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THE FORMATION AND FATE OF CARBONYL SULFIDE (COS) GAS IN ALUMINIUM SMELTING

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ABSTRACT

Carbonyl sulfide (COS) gas is emitted from aluminium smelters at concentrations of 1 – 8 ppmv or 0.2 – 1.6 kg t\(^{-1}\) Al produced. While COS emissions are relatively small compared to emissions of HF or SO\(_2\), previous measurements suggest that COS is not efficiently captured in the scrubbing systems used by aluminium smelters and it has been suggested that the industry is a significant anthropogenic emitter of COS. COS is a unique sulfur gas in the atmosphere, due to its stability, lifetime of several years and implication in ozone depletion.

The source of COS and other sulfur gases from aluminium smelters, is the 1 – 4 mass% S content of anodes, consumed during aluminium electrolysis. These anodes are primarily made from petroleum coke, a low value and therefore high sulfur product, of crude oil refining. This thesis examines aspects of the formation and fate of COS in aluminium reduction cells.

One thesis objective was to confirm the nature of sulfur species present in petroleum cokes and anodes. A XANES (X-ray Absorption Near Edge Structure) spectroscopy study of cokes from the major suppliers and anode core samples showed that organic sulfur containing ring structures were the dominant sulfur species, before and after anode baking and even after significant desulfurisation at 1500ºC.

Thermodynamic calculations performed using the HSC Chemistry© computer package agreed with previous smelter measurements that COS gas was the dominant sulfur gas to form at the anode face and SO\(_2\) became the dominant sulfur gas after the anode gases left the cell and mixed with an induced air draft in the cell hooding.

Previous smelter measurements showed that some COS (about 5 ppmv) did survive through the cell ducting into the dry scrubber and that there were only negligible reductions in COS concentration after dry scrubbing. The dry scrubber contains smelter-grade alumina, which adsorbs HF and other smelter gases, before the alumina is recycled to the cells.
Another objective of this thesis was to study the effect dry scrubbing had on COS emissions in greater detail in the laboratory to better understand any reactions that may be occurring. A thermodynamic analysis using HSC Chemistry© determined that alumina would reduce the stability of COS at a typical dry scrubbing temperature of 80°C. The dry scrubber was modelled in the laboratory using an alumina containing fluidised bed reactor, with the inlet and outlet gas composition monitored using mass spectrometry. Adsorbed species resulting from COS adsorption on alumina were studied separately using DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy).

Experiments showed that COS was stable in the fluidised bed apparatus in isolation. The presence of smelter-grade alumina led to the adsorption of COS in its molecular form and as adsorbed hydrogen thiocarbonate. The latter species is believed to be an intermediate in the hydrolysis of COS into H₂S on alumina. The effect of conditions which may vary in the dry scrubbing system, such as humidity, SO₂ and HF concentrations, were studied. The presence of optimum humidity levels ensured sustained hydrolysis of COS over several hours, but adsorbed SO₂ and HF interfered with COS conversion. This suggests that COS hydrolysis would be unlikely to occur to a great extent in commercial dry scrubbers used in the aluminium smelter industry.
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<td>$E^0$</td>
<td>V</td>
<td>Standard electronic potential for redox reaction</td>
</tr>
<tr>
<td>EDS</td>
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<td>Energy Dispersive Spectroscopy</td>
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<tr>
<td>EXAFS</td>
<td></td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FTIR</td>
<td></td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td></td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>FLY</td>
<td></td>
<td>Fluorescence Yield</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>Gaseous species</td>
</tr>
<tr>
<td>GC-MS</td>
<td></td>
<td>Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>HTC</td>
<td></td>
<td>Hydrogen thiocarbonate (adsorbed species)</td>
</tr>
</tbody>
</table>
### Symbol/Abbreviation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
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<tbody>
<tr>
<td>hv</td>
<td>eV</td>
<td>Energy of the x-ray source in XPS</td>
</tr>
<tr>
<td>I</td>
<td>torr/ppmv</td>
<td>Ionisation correction factor</td>
</tr>
<tr>
<td>k</td>
<td></td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>Equilibrium constant for reaction</td>
</tr>
<tr>
<td>KE</td>
<td>eV</td>
<td>XPS kinetic energy</td>
</tr>
<tr>
<td>L</td>
<td>mm</td>
<td>Fluidised alumina bed height</td>
</tr>
<tr>
<td>L_c</td>
<td>Å</td>
<td>Crystallite size</td>
</tr>
<tr>
<td>m/z</td>
<td></td>
<td>Mass to charge ratio of ions in mass spectrometer</td>
</tr>
<tr>
<td>p_a</td>
<td>torr</td>
<td>Partial pressure of gas ( a )</td>
</tr>
<tr>
<td>p_{ab}</td>
<td>torr</td>
<td>Background partial pressure of gas ( a )</td>
</tr>
<tr>
<td>p_{ac}</td>
<td>torr</td>
<td>Partial pressure of gas ( a ) at time of calibration</td>
</tr>
<tr>
<td>P_T</td>
<td>torr</td>
<td>Total pressure</td>
</tr>
<tr>
<td>r</td>
<td></td>
<td>Reaction rate</td>
</tr>
<tr>
<td>RH</td>
<td>%</td>
<td>Relative humidity</td>
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<tr>
<td>SEM</td>
<td></td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SRC</td>
<td></td>
<td>Synchrotron Radiation Center</td>
</tr>
<tr>
<td>TEY</td>
<td></td>
<td>Total Electron Yield</td>
</tr>
<tr>
<td>V_0</td>
<td>ms^{-1}</td>
<td>Superficial gas velocity in fluidised bed</td>
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<tr>
<td>[x]</td>
<td>ppmv, kmol</td>
<td>Concentration of species ( x )</td>
</tr>
<tr>
<td>XANES</td>
<td></td>
<td>X-ray Absorption Near Edge Structure Spectroscopy</td>
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<tr>
<td>XPS</td>
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<td>X-ray Photoelectron Spectroscopy</td>
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<td>X-Ray Diffraction</td>
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<td>XRF</td>
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<td>X-Ray Fluorescence</td>
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<tr>
<td>y_a</td>
<td></td>
<td>Mole fraction of gas ( a )</td>
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</tbody>
</table>