No.36 Vaporization and Coagulation of Metals upon the Recirculation of
Flue Gas Impurities (H₂O, HCl and SO₂)
During Victorian Brown Coal Oxy-fuel Combustion

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SYNOPSIS
Oxy-fuel combustion of a Victorian brown coal of Australia was carried out at 1000°C to experimentally quantify the vaporisation of organically bound metals and the coagulation of corresponding metallic vapors as a function of the concentration of gaseous impurities including H₂O, HCl and SO₂ in 27% O₂ balanced with CO₂. The results indicate that, organically bound metals are highly sensitive to the changes to the loading of gas impurities during lignite combustion. HCl re-circulation is the most crucial factor promoting the vaporisation of metals via chlorination. Re-circulation of SO₂ affected the vaporisation of Na via changing the SO₂/HCl ratio in flue gas. Co-existence of steam with HCl and SO₂ is more favorable for the conversion of chlorides into molten alumino-silicates rather than sulfate droplet, which however should be cautioned, as its side effect on coal oxidation rate would be significantly intensified.

1. Introduction
Oxy-fuel combustion is a technology which employs a mixture of oxygen and re-circulated flue gas (RFG) in place of air for coal combustion to generate a CO₂-rich gas stream that can be directly sequestered or stored with minimal further treatment. These impurities (HCl, SO₂ and steam) can be gradually accumulated when flue gas is continuously recycled back into a furnace, thereby potentially causing additional ash-related technical troubles and environmental pollutant emissions. Thereafter, it is of significance to understand the ash formation routes during retrofitting existing air-fired power plants. The present study aims at clarifying the influence of three gas impurities, SO₂, HCl and steam on the vaporization propensity of the coal-bound inorganic metals and the coagulation of metallic vapors during oxy-fuel combustion.

2. Experimental
2.1 Coal Sample Properties
A Loy Yang brown coal from Victoria, Australia, was tested. The coal sample was air-dried and sieved to 106–153μm. The ash composition of test coal was shown in Table 1. For XRF quantification, coal was first ashed at 600°C in muffle furnace. CCSEM analysis was however conducted directly on the raw coal, which is thus not able to detect the organically bound cations and even the nano-scale mineral grains that are embedded deeply in the closed voids in coal.

<table>
<thead>
<tr>
<th>Table 1 Ash compositions, wt%</th>
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<tbody>
<tr>
<td>SiO₂</td>
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<tr>
<td>XRF</td>
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<tr>
<td>CCSEM</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>Cl</th>
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<tbody>
<tr>
<td>XRF</td>
<td>5.44</td>
<td>2.53</td>
<td>1.49</td>
<td>0.69</td>
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<tr>
<td>CCSEM</td>
<td>0.3</td>
<td>2.5</td>
<td>0.4</td>
<td>0.7</td>
</tr>
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</table>

2.2 Experimental conditions
Coal combustion was carried out in a lab-scale DTF. The furnace / gas temperature and nominal gas residence time were fixed at 1273 K and 4 sec throughout this study, respectively. Coal at a feeding rate of 0.5 g/min was entrained by 1 L/min primary gas into the DTF. The pre-heated secondary gas of 9 L/min was also fed into the reactor. Elemental compositions of ash were quantified using XRF, Rigaku 2100. Crystalline structures in ashes were determined by X-ray Diffraction Spectrometer (XRD). The microstructures and compositions of individual ash particles were examined using scanning electron microscopy (SEM, JSM-6510) coupled with energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion
3.1 Influence of HCl and SO₂
As shown in Fig.1, doping HCl alone into 27% O₂/73% CO₂, caused a significant reduction on the coarse ash yield dropping steadily from 42.5% under the black condition (27% O₂ balanced with CO₂) to 32.5% with 500 ppm V HCl in flue gas. Since the variation of fine ash yield with HCl content is rather insignificant, it is apparent that the vaporisation of metals as gaseous chloride from char surface was greatly enhanced with...
increasing HCl content in flue gas. The resulting chloride mostly escaped the collection system, rather than condensing into fine ash particles. In contrast, doping SO₂ alone into 27% O₂/73% CO₂ shows a completely different tendency in terms of ash yield. Co-doping HCl (250 ppmV) and SO₂ (500 ppmV) into flue gas is more interesting, which shifted the yields of both coarse ash and fine ash fractions to a level falling between the results obtained from oxy-HCl (250 ppmV) and oxy-SO₂ (500 ppmV). This is a clear sign of the competition of HCl and SO₂ for the partitioning of metals.

![Fig. 1](image1.png)

Fig. 1 The yields of coarse ash and fine ash as a function of bulk gas composition. The symbol Air refers to pure air combustion.

3.2 Influence of Steam Addition
Adding 20% steam in flue gas is the most influential factor in terms of ash yields. As demonstrated in fig. 2, for the coarse ash fraction, wherever HCl and/or SO₂ is present in flue gas, replacing 20% CO₂ by steam caused a substantial increase in its yield. This apparently indicates the inhibitory influence of steam on the vaporization/chlorination of metals. One plausible explanation is the slow oxidation of coal and/or char in abundant steam, which in turn reduced the probability for the char-bound metals to expose into HCl in the gas phase. Moreover, steam has the potential to promote the conversion of chloride into refractory alumino-silicates metal oxides. The resulting Na alumino-silicate can melt at the furnace temperature to promote ash agglomeration. Reduction in the fine ash yield in oxy and oxy-SO₂ cases corresponds to the increase in the corresponding coarse ash fraction yield, further indicating the agglomeration of molten Na₂SO₄ and/or Na alumino-silicates into coarse ash.

![Fig. 2](image2.png)

Fig. 2 Influence of steam on the yields of coarse and fine ash fractions

4. Conclusions
In terms of the vaporization of metals, HCl re-circulation was the most crucial factor promoting the vaporization of metals via chlorination. Re-circulation of SO₂ affected the vaporization of Na via changing the SO₂/HCl ratio in flue gas. Co-existence of steam with HCl and SO₂ is more favorable for the conversion of chlorides into molten alumino-silicates than sulfate. Accordingly, the agglomeration extent of ash particles can be greatly intensified.

5. References