong></td>
<td>3.69</td>
<td>4.75</td>
<td>6.72</td>
<td>15</td>
</tr>
<tr>
<td><strong>Moisture (ar)</strong></td>
<td>49.12</td>
<td>49.12</td>
<td>51.03</td>
<td>50.88</td>
</tr>
</tbody>
</table>

### Table 2: Chemical composition of the coal sample ashes [mass.-%]

<table>
<thead>
<tr>
<th></th>
<th>HKN-S -</th>
<th>HKN-S +</th>
<th>HKS</th>
<th>HKT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>1.247</td>
<td>1.134</td>
<td>2.834</td>
<td>17.005</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.513</td>
<td>1.005</td>
<td>19.468</td>
<td>44.498</td>
</tr>
<tr>
<td>BaO</td>
<td>0.257</td>
<td>0.257</td>
<td>0.223</td>
<td>0.123</td>
</tr>
<tr>
<td>CaO</td>
<td>30.783</td>
<td>29.663</td>
<td>24.906</td>
<td>12.033</td>
</tr>
<tr>
<td>MgO</td>
<td>13.93</td>
<td>13.266</td>
<td>10.945</td>
<td>4.975</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.149</td>
<td>7.578</td>
<td>8.578</td>
<td>2.145</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.53</td>
<td>0.458</td>
<td>0.337</td>
<td>0.626</td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.144</td>
<td>5.931</td>
<td>8.492</td>
<td>2.292</td>
</tr>
</tbody>
</table>

### 2.2 Analytical methods

Alkali species release during gasification has been investigated by molecular beam mass spectrometry (MBMS). The MBMS system has been coupled to a high-temperature furnace. Fig. 1 shows the reactor for batch experiments, further information of the system can be found in WOLF.⁵,⁶

The main efforts of MBMS are that high reactive, condensable species are effectively quenched, so that no further condensation and reaction is possible. The released species are cooled down to several degrees Kelvin in very short time. Interaction with underground is inhibited by the high vacuum of the chamber systems inside the mass spectrometer and the big distance between the molecules in the so called molecular beam.

Small quantities of coal were gasified in batch mode in a corundum reactor and the gasification products were analyzed online by molecular beam mass spectrometry. The experimental setup for the gasification measurements is shown in Fig. 1. The reactor is made of alumina ceramic to prevent reactions between thermal conversion products and the reactor walls and to permit thermal cracking of the organic compounds at high temperatures. A platinum boat was filled with 50 mg of coal and connected with a 5 mm diameter alumina rod.
Fig. 1: Experimental setup during experiments with the tube furnace.

At the start of the experiment, this rod was inserted into an 18 mm inner diameter alumina reactor which was housed in a three-zone-furnace at constant temperature of 1400°C. A controlled gas flow of 3.7 l/min He and 0.3 l/min O₂ corresponding to 92.5% He and 7.5% O₂ was fed into the reactor to create a reducing environment. The oxygen concentration was chosen to get closer to autotherm gasification conditions. The gasification products flowed to the end of the reactor where they were analyzed by means of molecular beam mass spectrometry. MBMS is a reliable method for analyzing gases under high temperatures and pressures. For a detailed description of the MBMS-system the reader is referred to Wolf. Here, the system will only be briefly outlined. As shown in Fig. 2, it consists of three differentially pumped chambers. Gases enter the first chamber through a 0.3 mm diameter orifice. Due to the pressure difference between the reactor (p = 1 atm) and the first chamber (p = 4 • 10⁻² mbar), the gases undergo a supersonic free jet expansion. This nearly adiabatic expansion is responsible for a strong cooling of the gaseous species and the quenching of chemical reactions. About 10 orifice diameters downstream from the orifice the expansion has attained free molecular flow. The core of the free jet expansion is extracted by a conical skimmer of 1 mm diameter and directed into the third chamber. There ions are generated by electron impact ionization with a nominal electron energy of 30 eV. After passing the deflector, the ions are filtered in a quadrupole mass analyzer and detected by an off axis electron multiplier. The amplified signal is recorded by a complete computer and software package as a function of time and mass-to-charge ratio. In preliminary measurements, mass spectra from 10 to 150 amu were scanned to determine which species are present in the gas phase. During these measurements, NaCl but no Na₂SO₄ and no NaOH could be observed in the gas phase as Na-containing species. There was no evidence for the release of Na₂SO₄. Because of NaOH is difficult to detect as it has the same atomic mass of 40 amu as Ar which would result in an overlapping of the two peaks. Ar is always present in the gas phase to a small extent because the oxygen which is used for the experiments is slightly contaminated with Ar due to its production process. However, NaCl is one of the most dominant gas phase alkali species for temperatures up to 1400°C. NaOH exceeds NaCl only above this temperature. Therefore, the monitored species were H₂S⁺, O₂⁺, Cl⁻, K⁺, HCl⁺, NaCl⁺, SO₂⁺, and KCl⁺. In order to be able to monitor the gasification process with sufficient temporal resolution, 10 scans per second were acquired. Examples of typical intensity vs. time profiles are shown in Fig. 3 – 4 for the gasification of HKN-S⁺ at a temperature of 1400°C. At the beginning of each experiment, the sample boat was positioned in the cool front part of the furnace and a background spectrum was recorded for 20 – 30 s. The sample was then inserted into the hot zone of the furnace where it has been gasified. This resulted in a decrease of the
intensity of $O_2^+$ as oxygen was consumed and increases in the intensities of $H_2S^+$, $O_2^+$, $Cl^+$, $K^+$, $HCl^+$, $NaCl^+$, $SO_2^+$, and $KCl^+$ as these species were released. For the quantification of the release of the sampled species, the signal intensities were integrated over time and normalised to the $^{34}O_2$-signal from 0 – 20 s. To ensure reproducibility, five identical samples were measured and the results were averaged. The end of the alumina reactor was coupled to the sampling orifice of the MBMS device to sample the high temperature conversion products. The orifice extended into the furnace to maintain an elevated temperature to prevent condensation of gas-phase species on the tip of the orifice.

Fig. 2: Schematic representation of the MBMS system.

3 RESULTS AND DISCUSSION

The gas/solid interaction times in the alumina-tube flow reactor used in the experiments and the batch nature of the MBMS sampling experiments, with rapid quenching of the high temperature reaction products, are very short (0.15 - 0.3 s after sample insertion). Therefore, mainly fast gas/solid reactions and reactions occurring during char gasification are relevant for the obtained results and the results rather represent conditions in an entrained flow gasifier than in a fluidized bed gasifier.

MBMS pre-scans of the coal gasification products has been done for indication of the main released species. Hence, $H_2S^+$ (m/z 34), $HCl^+$ (m/z 36), $K^+$ (m/z 39), $NaCl^+$ (m/z 58), $SO_2^+$ (m/z 64) and $KCl^+$ (m/z 74) were qualitative and semi-quantitative investigated, because of their high signal intensity (reliable good signal/noise ratio) and the possibility to verify the species by comparing isotope ratios.

The results of the experiments are shown in Fig. 4 – 6. Two phases of gasification could be observed for all samples: pyrolysis and char reactions. The pyrolysis phase was generally much shorter than the char reaction phase. The main amount of the investigated species had been released during pyrolysis.
Fig. 3 shows two examples for intensity versus time profiles sampled during combustion and gasification of HKN-S + at 1400°C. Both under oxidising conditions and reduced oxygen content the thermo-chemical conversion of lignite started immediately after insertion of the sample, marked by the decrease of the m/z 34 signal. During pyrolysis volatile organic and inorganic matter is released from coal in only a few seconds. This matter instantly reacts with oxygen causing a lack of oxygen and extremely reducing conditions in the nearer environment of the coal particle in particular in the atmosphere with only 7.5%O₂. The lack of oxygen leads to the formation of highly deoxidised species, for example H₂S instead of SO₂. The graph in Fig. 3 shows the signal for m/z 34 which is occupied by ³⁴O₂ and ³⁴H₂S, indicating the release of H₂S during gasification. During char conversion the reactions are too slow to consume the complete O₂ resulting in slightly oxidising conditions and subsequently formation of SO₂ instead of H₂S.

Fig. 3: Intensity-time-profile at 1400°C in 20% O₂ and 7.5% O₂. The graph shows the signal for m/z 34 which is occupied by ³⁴O₂ and ³⁴H₂S. There is no release of H₂S under combustion conditions (20% O₂). The sharp rise of the peak (coloured in the lower graph) indicates the release of H₂S during pyrolysis under reduced oxygen content (7.5% O₂).
Fig. 4 and Fig. 5 show examples for intensity versus time profiles sampled during gasification of brown coals at 1400 °C. H₂S, HCl, K, and NaCl have been released with high intensity immediately after sample insertion. The release behaviour showed a very volatile character, since the bulk of the species was released during pyrolysis in the first seconds of the occurring reactions. This is distinctive for weakly bound species and species with a relative low decomposition temperature.

The organic material of brown coal contains many carboxylic groups which already start to decompose at moderate high temperatures at around 230-600°C during pyrolysis. Decomposition of carboxylic groups in combination with ion-exchange can lead to high release of HCl during pyrolysis phase⁴, for example:

\[ 2 \text{NaCl} + \text{HOOC-R} + \text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{CO}_3 + 2 \text{HCl} + \text{H-R} \]  

(1)

At higher temperature there are solid-solid reactions between alkali and alkaline earth metals with silica and aluminosilicate resulting in low intensity, long-term release of HCl during char reaction phase according to the following reaction equation examples:

\[ 2 \text{NaCl} + \text{SiO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{HCl} + \text{Na}_2\text{SiO}_3 \]  

(2)⁴

\[ 2 \text{NaCl} + \text{H}_2\text{O} + x\text{AlSi}_y\text{O}_z \leftrightarrow \text{Na-aluminosilicate} + 2 \text{HCl} \]  

(3)⁸,⁹

\[ 2 \text{KCl} + \text{H}_2\text{O} + x\text{AlSi}_y\text{O}_z \leftrightarrow \text{K-aluminosilicate} + 2 \text{HCl} \]  

(4)¹⁰,¹¹

Nearly all NaCl was released during pyrolysis at the start of the thermo-chemical conversion (Fig. 4 and 5). The formation of NaCl can be the result of volatilisation from species with a low melting or decomposition point or additionally by reaction of other released species (eq. 5). In addition, thermodynamic calculations showed that NaCl is more stable than NaOH at 1400°C as mentioned above.

\[ \text{NaOH} \text{ (g)} + \text{HCl} \text{ (g)} \leftrightarrow \text{NaCl} \text{ (g)} + \text{H}_2\text{O} \text{ (g)} \]  

(5)⁴

There has also been a second low intensity release for Na, K, and Cl containing species during char reaction phase (Fig. 4 and 5). During this phase species strongly bound in the coal matrix or mineral impurities were partly released during decomposition of the coal matrix, by formation of volatile species from mineral impurities and/or by char and ash reactions.

The high intensity of K as fragment originating from KCl or KOH during pyrolysis can be explained by the kind of K fixation in brown coals. In general brown coals have a very low K-aluminosilicate content, so most of the included K occurs in volatile forms, for example KCl or K₂SO₄·xFe₂(SO₄)₃. This is in agreement with the results shown in Tab. 1-2 and Fig. 6. HKT has a relative high K content but doesn’t show an unusually high release of K. At the opposite HKS contains 3.5 times less K than HKT, but HKT only released half of the K amount compared to HKS.

H₂S/SO₂ is released in two steps as shown in Fig. 3 – 5. The release of weak bound, mostly inorganic sulphur in form of mainly H₂S occurs in short-time and with high intensity during pyrolysis phase. The release of covalent in the coal matrix fixed sulphur and the formation of SO₂ from low volatile S-containing mineral matter (eq. 6-7) occurs over a long-time with low
intensity during char conversion phase according to the following solid-solid reaction between alkali and alkaline earth alkali metals with silica (eq. 8).

\[
\begin{align*}
2 \text{FeS}_2 & \leftrightarrow 2 \text{FeS} + \text{S}_2 \quad (6)^4 \\
\text{S}_2 + 2\text{O}_2 & \leftrightarrow 2 \text{SO}_2 \quad (7)^4 \\
\text{MeSO}_4 + \text{SiO}_2 & \leftrightarrow \text{MeSiO}_3 + \text{SO}_2 + 0.5 \text{O}_2 \quad (8)^8,^9
\end{align*}
\]

Even though there has been released a remarkable amount of \text{SO}_2, which should stabilize the formation of \text{Na}_2\text{SO}_4, there was no evidence for the release of \text{Na}_2\text{SO}_4 as shown in eq. 9. The reason is most likely a lack of \text{O}_2 which is still consumed by char reactions (Fig. 3-5).

\[
2 \text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + 0.5 \text{O}_2 \leftrightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl} \quad (9)^4
\]

Notable is also the release behaviour of \text{KCl}^+. \text{KCl}^+ has been released with very low intensity over a long-term during pyrolysis and char conversion. The signal intensity is not much above the background noise and must be interpreted with care. Nevertheless, the long-term release of \text{KCl} observed during gasification of all 4 brown coals can be explained via the replacement of \text{K} by \text{Na} in aluminosilicate at 1400°C (eq. 10):^4

\[
\begin{align*}
m\text{K}_2\text{O}^*\text{xSiO}_2^*\text{yAl}_2\text{O}_3 + 2 \text{NaCl} & \leftrightarrow (m-1)\text{K}_2\text{O}^*\text{Na}_2\text{O}^*\text{xSiO}_2^*\text{yAl}_2\text{O}_3 + 2 \text{KCl} \quad (10)^4
\end{align*}
\]

The averaged normalised peak area of the different species released at 1400°C is shown in Fig. 6. A comparison of these semi-quantitative results and the composition of the brown coals Table 1 and Table 2 reveals that, similar to former investigations on thermal conversion of coal and biomass, the amount of released species does not always directly correspond to the amount of corresponding elements found in the coal.\textsuperscript{7-14} Release mechanisms during gasification of coal are complex, correspond to different coal ingredients and can also alter depending on reaction conditions. Correlations between release behaviour and coal composition of the investigated brown coals had been checked by linear correlation as shown in Fig. 7. The underlying relationships may not always describe the behaviour correctly in all possible points, because some mechanisms are concurring. However, the results might be useful for predictions of the release behaviour of Na, K, Cl, and S species during coal gasification.

The release of \text{HCl} shows only a moderate positive correlation with the Cl content of the brown coals. Much more influence on the \text{HCl} release seems to have the Na/S and Ca/S ratio. The release of \text{HCl} is in good negative correlation with both the Na/S and Ca/S ratio. This can be explained by the capture of Na by S, leaving a higher amount of Cl for the formation of \text{HCl}. Also a high S content seems to prefer the formation of \text{HCl}. 


Fig. 4: Intensity versus time profiles of $^{16/18}\text{O}_2^+$, HCl$^+$, K$^+$, NaCl$^+$, and SO$_2^+$, and KCl$^+$ released during gasification of HKN-S + at 1400 °C in He 92.5% / O$_2$ 7.5%.
Fig. 5: Intensity versus time profiles of $^{16/18}$O$_2^+$, HCl$^+$, K$^+$, NaCl$^+$, and SO$_2^+$, and KCl$^+$ released during gasification of HKN-S - at 1400°C in He 92.5% / O$_2$ 7.5%.
The strong influence of Na/S and Na/Cl ratios on the release of NaCl can be very well observed for the two coals HKN-S - and HKN-S +. These coals are very similar in composition, the only big difference being the amount of S and Cl (HKN-S + contains 2 times more S and Cl, respectively). According to the results shown in Fig. 7 it seems that there is a strong influence of Na/S and Na/Cl ratios on the release of NaCl. This influence might be more important for the NaCl release as the S/Cl ratio because of the similar ratio for both HKN-S - and HKN-S +.

High total ash content, especially SiO$_2$ and Al$_2$O$_3$, reduced the amount of K released. The recapture of K by clay minerals had already been investigated during co-combustion of straw and coal by MÜLLER et al.\textsuperscript{7} Because of the lack of SiO$_2$ and Al$_2$O$_3$ in HKN-S +, HKN-S - and HKS there is a relatively high release of K. In comparison, HKT has a much higher K content, but also more SiO$_2$ and Al$_2$O$_3$, resulting in a relative low K release. Also much of the K might already be strongly fixed in K-aluminosilicates and therefore not available for release. On the other hand, a high content of basic oxides (CaO, MgO, FeO) of ash enhances the potassium release from aluminosilicates.\textsuperscript{4} This result had been found for a pulverized-coal flame and seems to be transferable to reduced oxygen content as the moderate correlation coefficient for the release of K from high basic brown coals (HKN-S -, HKN-S +, HKS) showed. HKT has a much higher acid content and therefore is able to capture more K and incorporate it in its aluminosilicate structure (Tab. 1-2, Fig. 6).

The release of KCl seems to be depended on the Cl content. There is a good positive correlation between the Cl content and the release of KCl. The K/S ratio showed a negative correlation, which again can be explained by capture reactions similar to eq. 9. K also seems to concur with Na for the formation of chlorides. High Na/Cl ratio leads to the formation of NaCl instead of KCl (Fig. 7).

Fig. 6: Integrated and to the $^{34}$O$_2$+ signal normalised peak areas for the release of HCl, K, NaCl, and SO$_2$, and KCl.
4 CONCLUSIONS

The aim of the work was to get a broader knowledge on the influence of fuel properties on the release of Na, K, Cl, and S containing species during gasification of lignite. Therefore, laboratory scale gasification experiments with four different brown coals have been performed at 1400 °C. Experiments have been conducted in a tube furnace with an atmosphere of 92.5% He and 7.5% O₂.

The release of H₂S, HCl, K, NaCl, and SO₂ has been investigated by molecular beam mass spectrometry. Molecular beam mass spectrometry has proven worthwhile in researching coal gasification at high temperatures. The method allows a detailed insight into alkali release during thermo-chemical conversion by analysing the released species in detail and time dependence. As main phases has been discovered: the pyrolysis phase during which the volatile matter and much of the species of interest were released and instantly converted, and the char conversion phase during which the solid char is converted into gas products and another usually smaller amount of the investigated species were released.

The main amount of HCl, K, and NaCl has been released during pyrolysis. H₂S/SO₂ were released in two remarkable steps during pyrolysis and char reaction phase. The fuel composition has an important impact on the amount of released species as was shown by

Fig. 7: Linear correlation coefficients for coal composition and the release of HCl, K, NaCl, SO₂, and KCl during gasification of lignite in tube furnace experiments at 1400°C.
linear correlation. The release of NaCl is dependent on the Na/Cl and Na/S ratios. High Ca/S and Na/S ratios seem to reduce the SO$_2$ release during gasification. The study has provided information on the influence of fuel composition on gas phase release of Na, K, Cl and S during gasification of different coals. This is important to understand corrosion and slagging processes while developing improved coal gasification technique.

Acknowledgement
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5 REFERENCES