



**ANLECR&D project**

**Milestone Report for Project 6-1212-0221 on  
“Gas quality impacts, assessment and control in oxy-fuel technology for  
CCS: Part 2. Mercury removal with SO<sub>3</sub> in the fabric filter and with NO<sub>x</sub>  
as liquids in CO<sub>2</sub> compression”**

# **Mercury and SO<sub>3</sub> capture by the fabric filter in oxy-fuel technology**

by

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## Executive Summary

The ANLECR&D project - Gas quality impacts, assessment and control in oxy-fuel technology for CCS: Part 2. Mercury removal with SO<sub>3</sub> in the fabric filter and with NO<sub>x</sub> as liquids in CO<sub>2</sub> compression - is based on reduction of cost and risk associated with CO<sub>2</sub> gas quality in the Callide Oxyfuel Project (COP) and for future oxyfuel technology deployment. The present report details the component on mercury removal with SO<sub>3</sub> in the fabric filter. The removal of mercury is critical in avoiding the cost and risk of corrosion in brazed aluminium cryogenic heat exchangers of the CO<sub>2</sub> Processing Unit (CPU). SO<sub>3</sub> determines the acid dew point temperature and therefore the exit flue gas temperature and its associated energy loss. Both mercury and SO<sub>3</sub> are known to be partially removed in the fabric filter.

The aim of the research is that by testing “real” oxyfuel flue gas passing the fabric filter at the COP together with related controlled laboratory measurements on “synthetic” flue gas contacting ash the work will quantify and provide understanding of the impact of Hg and SO<sub>3</sub> capture by ash in the fabric filter prior to the CPU.

Previous experiments funded by Glencore (formerly XSTRATA Coal) have been conducted for the University of Newcastle at the University of Stuttgart to investigate oxy-fuel process configurations on a once-through pilot-scale furnace to simulate different extents of oxy-fuel recycle gas treatment and associated capture of mercury and SO<sub>3</sub> by fly ash. These experiments used the same coals (but different samples) as used in the Aioi test furnace of IHI used for the COP feasibility study, and they provided the ash samples for the present controlled laboratory measurements.

The analysis of fly ash collected in the Stuttgart experiments with oxy-firing showed greater sulfur and mercury levels than those for air firing, both conditions had low carbon-in-ash levels.

*..... Greater capture of both mercury and sulfur gases is expected by “clean” ash with C-in-ash levels less than 0.1% in oxy-firing compared to air-firing, with the difference being coal specific.*

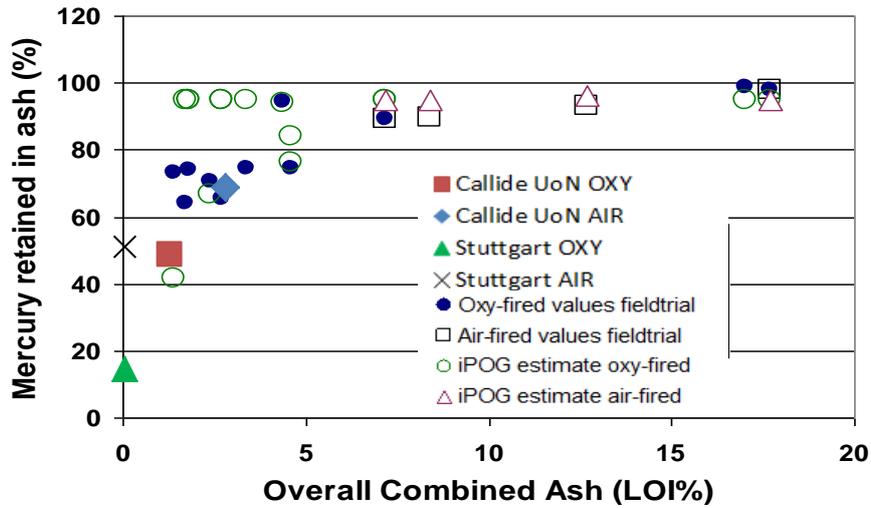
In experiments on the COP fabric filter, mercury in the flue gas passing the filter was collected on activated carbon beds for average measurements over a defined period, and an Ohio Lumex RA-915+ Elemental Hg Analyser logged continuous mercury data. SO<sub>3</sub> was measured by the Controlled Condensation Method. Thus the degree of oxidation and capture of gaseous mercury was estimated, as oxidised mercury species (Hg<sup>2+</sup>) are generally water soluble and can be removed during scrubbing of the flue gas, prior to compression whereas the non-oxidised mercury (ie elemental Hg<sup>0</sup>) is not soluble. The COP fabric filter tests on 30/06/14 and 01/07/14 also involved measurements taken on the stack during Air-Oxy transitions.

A summary of the results for capture in experiments relevant to fabric filtration at pilot and laboratory scale as well as from the COP is given in the Table 1, followed by conclusions and practical implications, on the measured capture, acid dew-point implications and measurements during transitions of air-oxy firing. As the ash amount and contact time differs between the three scales, only trends in capture can be compared, not magnitudes.

**Table 1: Summary of mercury and SO<sub>3</sub> capture by filter ash experiments completed at the University of Newcastle, Stuttgart and Callide Oxyfuel Project (COP). ND-not determined**

		<b>Laboratory experiments</b>	<b>Pilot-scale at Stuttgart</b>	<b>Full scale FF tests at COP</b>
Aim		Determine sensitivity on mercury capture to gas composition and temperature for low C-in-ash and synthetic gas of Hg <sup>0</sup> , SO <sub>2</sub> , SO <sub>3</sub> , H <sub>2</sub> O	Determine capture for low C-in-ash and doped combustion gas	Determine practical capture on FF with real oxyfuel gas
Overview		Synthetic gas passed through ash collected at pilot scale at Stuttgart	Flue gas from once-through combustion doped with Hg <sup>0</sup> and SO <sub>2</sub> in oxidant – both inlet and outlet gas of FF measured	Measurements of gas exiting COP FF fired with Callide coal – no inlet gas measurements
Expt variables, upstream gas comp range	Ash	Ash from Callide coal	From 3 coals, including Callide	From Callide coal
	SO <sub>3</sub> in, ppm	0, 10, 15	10-30	ND, ~ 9 ppm from calculation
	Hg in ug/m <sup>3</sup>	0, 5, 10 as Hg <sup>0</sup>	9-32, with Hg <sup>++&gt;</sup> Hg <sup>0</sup>	ND
	C-in-ash, %	<0.1	<0.1 with <0.2 for one coal	1.5
	Temp, °C	90, 120, 150, 200	195-225	150, and variable during air/oxy transitions
Measured capture by ash, %; downstream gas comp range	SO <sub>3</sub> %; ppm	ND	24-69%; 2-15 ppm	16% capture of SO <sub>2</sub> , SO <sub>3</sub> <0.03 ppm indicating >90% capture
	Hg %; ug/m <sup>3</sup>	Systematic reduction in capture with temperature increase, increase by H <sub>2</sub> O, variable sensitivity to SO <sub>3</sub> in experiments, with gas/ash reaction indicated at high SO <sub>3</sub>	13-52%, with HgO capture > Hg <sup>2+</sup> capture; 5-20 ug/m <sup>3</sup>	92-99%, based on full release of coal Hg on combustion, with Hg <sup>2+</sup> commonly > 80% of Hg; <0.01 ug/m <sup>3</sup> as Hg <sup>0</sup>
Competition between SO <sub>3</sub> and Hg capture		Observed, but FF temperature more sensitive	Not observed	Not observed

*Mercury capture.* Figure 1 presents the mercury capture data. The laboratory and pilot-scale Stuttgart measurements are associated with ash with very low C-in-ash, and therefore provide results for mercury capture by ash, rather than the well-known retention by its unburnt char. The sensitivity to temperature was found to be most significant. The COP experiments agree with the data obtained at the COP in a previous ANLECR&D study by Macquarie University (here fieldtrial) where >80% removal is achieved with a C-in-ash > 5%. The iPOG predictions also reported by Macquarie University generally under predict the measurements.



**Figure 1: The mercury retained on ash for various ash carbon contents from [26], and including current Stuttgart and COP data.**

The intercept on Figure 1 is for “clean” ash with low C-in-ash, with low mercury capture.

..... *The results emphasise that for C-in-ash > 5%, mercury capture by a fabric filter is high (>80%) with little impact on ash quality.*

*SO<sub>3</sub> capture by fabric filter ash and acid-dew point (ADP) temperature.* Based on measured SO<sub>3</sub> concentrations, the H<sub>2</sub>SO<sub>4</sub> dew point temperatures were measured and also calculated according to ZareNehzhad’s [18] correlation, which gives the lines of Figure 2, indicating regions for air and oxyfiring from the pilot-scale Stuttgart measurements, estimates for the COP based on 1% conversion of SO<sub>2</sub> to SO<sub>3</sub> and the capture limit for the condenser temperature used at the COP experiments. The COP SO<sub>3</sub> levels and ADP temperatures are less than the Stuttgart values. This is partially due to differing air leakage at the two scales, but most COP measurements fell below the 0.03ppm capture limit, which may be due to condensation prior to the fabric filter outlined on Figure 3.

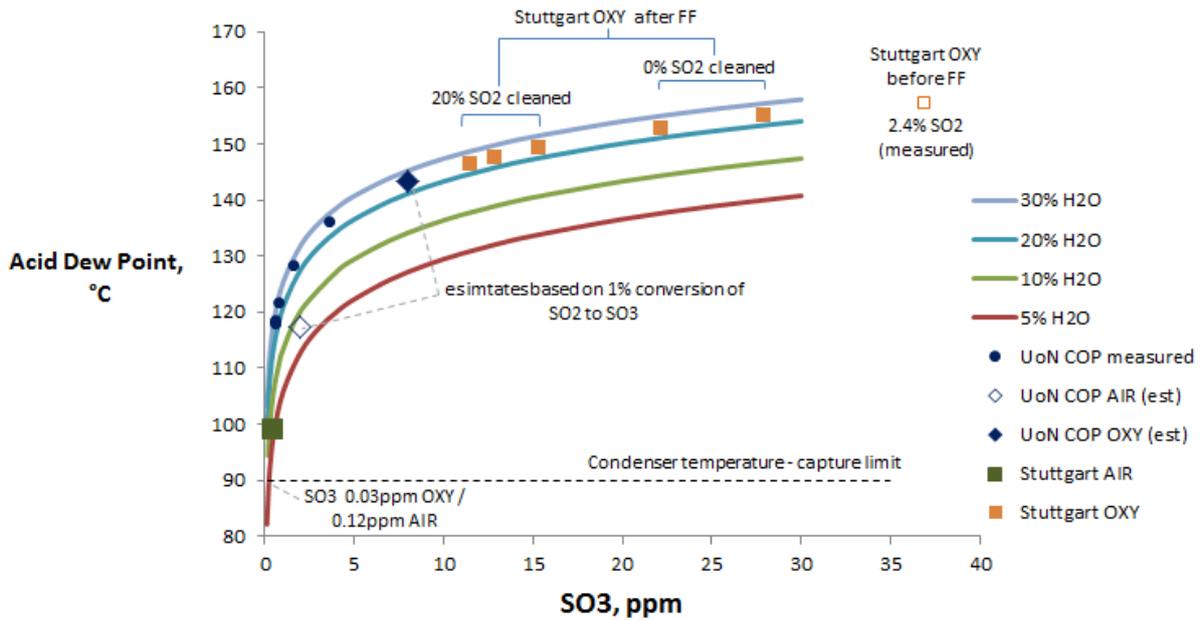


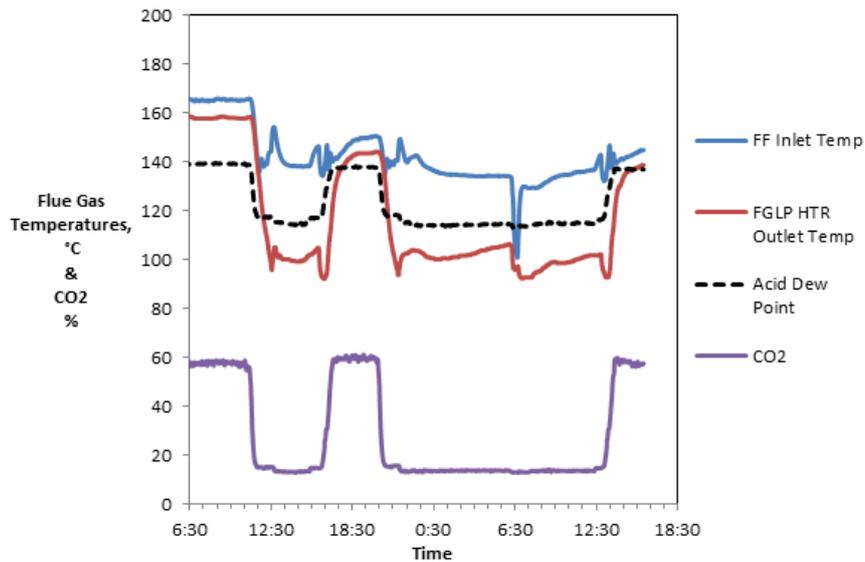
Figure 2. Acid dew point calculations for different  $SO_3$  and  $H_2O$  levels. UoN estimates of COP acid dew point are based on 1% conversion of measured  $SO_2$  (based on Table 11) and assume no  $SO_3$  capture across the Fabric Filter. Stuttgart results are taken from  $SO_2$  injection levels to match configuration cases of 0%  $SO_2$  cleaning and 20%  $SO_2$  cleaning of the recycled flue gas using measurement taken before and after the Fabric Filter. At the condenser temperature of  $90^\circ C$  used for “controlled condensation” of  $H_2SO_4$  (see Figure 20) the minimum  $SO_3$  detectable is shown to be 0.03 and 0.12 ppm respectively for oxy and air-firing.

..... The sensitivity of the acid dew point temperature can be related the gas composition using ZareNehzhad’s correlation, which gives a sensitivity to increased  $SO_3$  and  $H_2O$  levels, both being higher on oxy-firing compared to air firing.

Competition between mercury and  $SO_3$  capture. The pilot-scale and COP experiments did not indicate competition for their capture, but the “scientific” laboratory involving low C-in ash samples.

..... The results indicate that competition between mercury and  $SO_3$  by ash can be neglected for practical C-in-ash (2%) levels.

Transitions between air and oxy-firing:  $SO_3$ : The measured  $CO_2$ , FF inlet and temperatures at the outlet of FGLP heater located prior to the fabric filter are given on the figure under, with the estimated ADP.



**Figure 3: Flue gas temperatures and flue gas CO<sub>2</sub> content during COP measurements of transition between air and oxy-firing.**

During the transitions the ADP temperatures are seen to fall below the FGLP outlet gas temperatures so that acid gas condensation will occur. Thus the SO<sub>3</sub> of the inlet to the fabric filter will be reduced, and the measurements of the flue gas exiting the fabric filter will not be related to ash capture of SO<sub>3</sub> alone.

..... *The results emphasise that process units that may operate at temperatures below the ADP will be prone to acid attack, and are a practical issue in oxyfuel technology, as suggested here during transitions (and also previously during weekly start up and shut down at the Vattenfall pilot-plant) .*

*Transitions between air and oxy-firing: Hg:* The experimental data obtained during the transitions may be split into two regimes based on the measured CO concentrations during the transitions. During periods of high CO, the effect of lower burnout and (inferred) higher levels of carbon-in-ash resulting in high mercury capture levels. During periods of low CO, the capture extent is lower due to (inferred) lower carbon-in-ash.

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## 1 Background

With a growing awareness on the increased greenhouse gas emissions and their contribution to climate change, CO<sub>2</sub> capture and storage (CCS) technologies for coal-fired power generation were developed to concentrate the CO<sub>2</sub> for processing and sequestration. Oxy-fuel combustion is one of these CCS technologies. In oxy-fuel operation, coal is burned with a mixture of oxygen and recirculated flue gas, instead of air. The mixing of O<sub>2</sub> with recirculated flue gas is, among other issues, necessary to lower the temperature in the furnace which otherwise would exceed the limits of construction materials of the boiler [1]. Due to the lack of dilution of the flue gas by airborne nitrogen in oxy-fuel operation, the concentrations of flue gas components such as CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O generally increase considerably by a factor of around 4 [2, 3].

Various oxy-fuel process configurations (wet/dry recycle, environmental control units) as well as process conditions (recycle rate, residence time and thermal profile) are possible and have a significant impact on the concentration and reactions of impurities, such as NO<sub>x</sub>, SO<sub>x</sub> and Hg [4, 5]. For safety and corrosion protection, these impurities must be controlled and the choice of control units will ultimately affect plant cost and waste streams.

During combustion and along the flue gas path, SO<sub>3</sub> is formed from SO<sub>2</sub> in a homogeneous (bi- or trimolecular) gas phase reaction (Eq. (1)) or in a heterogeneous, solids catalysed reaction for example on iron oxide in ash [6, 7].



The following parameters generally have a significant influence on the formation of SO<sub>3</sub>:

- sulfur content of coal (SO<sub>2</sub> partial pressure)
- alkaline/earth-alkaline content of the ash
- oxygen partial pressure
- content of catalytic active compounds in the ash (e.g. Fe<sub>2</sub>O<sub>3</sub>)
- temperature-residence time profile of the plant
- application of gas cleaning equipment (SCR, FGD, filters, sorbent injection)

The sulfur content of the coal, which affects directly the SO<sub>2</sub> partial pressure, is the most important parameter, influencing the concentration of SO<sub>3</sub>. Higher sulfur contents cause higher SO<sub>2</sub> and therefore higher SO<sub>3</sub> concentrations [8]. Another very important parameter is the content of alkaline and earth-alkaline compounds in the ash which can capture SO<sub>3</sub> in the flue gas forming sulfates. SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> can also be separated from gas phase effectively by adsorption or by condensation on fly ash particles at temperatures near or below the sulfuric acid dew point temperature [9]. The SO<sub>3</sub>

formation is also influenced by the content of catalytically active compounds in the ash (e.g.  $\text{Fe}_2\text{O}_3$ ), with higher contents leading to higher  $\text{SO}_3$  formation [7].

Catalytic  $\text{SO}_3$  formation is highly dependent on temperature, with a maximum of the  $\text{SO}_2/\text{SO}_3$  conversion at about  $700^\circ\text{C}$  [10] and takes place on entrained fly ash particles, as well as on ash deposits [11]. The homogeneous formation, just as the catalytic  $\text{SO}_3$  formation, clearly shows a temperature-dependent behaviour [8]. Both are relatively slow [7], which is the reason why in practical firing systems, no equilibrium concentrations of  $\text{SO}_3$  can be observed. Therefore, the temperature-residence-time-profile of the flue gas in a plant is one of the main influencing factors on the  $\text{SO}_3$  formation [6, 8]. Also, the  $\text{O}_2$  concentration in the flue gas has a direct influence on the  $\text{SO}_3$  formation rate, which increases with increasing oxygen content [8, 12]. Besides the above mentioned fuel properties and operating parameters, installed flue gas cleaning equipment has a considerable impact on  $\text{SO}_3$  concentrations. For example, 0.5-2% of the  $\text{SO}_2$  can be catalytically oxidized to  $\text{SO}_3$  in SCR De $\text{NO}_x$  systems, leading to increased  $\text{SO}_3$  concentrations [7, 9]. In flue gas cleaning systems, such as FGDs, ESPs, baghouse filters or by injection of sorbents,  $\text{SO}_3$  concentrations can also be reduced considerably [6].

In practice,  $\text{SO}_2/\text{SO}_3$  conversion rates between 1 and 5% [13] with  $\text{SO}_3$  concentrations up to about 40 ppm in air-fired and over 180 ppm in oxy-fuel-fired facilities have been observed [14, 15]. However, in a comprehensive study by Fleig et al. [8], no clear trend was observed on the conversion rates between air and oxy-firing.

At temperatures below about  $400^\circ\text{C}$  gaseous sulfuric acid ( $\text{H}_2\text{SO}_4$ ) starts to form from the reaction of  $\text{SO}_3$  and water vapour and reaches complete transformation at approximately  $200^\circ\text{C}$  [16, 17]. The dew point of the formed  $\text{H}_2\text{SO}_4$  depends on the concentrations of  $\text{H}_2\text{O}$  and  $\text{SO}_3/\text{H}_2\text{SO}_4$ . It can be calculated based on those species according to ZareNehzhad [18]. In power plants,  $\text{H}_2\text{SO}_4$  dew points typically range between  $95$  and  $160^\circ\text{C}$ . With increased  $\text{H}_2\text{O}$  and  $\text{SO}_3/\text{H}_2\text{SO}_4$  concentrations in oxy-fuel, considerably higher dew points can be found. When temperature falls below the  $\text{H}_2\text{SO}_4$  dew point,  $\text{H}_2\text{SO}_4$  from gas phase starts to condense. In power plants, relevant temperatures are found in the region of air pre-heaters, where substantial problems due to low temperature corrosion can occur [18]. Therefore, generally the air/oxidant pre-heater outlet temperature is limited to temperatures above the acid dew point, which limits the utilization of the flue gases' sensible heat and thereby lowers the plant's efficiency. In cold parts of power plants, fouling by sulfate deposits can be a severe problem triggered by  $\text{SO}_3/\text{H}_2\text{SO}_4$ .

Mercury speciation during combustion, that is the partitioning of mercury as elemental ( $\text{Hg}^0$ ) and oxidized ( $\text{Hg}^{2+}$ ) vapor and particulate-Hg ( $\text{Hg}^P$ ), is thought to determine its retention in gas cleaning

technologies. This is proven for scrubbers, as  $\text{Hg}^{2+}$  is soluble, whereas  $\text{Hg}^0$  is not. For fabric filters it is less certain.

Unburnt carbon (i.e. coal char, or carbon in ash on filters) is known to collect mercury due to its high surface area [19], but the relative collection of  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  appears to depend on coal rank. If the collection process involves physical adsorption, then other species such as  $\text{SO}_3$  will compete with mercury compounds.

## 2 Objective

The overall objective of this project is to provide new knowledge that can be applied to reduce the cost and risks associated with  $\text{CO}_2$  gas quality in the Callide Oxyfuel Project (COP) and to future oxyfuel technology deployment in Australia and elsewhere. The removal of mercury species prior to  $\text{CO}_2$  liquefaction is critical in avoiding the cost and risk of corrosion in brazed aluminium cryogenic heat exchangers of the CPU.

The method applied in this research has been to test “real” oxyfuel flue gas at the COP together with related controlled laboratory measurements on “synthetic” gas in order to:

- (i) Quantify and provide understanding of the impact (reduction) of Hg capture due to  $\text{SO}_2/\text{SO}_3$  with associated high acid dew point temperature by ash in the fabric filter in oxyfuel combustion; and
- (ii) Quantify and provide understanding of Hg removal in oxyfuel flue gas compression and the stabilisation of the liquid during pressure reduction required for its disposal.

This report specifically details the research work undertaken on item (i) above only.

As oxyfuel flue gas passes a fabric filter it is expected that  $\text{SO}_3$  and mercury gases are partially captured, thereby also reducing the acid dew point temperature which is determined by  $\text{SO}_3$ . However,  $\text{SO}_3$  affects mercury capture, and so it is possible that the reduction of both gases will decrease compared to their capture without the other gas. It is well known that mercury attaches to unburnt carbon and the present study attempts to eliminate this variable by using ash with low levels of unburnt carbon.

The controlled laboratory measurements includes further analysis of ash samples collected in the Stuttgart experiments and apparatus to examine capture of sampled ash which was assembled for the Callide tests [20]. The project continues work reported in a previous ANLECR&D project [21].

### **3 Experiments of sulfur and mercury capture by ash during air-fired and oxy-fuel combustion**

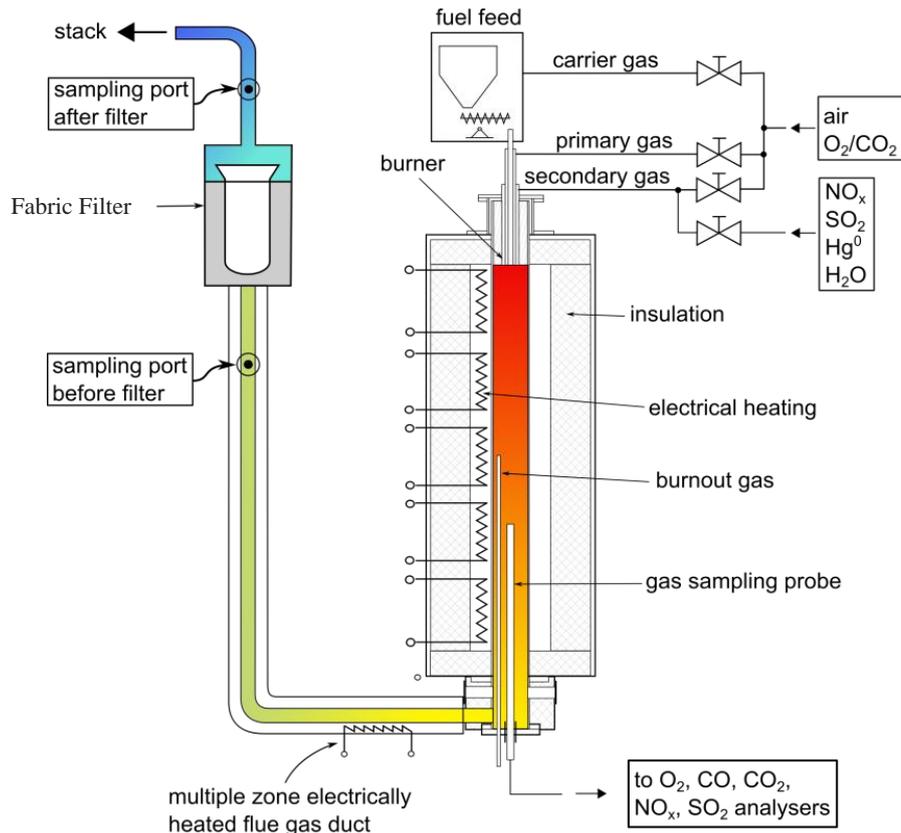
Experiments previously conducted by the University of Stuttgart for the University of Newcastle [20] to investigate oxy-fuel process configurations, with impurities injected to the oxidant gas, were completed on a once-through reactor to simulate different extents of oxy-fuel recycle gas treatment. Three Australian coals, which have previously been tested in the Aioi furnace of IHI by CCSD [3], were used in the experiments. The capture of  $\text{SO}_x$  and Hg in a baghouse filter was evaluated.

The collected ash has been characterized in the present study and also has been used in further experiments to study the capture of sulfur and mercury gases. The measurements for sulfur capture were also converted to acid dew point temperatures to allow for the determination of plant efficiency impacts.

#### **3.1 Capture measured at the University of Stuttgart pilot-plant**

Experiments were carried out utilising a 20 kW electrically heated once-through combustion rig (Figure Figure 4) of the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany. The electrically heated furnace was operated at a wall temperature of 1350°C. Some of the generated flue gases were drawn through an electrically heated flue gas duct (remaining gas going to an exhaust), in which the gas temperature drops from approx. 700°C to 200°C in approximately 4 seconds. Flue gas enters the heated bag-house filter at gas temperatures of approximately 190°C to 270°C and exits at about 185°C to 205°C. The fabric filter was cleaned regularly to counteract a drop in the flue gas flow rate and therefore in the flue gas residence time in the system. Comprehensive  $\text{SO}_3$  and Hg measurements were performed before and after the bag-house filter. The bag filter was cleaned prior to each  $\text{SO}_3$  sampling.

To simulate the flue gas recycle of an oxy-fuel process with impurities present in the recycled gas, the oxidant gas was doped with desired amounts of  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{Hg}^0$  and  $\text{H}_2\text{O}$ . This highly flexible method allows for an investigation of oxy-fuel combustion with simulation of different extents of recycle gas treatment (e.g.  $\text{SO}_2$  removal rate) and impurity levels in coal.



**Figure 4: Schematic of the experimental combustion rig used for air and oxy-fuel investigations at IFK showing the filter simulating the fabric filter and for collection of ash samples, with sampling ports before and after the filter**

To enable a comparison of the results with previous studies, the three Australian coals (A, B and C) used in this study came from similar sources as those previously tested by IHI [3]. The coals are from the same mine as the samples tested by IHI but are different samples. Coal properties are listed in Tables 2 and 3.

**Table 2: NCV, proximate, elemental and Hg analyses of the three investigated Australian coals**

Coal	NCV [kJ/kg]	W [% ad]	A [% db]	V [% daf]	FC [% daf]	C [% daf]	H [% daf]	N [% daf]	S [% daf]	O <sup>1</sup> [% daf]	Hg [mg/kg, daf]
Coal A	18026	3.9	32.5	35.9	64.1	73.8	4.3	1.1	0.3	20.5	0.07
Coal B	24956	1.5	23.0	50.6	49.4	78.3	6.7	1.1	0.7	13.2	0.04
Coal C	26748	3.7	9.8	35.9	64.1	77.2	5.2	2.0	0.7	15.0	0.02

<sup>1</sup> Calculated by subtraction

**Table 3: Analysis of coals by ICP-OES for main ash forming elements (based on a direct analysis of raw, unmilled coal samples for ash forming minerals, without previous ashing)**

Coal	SiO <sub>2</sub> [%]	Al <sub>2</sub> O <sub>3</sub> [%]	Fe <sub>2</sub> O <sub>3</sub> [%]	CaO [%]	MgO [%]	SO <sub>3</sub> [%]	K <sub>2</sub> O [%]	Na <sub>2</sub> O [%]	TiO <sub>2</sub> [%]	P <sub>2</sub> O <sub>5</sub> [%]
Coal A	58.9	26.2	6.8	1.2	0.7	3.0	0.4	0.1	2.4	0.2
Coal B	64.4	21.5	1.2	0.4	0.7	7.2	0.4	0.2	3.9	0.0
Coal C	33.2	23.0	11.4	7.0	1.8	22.7	0.9	1.3	1.2	1.8

The differences between the oxy-fuel experiments were established by the injection rates of the flue gas impurities H<sub>2</sub>O, NO, SO<sub>2</sub> and Hg<sup>0</sup>. By variation of the injection, different removal rates of the impurities from the recycled gas between 0 and 100% were simulated.

**Table 4: List of experimental settings and simulated removal rates**

Index	Coal	Experimental settings					
		air/oxy	Simulated capture rates [%]			Simulated NO conc. in rec. flue gas [ppm, dry]	
			H <sub>2</sub> O	SO <sub>2</sub>	Hg		
<b>A-A</b>		“air”	-	-	-	-	
<b>A-OC</b>		Oxy28 – “clean”	100	100	100	-	
<b>A-O2S5H</b>	Coal A	Oxy28 – called “oxy”	23	23	44	962	
<b>A-O5S5H</b>		Oxy28	23	52	44	962	
<b>A-O2S8H</b>		Oxy28	23	23	79	962	
<b>A-O0S5H</b>		Oxy28	23	4	44	962	
<b>A-O2S0H</b>		Oxy28	23	23	7	962	
<b>A-O0S0H</b>		Oxy28	23	4	7	962	
<b>B-A</b>			“air”	-	-	-	-
<b>B-OC</b>		Coal B	Oxy28 – “clean”	100	100	100	-
<b>B-O2S5H</b>	Oxy28- called “oxy”		24	24	51	949	
<b>C-A</b>		“air”	-	-	-	-	
<b>C-OC</b>	Coal C	Oxy28 – “clean”	100	100	100	-	
<b>C-O2S5H</b>		Oxy28- called “oxy”	23	23	62	959	

Coals were fired in 28% O<sub>2</sub>, with the balance being CO<sub>2</sub>, this corresponding to the IHI tests [3] and are based on a matched radiative heat transfer in the furnace with air firing. The O<sub>2</sub> (dry) of the flue gas was set at 3%.

The experimental settings for experiment O2S5H listed in Table 3 are considered the “practical” oxy-fuel settings where recycled flue gas is separated into primary and secondary gases, with the primary gasses passing a cooler condenser before entering the crushing mill (removing a nominal 20% of H<sub>2</sub>O and SO<sub>2</sub>). Hg is also removed in, for example, a fabric filter at the COP with a nominal 50% removal. NO is also reburnt by volatile matter and char in the furnace, with a nominal 1000 ppm representing a “practical” condition. Table 4 gives the exact settings and resulting capture rates simulated in the experiments.

The “practical” settings are called “oxy” here for convenience.

### 3.1.1 SO<sub>3</sub> capture

Figure 5 shows SO<sub>3</sub> capture rates calculated based on measured SO<sub>3</sub> concentrations before and after the combustion rig fabric filter. In the plot capture rates calculated from very low concentrations and the ones from experiments A-O2S5H and A-O0S0H, with unexpectedly high SO<sub>3</sub> concentrations after filter are represented in a light grey colour. It shall be highlighted that those values are of limited significance. Those SO<sub>3</sub> capture rates and the one for the B-OC experiment are relatively low compared to the other experiments.

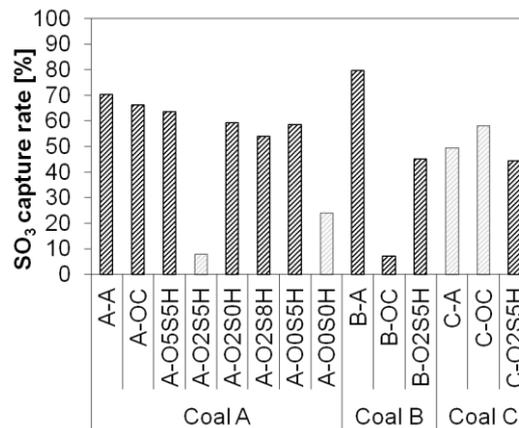


Figure 5: Calculated SO<sub>3</sub> capture rates on the fabric filter

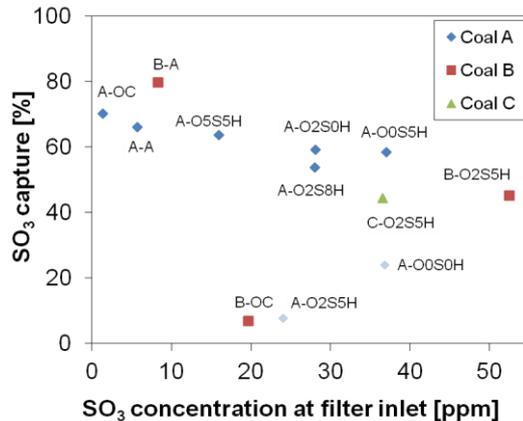


Figure 6: SO<sub>3</sub> capture rate on the fabric filter vs. SO<sub>3</sub> concentrations at the fabric filter inlet for various experiments

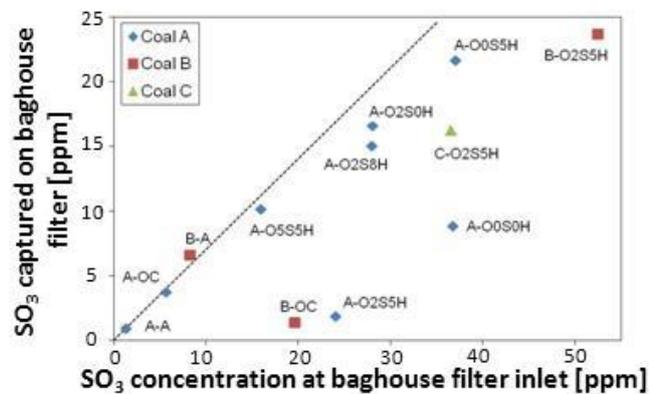


Figure 7: SO<sub>3</sub> capture on the fabric filter vs. SO<sub>3</sub> concentrations at the fabric filter inlet for various experiments.

Under air firing conditions coal B generated the highest capture rate overall, almost 80%. All other oxy-fuel combustion settings generated SO<sub>3</sub> capture rates between about 45 and 65%. For coal A, a tendency of decreasing SO<sub>3</sub> capture rates with decreasing simulated SO<sub>2</sub> removal rates (increasing SO<sub>2</sub> concentrations) was observed, though the actual amount captured increased. This effect is possibly due to the saturation behaviour of the ash on the filter for SO<sub>3</sub> capture, or by an insufficient residence time of the flue gas in the fabric filter for capture of higher amounts of SO<sub>3</sub>. In Figure 6,

SO<sub>3</sub> capture rates are plotted versus SO<sub>3</sub> measured at the fabric filter inlet. It seems that SO<sub>3</sub> capture rates on the fabric filter decrease with increasing SO<sub>3</sub> concentrations at the fabric filter inlet. Figure 7 shows the same data as in Figure 6 but as a concentration rather than a percentage.

In Figure 8 molar Ca/S, Mg/S and (K+Na)/2S ratios of coals A, B and C are related to the SO<sub>3</sub> capture on the filter. It seems that the Ca/S ratio of the coal has a limited influence on the SO<sub>3</sub> capture of the baghouse filter, since coals B and C show very similar SO<sub>3</sub> capture rates even though they differ in their Ca/S ratios by around 680%. Based on the current experiments, it is difficult to conclude whether the Mg/S, the (K+Na)/2S, or both are more relevant to the SO<sub>3</sub> capture on the filter. Both the Mg/S and the (K+Na)/2S ratio of coals B and C are very similar, so as their SO<sub>3</sub> capture rates; while coal A, with higher capture rates shows also higher Mg/S and (K+Na)/2S ratios.

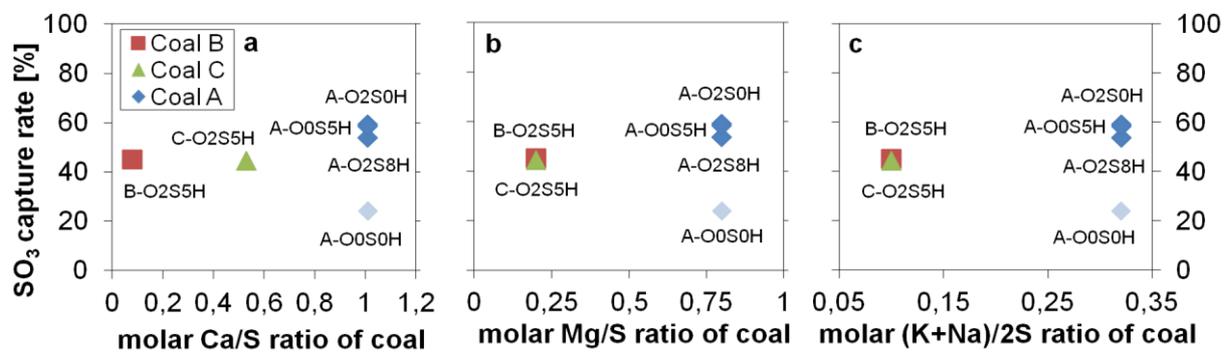


Figure 8: SO<sub>3</sub> capture vs. molar Ca/S (a), molar Mg/S (b) and molar (K+Na)/2S (c) ratios (only experiments with similar SO<sub>3</sub> concentrations at the filter inlet are compared).

### 3.1.2 Calculated Acid Dew Point temperatures/efficiency implications

Based on measured SO<sub>3</sub> concentrations, the H<sub>2</sub>SO<sub>4</sub> acid dew point temperatures (ADP) were calculated according to ZareNehzhad's correlation [18]. The results obtained under air (A), clean oxy-fuel (OC) and the oxy (O2S5H) setting with impurity injection for all 3 coals are shown in Figure 9. ADP temperatures of 93 to 163°C were calculated before the filter and 86 to 157°C after the filter, with coal B, which has the lowest molar Ca/S ratio, having the highest APDs. H<sub>2</sub>SO<sub>4</sub> dew point temperatures under air conditions were 12-27 K below those of the clean oxy-fuel and 41 to 67 K below those of the oxy-fuel configurations with SO<sub>2</sub> and H<sub>2</sub>O injection. The SO<sub>3</sub> capture on the filter was equivalent to a reduction of the H<sub>2</sub>SO<sub>4</sub> dew point temperature between 1 and 16 K.

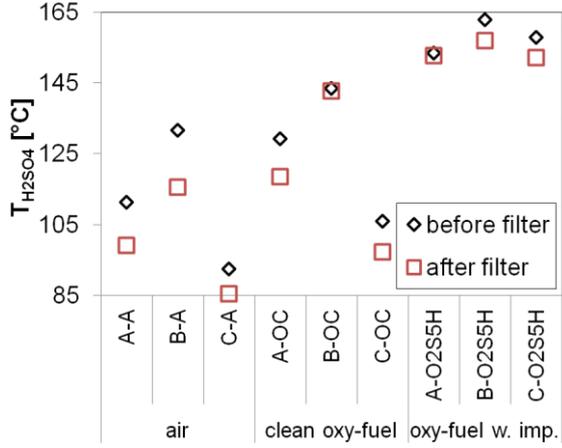


Figure 9: Calculated H<sub>2</sub>SO<sub>4</sub> dew points before and after filter for coals A, B and C

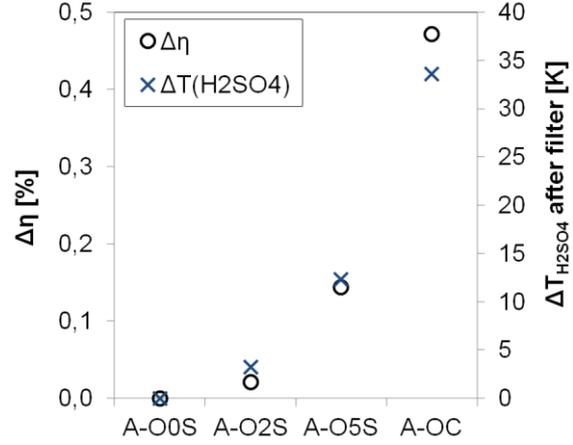


Figure 10: Differences in acid dew point temperatures and respective process efficiencies for coal A oxy-clean (OC) and 20% (O2S) and 50% (O5S) SO<sub>2</sub> removal settings, compared to an uncleaned recycle configuration O0S

In Figure 10 differences in the acid dew point temperatures of the experiments with 50 and 20% SO<sub>2</sub> removal (O5S, O2S) and the clean oxy-fuel experiment (OC) compared with the experiment without SO<sub>2</sub> removal (O0S) are presented. At lower ADPs, the oxidant pre-heater can be safely operated at lower temperatures, which can increase a plant's efficiency. Based on ADPs, the flue gas composition and the NCV of coal A, equivalent efficiency gains ( $\Delta\eta$ ) on the basis of the configuration without SO<sub>2</sub> removal were calculated, according to equation (3).

$$\Delta\eta = \frac{m_{FG,O0S}c_{p,FG,O0S}T_{H_2SO_4,O0S} - m_{FG,1}c_{p,FG,1}T_{H_2SO_4,1}}{NCV} \times 100 \quad (3)$$

Where:

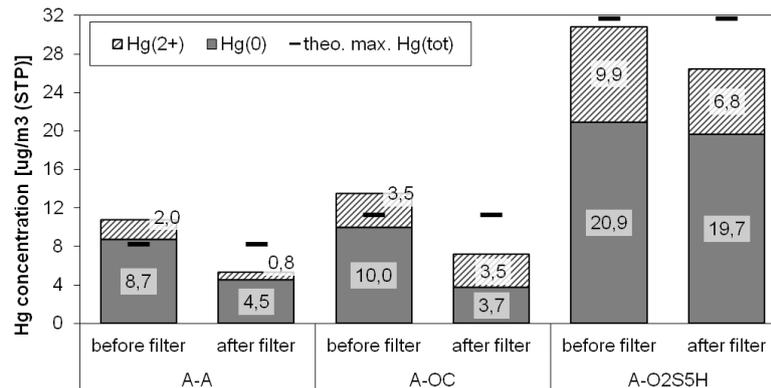
$m$  refers to the mass flow of flue gas,  $C_p$  is the specific heat of the flue gas and  $T_{H_2SO_4}$  is the acid dew point temperature at conditions of different SO<sub>2</sub> cleaning (ie FG,O0S) compared with no SO<sub>2</sub> cleaning (ie. FG,1)

One observes a minor efficiency benefit of 0.02% from partial (20%) recycle gas desulfurization and a considerable benefit of 0.14% for 50% desulfurization. The clean oxy-fuel configuration has an efficiency benefit potential of 0.47%, which is relatively high due to a combined effect of low SO<sub>3</sub> and low H<sub>2</sub>O concentrations. It should be considered that the efficiency benefit of the clean oxy-fuel configuration is of limited significance, since a complete H<sub>2</sub>O and SO<sub>2</sub> removal from recycled flue gas would require a cooling of the gas to temperatures far below the H<sub>2</sub>SO<sub>4</sub> dew point. The equivalent efficiency gain by allowing for lower oxidant pre-heater outlet temperatures due to the reduction of the SO<sub>3</sub> concentrations when passing the fabric filter were also calculated and reached between 0.3

and 0.7 % for air and between 0.01 and 0.11 % oxy-firing conditions. These numbers illustrate the potential that sorbents for SO<sub>3</sub> reduction might have to improve the oxy-fuel process efficiency.

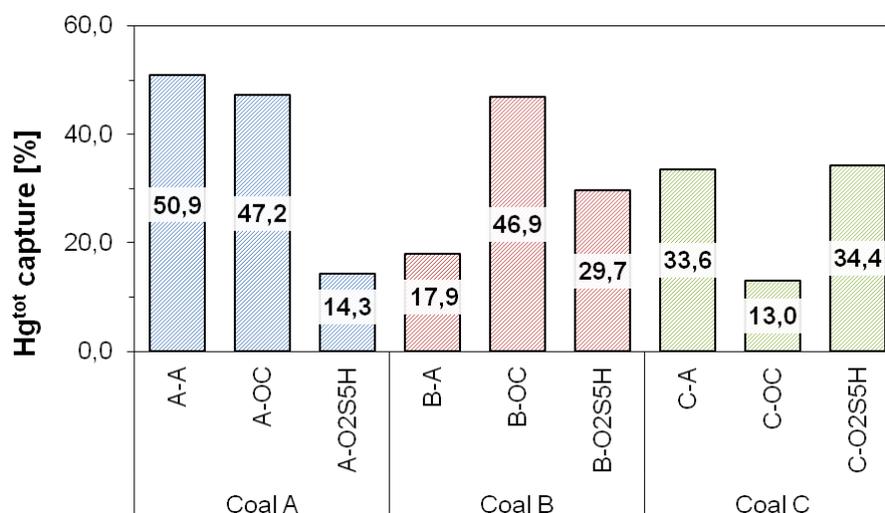
### 3.1.3 Mercury capture

Figure 11 gives Hg<sup>0</sup> and Hg<sup>2+</sup> concentrations before and after the fabric filter for the air, clean oxy-fuel and oxy (O2S5H) experiments with coal A. Hg<sup>0</sup> is seen to dominate the Hg species from in the flue gas entering the filter, both Hg<sup>0</sup> and Hg<sup>2+</sup> being removed as the gases pass the ash on the filter.



**Figure 11: Measured Hg<sup>0</sup> and Hg<sup>2+</sup> concentrations before and after the fabric filter measured during air (A-A), clean oxy-fuel (A-OC) and oxy (A-O2S5H) combustion of coal A. In addition, corresponding theoretical maximum Hg concentrations are shown.**

In all experiments considerable amounts of mercury were captured on the fabric filter. Based on the measured Hg<sup>0</sup> and Hg<sup>2+</sup> concentrations before and after the fabric filter, the capture rates of all mercury species (Hg<sub>tot</sub>) were calculated. Figure 12 shows the Hg<sub>tot</sub> capture rates for coals A, B and C in air, clean oxy-fuel and oxy (O2S5H) operation.



**Figure 12: Hg<sub>tot</sub> capture rates for coals A, B and C in air, clean oxy-fuel and oxy (O2S5H) operation**

Capture rates between 13 and 52% were obtained. A clear difference between air and oxy-fuel settings could not be observed, but different coals produced different behaviours.

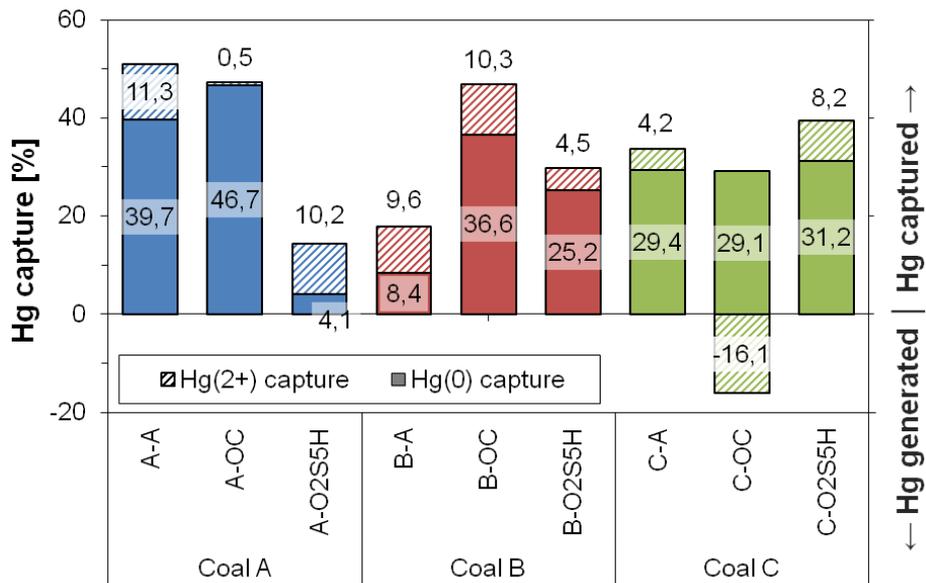


Figure 13: Contribution of  $Hg^0$  and  $Hg^{2+}$  capture to the total capture rates for coals A, B and C in air, clean oxy-fuel and oxy (O2S5H) operation.

The capture of the different Hg species was evaluated in greater detail by calculation of individual  $Hg^0$  and  $Hg^{2+}$  capture rates on the fabric filter. The results are presented in Figure 14. It is observed that in most experiments the  $Hg_{tot}$  reduction is mainly caused by a reduction of elemental Hg ( $Hg^0$ ). In most cases the reduction of  $Hg^{2+}$  accounts only for about 20% or less of the  $Hg_{tot}$  reduction. In one case, even an increase of the  $Hg^{2+}$  concentration was measured. Such behaviour can be explained assuming that the fabric filter is working not only as a Hg capture unit, but also oxidizing  $Hg^0$  to  $Hg^{2+}$ .

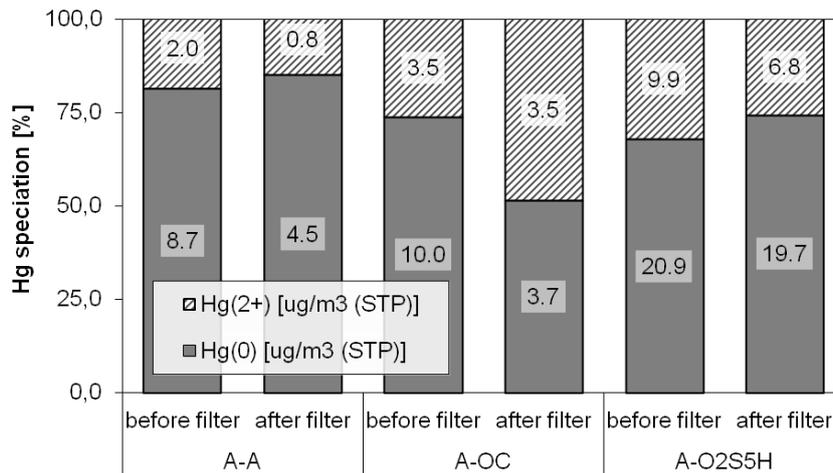


Figure 14: Ratios between elemental and oxidized Hg forms measured for coal A and the air, the clean oxy-fuel and the oxy (O2S5H) setting (numbers in the plot represent concentrations of  $Hg^0$  and  $Hg^{2+}$ ).

Figure 14 shows the ratios between elemental and oxidized mercury forms measured for coal A. It can be observed that in many cases the ratio between  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  shifts towards  $\text{Hg}^{2+}$  when the flue gas passes through the filter.

### 3.1.4 Competition for capture by ash between sulfur and mercury gases

*SO<sub>3</sub> capture* was measured on the fabric filter. Capture rates were, except for few instances, in the ranges between 45 and 65 %. A clear difference between different combustion regimes (e.g. air, clean oxy-fuel, oxy-fuel with injection of  $\text{SO}_2$ ) was not observed. The extent of  $\text{SO}_3$  capture rates on the baghouse filter reduced slightly with increasing  $\text{SO}_3$  concentrations at the filter inlet. This suggests some kind of saturation behaviour of the capture mechanism.

*Hg was captured* when the flue gas passed through the fabric filter. Capture rates between approximately 10 and 50 % were measured, with most of the settings having capture rates between about 20 and 30 %. In almost all experiments, the ratio between  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  shifts towards  $\text{Hg}^{2+}$  when the flue gas passes through the fabric filter. In some cases, this goes together with an increase of the absolute  $\text{Hg}^{2+}$  concentrations, while  $\text{Hg}^0$  concentrations are decreasing in all cases. A possible explanation for this behaviour is that in the fabric filter  $\text{Hg}^0$  could be oxidized to  $\text{Hg}^{2+}$  along with the capture of both species.

*A competition between  $\text{SO}_3$  and Hg for sorption sites in the ash* and therefore a decreasing capture of Hg with increasing  $\text{SO}_3$  concentrations *was not observed*. Possibly, due to the high ash content of coal A, a saturation of sorption sites was not reached in the performed experiments.

## 4 Laboratory measurements for capture of sulfur and mercury by fly ash

### 4.1 Ash characterisation related to capture

Ash samples from the Stuttgart experiments were analysed to characterise the capture of sulfur and mercury, these being collected in the bag filter located as detailed on Figure 4.

#### 4.1.1 Ash analysis

Table 5 presents the ash analysis and unburnt carbon analyses.

**Table 5: Ash oxide and Unburnt Carbon Analysis of the Fly Ash Samples used in the experiments.**

Dry Basis %	Fly Ash Sample					
	A		B		C	
	Air (A-A)	Oxy (A-O2S5H)	Air (B-A)	Oxy (B-O2S5H)	Air (C-A)	Oxy (C-O2S5H)
SiO <sub>2</sub>	55.2	52.9	68.7	69	53.8	53
Al <sub>2</sub> O <sub>3</sub>	33.3	34	25.2	24.2	25.9	26.5
Fe <sub>2</sub> O <sub>3</sub>	6.55	7.13	1.62	2.16	8.55	8.34
CaO	0.95	1.41	0.73	0.87	4.55	4.66
MgO	0.741	0.98	0.716	0.737	1.558	1.667
Na <sub>2</sub> O	0.144	0.158	0.25	0.275	0.971	0.979
K <sub>2</sub> O	0.512	0.518	0.627	0.604	1.11	1.058
TiO <sub>2</sub>	2.06	2.16	1.77	1.65	1.15	1.13
MnO <sub>2</sub>	0.097	0.113	0.002	0.008	0.04	0.041
P <sub>2</sub> O <sub>5</sub>	0.178	0.275	0.134	0.176	1.364	1.508
SO <sub>3</sub>	0.132	0.243	0.186	0.28	0.932	0.969
BaO	0.042	0.056	0.067	0.063	0.067	0.072
SrO	0.049	0.069	0.034	0.036	0.094	0.1
<b>Total</b>	100	100	100	100	100	100.0
% Carbon (Unburned)	< 0.1	< 0.1	0.106	< 0.1	0.134	0.199

The ash samples produced in the oxy-fired experiments contain higher sulfur levels compared to air-fired samples. This is expected due to the higher SO<sub>2</sub> levels in the flue gas during the experiments, given on Table 6.

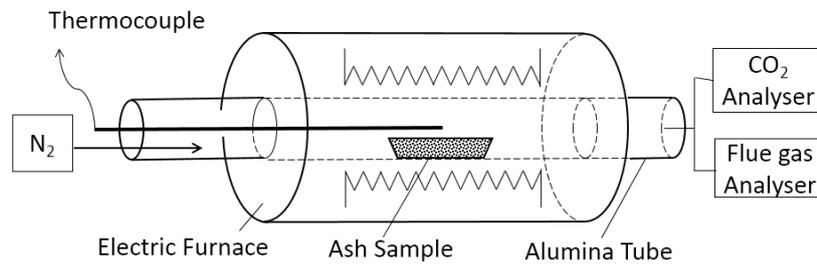
**Table 6: SO<sub>2</sub> concentrations in the oxidant and flue gas entering the bag filter during University of Stuttgart experiments**

Coal Sample	SO <sub>2</sub> in the oxidant ppm (dry)		SO <sub>2</sub> in flue gas ppm (dry)	
	Air (-A)	Oxy (-O2S5H)	Air (-A)	Oxy (-O2S5H)
<b>A</b>	0	824	199	1235
<b>B</b>	0	1569	367	2578
<b>C</b>	0	1723	444	2802

#### 4.1.2 Ash heating experiments – sulfur release

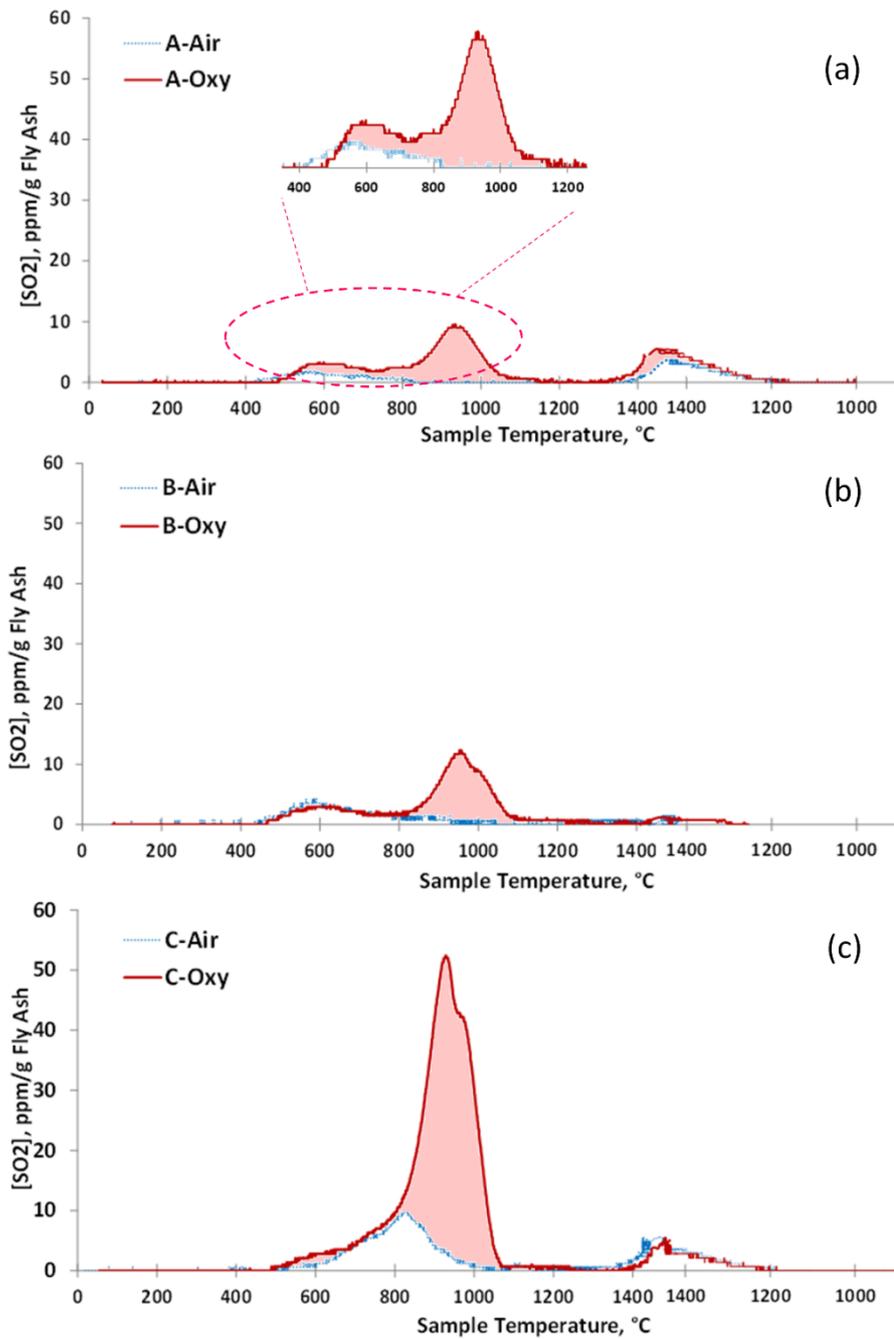
The collected fly ash samples were characterised by thermal decomposition in a horizontal tube furnace. In all experimental runs, a nitrogen carrier gas was used with a flow rate of 1.5 L/min, maintained using a calibrated Dwyer rotameter. Two 3 ml alumina crucibles containing a combined mass of approximately 1.0 gram of ash were placed in the reactor tube and heated at a rate of 5°C/min to 1400°C ± 20 K. This heating rate was selected based on previous experiments to optimize the operating conditions. The samples filled the crucibles to roughly half the crucible height and the sample temperature was measured by a type K thermocouple supported next to the ash samples. To ensure that decomposition of the samples were complete, the samples were maintained at 1400°C for a minimum period of at least 2 hours. Decomposition gases were passed on through CO<sub>2</sub> infrared analyser (Vaisala) and a Gas Analyser (Testo 350XL) to continuously measure the concentration of

the different gases ( $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$ ). All experiments were completed at atmospheric pressure. Figure 15 shows a schematic of the experimental setup.



**Figure 15** The experimental equipment used in decomposition experiments used to determine the sulfur absorbed on the fly ash samples.

Figure 16 shows the experimental results for the ash samples produced in air and oxyfuel conditions for each of the three coals. It can be noted that for all fly ash samples used, changing conditions from Air to Oxy firing has increased the amount of sulfur species (as  $\text{SO}_2$ ) evolved during the decomposition. The light, dotted (blue) lines in the figures show air-firing derived fly ash whilst the solid (red) lines represent the fly ash derived from oxy-firing.



**Figure 16: Thermal Gas Evolution from the Decomposition of Fly Ash under an inert atmosphere ( $N_2$ ). The shaded region represents the difference between sulfur evolved from Oxy and Air fired fly ash for samples A, B and C.**

Five main points can be deduced from this plot:

- (1) The evolution of sulfur species was found to be aligned when the plots were drawn against one another indicating that similar sulfur species evolve at similar temperatures from air and oxy-fired samples with only a slight shifting of the evolution temperature which is probably due to small changes in ash composition.
- (2) Oxy fly ash  $SO_2$  release is 2-3 times greater compared to Air fly ash, as evident by integration of the area under the curve.

- (3) Between 400°C and 800°C, a wide primary peak of sulfur release with a smaller shoulder peak is observed from all fly ash samples (see enlarged image in Figure 16).
- (4) Between 800°C and 1100°C, a strong secondary can be observed which is more significant in oxy-fuel fly ash.
- (5) It can be noted that a third set of peaks occurs at temperatures higher than 1300°C. This may indicate that during the sintering of the fly ash, some high temperature sulfur species, possibly associated with slag particles are evolved.

The temperatures of decomposition peaks give an indication of the sulfur species present. For sulfates as the dominant species, decomposition will be found between 400°C and 800°C for iron, aluminium and magnesium sulfates; and higher than 1000°C for potassium, sodium and calcium sulfates.

### 4.1.3 Ash sample total sulfur

By integrating the area under the curves of the experimental results of the ash heating experiments, detailed in Section 4.1.2 above, the total amount of sulfur released was determined. This represents the sulfur present in species that can decompose (up to 1400°C) and is compared to the total amount of sulfur present in the ash, determined by the Eschke method [22]. The Eschke method is a gravimetric technique which digests the sample using acid, converting all sulfur into sulfate, which is then precipitated as barium sulfate. The Eschke method was used for total sulfur because a significant portion of the sulfur may be trapped in the amorphous (eg glassy) fraction of the fly ash. This amorphous material may not release the sulfur prior to 1400°C (as observed in Figure 16). Importantly, the Eschke method uses acid digestion rather than high temperature to remove the sulfur species and thus provides an improved measurement of the total sulfur in the fly ash.

**Table 7: Comparison of the total sulfur in the fly ash samples with the amount of sulfur that is released upon heating.**

Fly Ash Sample	Sulfur Content		Percent of sulfur that is decomposable (%)
	mg S/g FA		
	Total sulfur (Eschke)	Decomposable sulfur	
A-Air (A-A)	1.71	0.85	50%
A-Oxy (A-O2S5H)	2.00	1.67	83%
B-Air (B-A)	1.29	0.48	38%
B-Oxy (B-O2S5H)	1.59	1.09	68%
C-Air (C-A)	4.21	1.65	39%
C-Oxy (C-O2S5H)	4.95	4.05	82%

Sulfur-retention behaviour of fly ash from Oxy-fuel experiments is greater than that of its air-firing counterpart. However, a significant proportion of the sulfur is not released when the ash is heated, indicating that this sulfur is present in a form which does not decompose at temperatures below

1400°C. This may be due to the slagging of the fly ash, resulting in the encapsulation of sulfur in the slag.

#### 4.1.4 Total mercury in ash – Ash heating experiments – mercury release

Filter ash from the University of Stuttgart experiments produced during air combustion contained less mercury than ash produced in oxy-fuel experiments. For Coal A, shown in Table 8, air combustion ash contained 0.0043 µg Hg/g ash, while the ash produced during oxy-fuel combustion (experiment A-O2S5H) contained 0.0056 µg Hg/g ash. This is an increase in mercury content of 31%. The difference in mercury content of Coal C from the two firing modes was 218%. Increased mercury capture by fly ash during oxy-fuel combustion is expected due to the simulated partial recycle of the gas stream containing mercury, resulting in an increase in total mercury of 56% in the flue gas of the –O2S5H oxy-fuel experiments. Variability in the difference in the amount of mercury captured by the oxy-fuel experiments and the air experiments, listed in Table 8, is due to the amount of unburnt carbon in the ash samples. Unburnt carbon captures mercury most efficiently. Samples produced in the experiments B-A, C-A and C-O2S5H contained a small amount of unburnt carbon, listed in Table 5.

**Table 8: The mercury content of bag filter ash samples.**

Fly ash sample	Hg Content	
	ng Hg/g FA	
	Air (-A)	Oxy (-O2S5H)
A	4.292	5.637
B	1.243	1.482
C	0.819	2.602

Flue gas flowrates through all the experiments were maintained at 9-10 m<sup>3</sup>/h and so variation in total gas volume, resulting in lower flowrates and longer residence times across the filter cannot explain the differences observed in the results.

## 4.2 Laboratory capture experiments at the University of Newcastle

The University of Stuttgart experiments show that mercury is captured by fly ash though the mechanism is unclear and the rates of capture in air and oxyfuel appears to be dependent on the coal fired. Speciation of the mercury before and after the bag filter also appears to be dependent on the components of the flue gas. While the oxy experiment simulating the complete cleaning of the flue gas before recycle and the air experiment found a significant reduction in the Hg<sup>0</sup> species in the flue gas across the filter, the experiment simulating oxyfuel combustion with flue gas recycled without cleaning produced a reduction in the Hg<sup>2+</sup> across the filter. Though it was postulated that this may be due to the presence of sulfur species in the gas, further experiments with different levels of sulfur in

the flue gas did not show consistent results. Further work was clearly required to understand the mercury and sulfur capture by ash.

An apparatus was constructed for experiments to quantify the capture of sulfur and mercury from “synthetic” flue gas by ash on the Fabric Filter. Oxy-fuel derived ash was used from the University of Stuttgart experiments. This apparatus also has the same gas analysis train used in experiments at the COP, and so was also utilised to develop analytical techniques for these tests.

#### 4.2.1 Laboratory apparatus for capture of mercury and SO<sub>2</sub>/SO<sub>3</sub> by ash simulating a bag filter and gas analysis train (also used for COP tests).

Figure 17 is a schematic of the laboratory apparatus used for the ash capture experiments, comprising SO<sub>2</sub> injection, SO<sub>3</sub> generation, Hg<sup>0</sup> injection, ash in the bag filter simulator then gas analysis. Nitrogen containing 1000 ppm SO<sub>2</sub> is passed at 2 L/min through a water bath at 30°C to saturate the gas to 2% H<sub>2</sub>O. Mass flow controllers were used to maintain accurate gas flows. The saturated gas was then passed through a packed bed of fly ash (2 grams) collected from the filter of the University of Stuttgart experiments, held in a 1 inch O.D. quartz tube, heated to 700°C by an electrically heated tube furnace. This arrangement was found to catalytically produce SO<sub>3</sub> at a concentration of 18 ppm, which is diluted further to 10-12 ppm before reaction with filter ash.

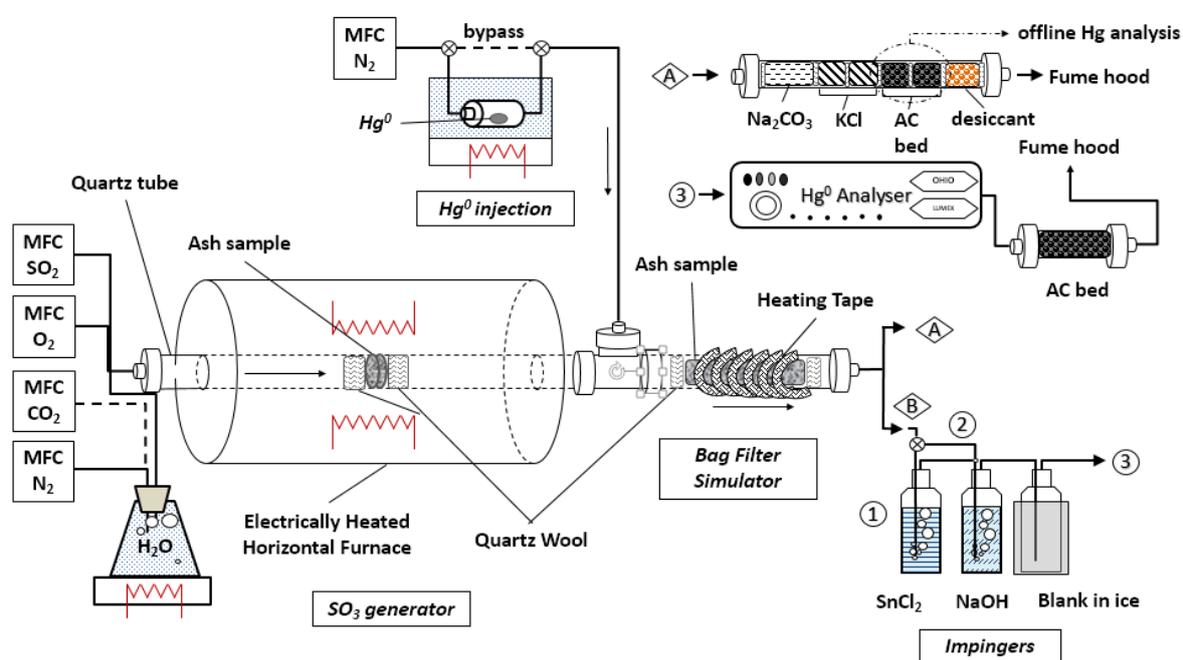


Figure 17: Experimental apparatus for determining the capture of SO<sub>3</sub> and Hg on bagfilter ash.

Mercury was injected into the gas stream after the SO<sub>3</sub> generating ash by passing 1 L/min of N<sub>2</sub> across a mercury permeation tube situated in a water bath maintained at 30°C. This produced a flow of Hg<sup>0</sup>

gas at 15000 ng/m<sup>3</sup> in the Hg injection line and 5000 ng/m<sup>3</sup> in the combined combined gas line at 3 L/min. Increasing the temperature of the mercury permeation tube to 40°C increased the mercury concentration in the combined gas line at 3L/min to 10,000 ng/m<sup>3</sup>. The gas mixture of N<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub> and Hg<sup>0</sup> was then allowed to pass through a second packed bed of ash (2 grams) held in a 1 inch O.D. quartz tube to simulate the interaction between flue gas and fly ash at the bag filter. The second packed bed of fly ash was maintained at temperature by a heating tape wrapped around the quartz tube. Four temperatures: 90°C, 120°C, 150°C and 200°C were used in this investigation, simulating the temperatures of a bag filter.

To complete the analysis of the fluegas stream, the gas was allowed to pass through a solution of equal volumes of 0.05 molar SnCl<sub>2</sub> and 0.1 molar HCl, which converts Hg<sup>2+</sup> to Hg<sup>0</sup>. The gas was then made to pass through a solution of NaOH with a pH greater than 10 to capture any sulfur present in the gas stream before the gas passed through an empty impinger in an ice bath to condense water from the gas. The total mercury in the gas stream was then measured by an on-line Ohio Lumex RA-915+ mercury spectrometer.

To measure the Hg<sup>0</sup> in the gas stream coming from the bag filter ash, rather than the total mercury present in the gas, the SnCl<sub>2</sub> impinger was removed from the gas train. Being soluble in water, any Hg<sup>2+</sup> was collected by the NaOH impinger. Hg<sup>2+</sup> was then calculated by difference between the total mercury and the Hg<sup>0</sup> measurements.

Mercury collected by the “bagfilter” ash samples was determined at the end of the test by heating 0.7g of the ash in the solids tray of the OhioLumex RA-915+ mercury spectrometer. The remainder of the ash sample was used to determine the sulfur collected by the ash. This was completed by the Eschke total sulfur analysis [22].

A second analysis option is also outlined in Figure 16 as option A. This method was not used in the tests completed here due to the resulting pressure drop across the cartridge which was too large for the quartz tubing used in the experimental setup, but was nonetheless trialled during development of the experiment and used in the COP tests. In this technique the gas is passed through a ½ inch O.D. PFA tube packed with granular Na<sub>2</sub>CO<sub>3</sub> (for S removal), followed by KCl (to convert Hg<sup>2+</sup> to Hg<sup>0</sup>), then several layers of activated carbon (for Hg<sup>0</sup> capture prior to analysis) and finally a desiccant to absorb moisture from the gas. Each layer of the packing was separated by quartz wool. Several layers of activated carbon are used to ensure all mercury in the gas stream was collected; achieved when the final layer of activated carbon does not contain any absorbed mercury. This method provides a total measurement of mercury, or Hg<sup>2+</sup> if the KCl is eliminated from the tube.

The ash samples used in the experiments were from the University of Stuttgart experiments for coal A as collected in the baghouse filter of Figure 4, with analyses of Table 5.

For the COP tests where gas samples were made in the stack, following the bag filter, the same analysis train was used, again with options A and B for batch and continuous measurements. The NaOH used in the impinger train was exchanged for 0.1 molar NaCO<sub>3</sub> to avoid capture of CO<sub>2</sub> from the flue gas which would bias final Hg concentrations.

#### 4.2.2 SO<sub>3</sub> estimation

Initially, the amount of SO<sub>3</sub> generated by the first packed bed of ash when SO<sub>2</sub> was passed through it at 2 L/min was determined by collecting the H<sub>2</sub>SO<sub>4</sub> condensate at 80°C using a water cooled condenser packed with quartz wool. H<sub>2</sub>SO<sub>4</sub> forms from the reaction of SO<sub>3</sub> and H<sub>2</sub>O. The reaction is complete when excess water is present [23-25]. No water is expected to be condensed at this temperature as it is above the dew point for water of 60°C. After collection, the H<sub>2</sub>SO<sub>4</sub> is washed out with distilled water and made up to 100mL in volume. The SO<sub>4</sub><sup>2-</sup> concentration is then determined by ion chromatography and back-calculated to a SO<sub>3</sub> concentration using the gas flow rate and sampling time. With standard water analysis detection limits of 1mg SO<sub>4</sub><sup>2-</sup>/L, a 30 minute sampling time from a 2L/min flow gives a minimum detection limit of 0.42 ppm SO<sub>3</sub>.

For the COP tests, a condenser temperature of 90°C was used to account for the higher water content in the real oxyfuel flue gas. A higher sampling flow rate of 3.5L/min was used to collect more H<sub>2</sub>SO<sub>4</sub>, bringing the quantification limit down to 0.24 ppm SO<sub>3</sub> for the 30 minute samples during transition and 0.06 ppm SO<sub>3</sub> for the 2 hour samples taken during the steady state before and after transition. Preliminary testing in the laboratory of the short sampling times used for the COP tests confirmed that the lower amount of collected material was able to measure the same concentrations of SO<sub>3</sub> as with larger time intervals.

#### 4.2.3 Capture of mercury and SO<sub>x</sub> by ash

The aim of the laboratory experiments was to establish the sensitivity to mercury capture due to SO<sub>3</sub>. Four variables were identified that may change the amount of mercury captured by the fly ash: the amount of mercury present in the flue gas, the SO<sub>3</sub> concentration in the flue gas which is altered by the SO<sub>2</sub> and H<sub>2</sub>O concentrations, and the temperature of the collecting ash. Each of the variables are listed in the experimental design shown in Table 9. All experiments contacting gas with ash were completed over 30 minutes.

**Table 9: Details of the laboratory experiments for mercury and SO<sub>3</sub> capture by bag filter (BF) ash, giving inlet gas compositions**

<b>Experiment type</b>	<b>Hg(0) μg/m<sup>3</sup></b>	<b>SO<sub>2</sub> (SO<sub>3</sub>) ppm</b>	<b>H<sub>2</sub>O %v</b>	<b>BF Temp °C</b>
1: Variable Hg	0, 5, 10	667 (10)	2	150
2: Variable SO <sub>x</sub>	5	0 (0), 667 (10), 1000 (15)	2	150
3: Variable H <sub>2</sub> O	5	667 (10)	0, 2	150
4: Variable BF Temp	5	667 (10)	2	90, 120, 150, 200

Figure 17 shows the mercury species measured in the flue gas of the experiments when the SO<sub>3</sub> concentration was held at 12 ppm and the temperature of the capturing ash was changed from 90°C to 200°C. The majority of the mercury remains in the gas as Hg<sup>0</sup>, with a small conversion to Hg<sup>2+</sup> observed for the lower temperatures. At 150°C and 200°C the measurement of Hg<sup>0</sup> alone provided a larger value than the measurement of Hg<sup>0</sup> & Hg<sup>2+</sup> together.

“Hg captured” on Figure 18 represents the amount of mercury no longer found in the gas stream, a measurement by difference. Capture of mercury by the ash was also measured by heating the ash at the end of the experiment to 680°C and measuring the amount of mercury emitted, though this is not shown in the figure. The mercury released from the ash decreased from 9% of the injected mercury at 90°C to 1% at 200°C. The remainder of the mercury could not be accounted for and this gap in the mass balance varied between 12.2% at 90°C and 0.5% at 200°C. It is possible that mercury was collected on surfaces within the experimental train even though effort was made to eliminate this risk. Experimental error is also included in these values. Capture of mercury, measured both by difference between the feed mercury and the flue gas concentration and by direct measurement of the mercury remaining in the ash at the end of the experiment, decreased with increasing temperature. Therefore the lower the temperature of the bag filter, the better the capture of mercury by the ash.

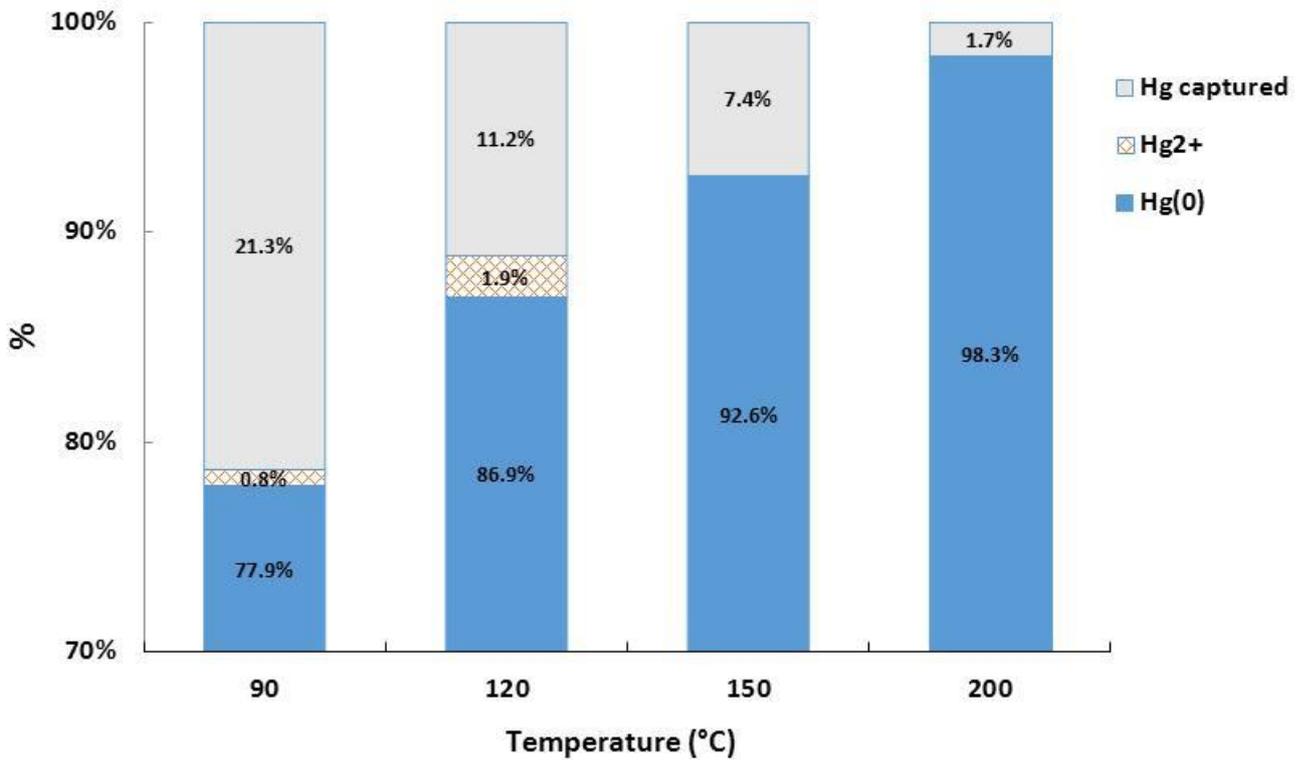


Figure 18: The speciation of mercury in the exit gas ( $\text{Hg}^0$  and  $\text{Hg}^{2+}$ ) after ash contact and mercury not observed in the flue gas (Hg captured) in laboratory experiments with 12 ppm  $\text{SO}_3$ .

Doubling the amount of mercury in the experiment reduced the proportion of mercury in the flue gas, while the amount of mercury retained in the experiment, either on the ash or other surfaces increased from 38 ng (7.4%) to 208 ng (20.9%), shown in Figure 19. No oxidation of mercury was observed in these experiments, consistent with other experiments completed at 150°C and 12 ppm  $\text{SO}_3$ .

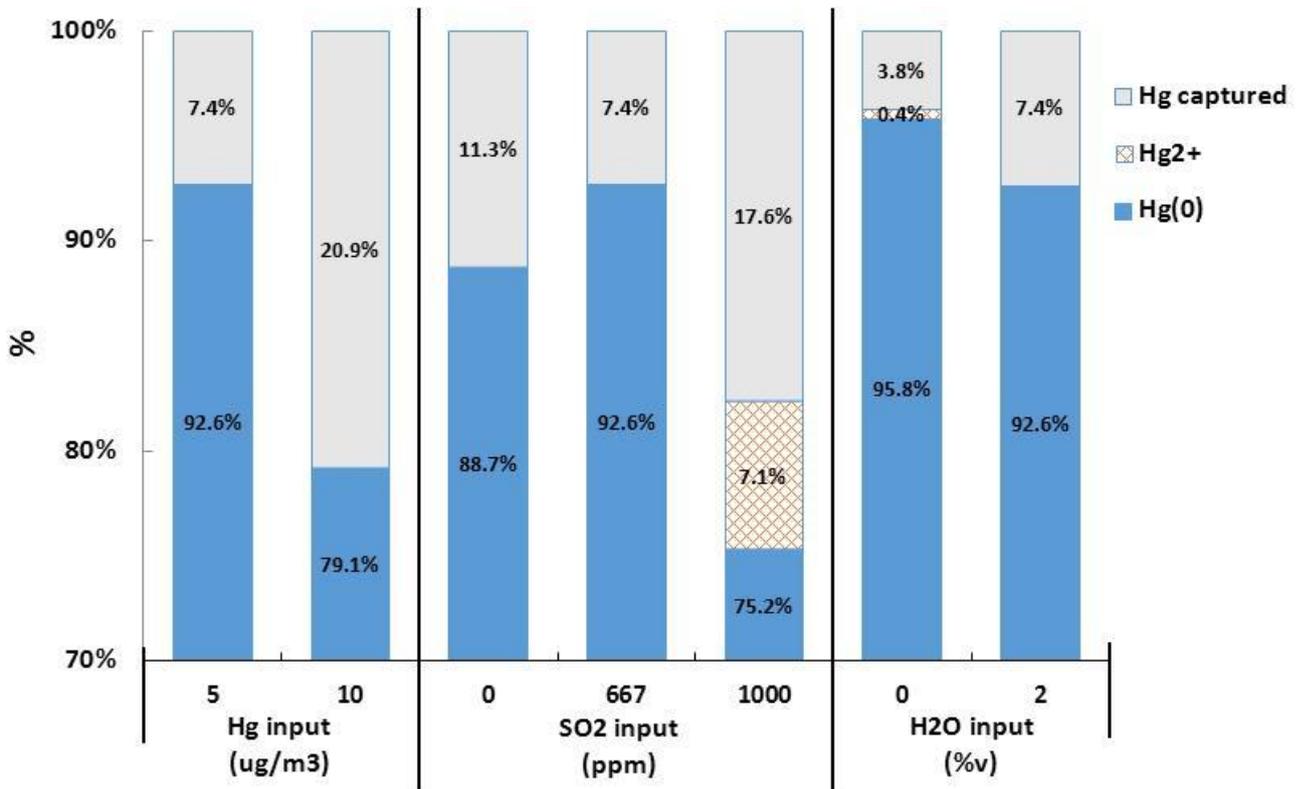


Figure 19: The mercury speciation in the exit gas after ash contact ( $Hg^0$  and  $Hg^{2+}$ ) and mercury not observed in the flue gas (Hg captured) with changing Hg and  $SO_2$  (with associated  $SO_3$  changes from Table 9) and with and without the presence of water in the experimental feed gases. For each of these experiments the filter ash was held at  $150^\circ C$ , other inputs on Table 9.

Increasing the concentration of  $SO_2$  in the feed gas resulted in an increase in the  $SO_3$  concentration produced by the  $SO_3$  generating packed ash bed. Figure 18 shows the changing flue gas mercury species when the feed gas concentration of  $SO_2$  changes from 0 to 667 ppm (or 12 ppm  $SO_3$ ) to 1000 ppm  $SO_2$  (or 15 ppm  $SO_3$ ). Oxidised mercury,  $Hg^{2+}$ , only appears to occur in the flue gas at the highest  $SO_2/SO_3$  concentrations considered. Sulfur species are known to compete for capture sites on activated carbon. It is unclear if the same competition occurs on fly ash with very little carbon content, as in these ash samples. With a “small” amount of sulfur in the gas the amount of mercury assumed to be captured is reduced but with an increased amount of sulfur species the capture is improved.

Figure 19 indicates that the capture by “clean” ash with little carbon is complex, as the data implies reactions between gas and ash which differ with gas composition - note the formation of  $Hg^{2+}$  at high  $SO_2$ .

When the experiment was completed with no water in the feed gases, though the  $SO_2$  concentration was maintained at 667 ppm in the combined gas line before the second packed bed of ash, simulating

a bag filter, the amount of mercury captured by the ash decreased from 7.4% to 3.8%. This indicates that the presence of  $\text{H}_2\text{SO}_4$  does increase the amount of mercury captured, for without water present in the gas stream, no  $\text{H}_2\text{SO}_4$  would form.

#### 4.2.4 Conclusions of the laboratory experiments of Mercury ( $\text{Hg}^0$ ) and $\text{SO}_x$ capture by ash

The following conclusions can be drawn from the laboratory experiments involving ash with low C-in-ash:

- Mercury capture by the ash increases systematically with decreasing temperature, increasing mercury and  $\text{SO}_2/\text{SO}_3$  concentration in the flue gas.
- Only at higher  $\text{SO}_2/\text{SO}_3$  concentrations or low filter temperatures is  $\text{Hg}^{2+}$  observed in the flue gas.
- The formation of  $\text{H}_2\text{SO}_4$  appears to improve mercury capture.

The ash samples used in the laboratory experiments contained very little unburnt carbon. Carbon in ash is known to be highly effective in capturing mercury and would be expected to dwarf the trends found above for the capacity of ash to capture mercury.

### 4.3 Experiments on Hg and $\text{SO}_3$ removal by Fabric Filter at the Callide Oxyfuel Project

#### 4.3.1 Introduction

The University of Newcastle (UoN) has performed three test campaigns at the Callide Oxyfuel Project; the first test campaign using a slip stream of flue gas on a laboratory compressor (October 2013) and the second and third test campaigns for the current ANLEC R&D project focussing on mercury and  $\text{SO}_3$  in the flue gas (May-July 2014). Here, the emphasis is on the third campaign, with Fabric Filter tests running on 30/06/14 and 01/07/14. This involved measurements taken on the stack during Air-Oxy transitions; other measurements testing the volatility of liquid waste products from the CPU will be detailed in a subsequent report.

The Fabric Filter is a well-known mercury removal unit, providing a packed bed of fly ash and unburned carbon with extended ash residence time for the adsorption of gaseous mercury species from the flue gas. The extent of removal is uncertain but the level of residual carbon-in-ash is an accepted adsorption site due to its significant surface area. The basis for the third test campaign was to examine the impact of oxyfuel conditions on mercury concentration and speciation. In particular,

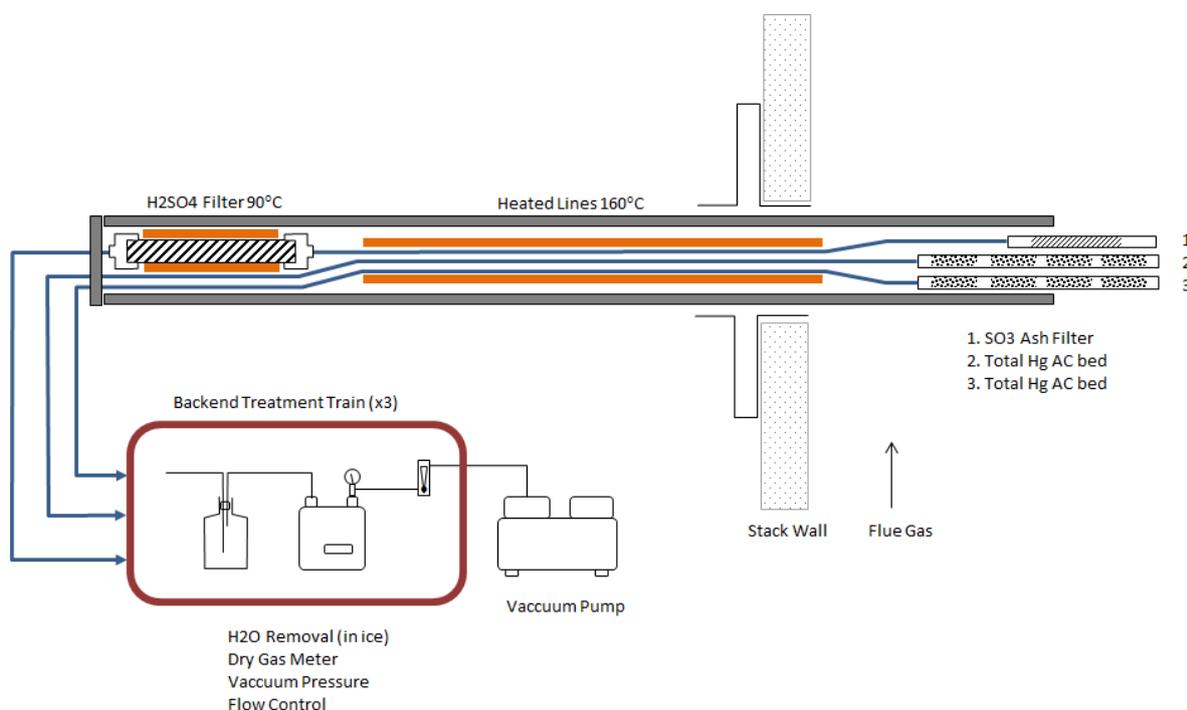
the change in SO<sub>2</sub> concentration (due to recycle) was expected to increase SO<sub>3</sub> concentration and compete for mercury adsorption sites in the fly ash. In a practical application, the level of SO<sub>3</sub> and H<sub>2</sub>O govern the acid dew point (as H<sub>2</sub>SO<sub>4</sub>) and it is expected that oxyfuel conditions will raise the acid dew point by approximately 40-60°C [2], exposing the bag filters to higher temperatures and potentially reducing the adsorption of mercury captured in the fly ash. Reduced mercury capture at the fabric filter has downstream impacts for CO<sub>2</sub> processing, increasing the level of carry over and placing greater emphasis on secondary Hg control measures.

The degree of oxidation of mercury in the gas phase can also have implications downstream as oxidised mercury species (Hg<sup>2+</sup>) are generally water soluble and can be easily removed during the initial quenching and scrubbing of the flue gas, prior to compression. The non-oxidised mercury (ie elemental Hg<sup>0</sup>) is not soluble and will be carried over into compression, requiring tertiary control measures such as passive NO<sub>2</sub> oxidation (tested by UoN) or placement of activated carbon beds. Overall, the uncertainty surrounding the capture of mercury and its speciation in the oxyfuel boiler block has significant downstream ramifications which will ultimately affect commercial design and cost of operation. Targeting the transition period between air firing and oxyfuel firing provided a unique opportunity to establish if there is a causal link between SO<sub>3</sub> levels and mercury capture.

#### ***4.3.2 Experimental Sampling Apparatus***

The sampling of gas phase mercury was taken from the stack using two custom built sampling probes. The first probe (shown in Figure 20) was used for interval sampling of SO<sub>3</sub> and Total Mercury (Hg<sup>2+</sup> and Hg<sup>0</sup>). This probe combined the measurement principles of Method 30b [28] for mercury and the Controlled Condensation Method for SO<sub>3</sub> [29]. Both methods collect a certain amount of sample over time and measure the volume of gas sampled, enabling an average concentration to be calculated. In this case, the mercury in the flue gas was collected on activated carbon beds (in duplicate) which were located at the end of the probe and directly inserted into the hot gas stream. The SO<sub>3</sub> sample was initially filtered in stream followed by collection in a quartz wool filter with a heater control set to 90°C, allowing SO<sub>3</sub> to be collected as condensed H<sub>2</sub>SO<sub>4</sub> without condensing H<sub>2</sub>O. The three gas streams were then passed through an ice bath to condense the water prior to measuring the volume with a dry gas meter. Vacuum pressure and gas temperature was measured after each dry gas meter and the sample flow rates were regulated by rotameter. The activated carbon (AC) beds and SO<sub>3</sub> filter were made from ½” PFA tubing and the sample lines were made from ¼” PFA tubing, with connections between each component made with standard swagelok tube fittings. Combining both interval measurements in a single heated lance allowed for shorter more frequent measurements to be

made and in practice three 30 minute samples were made during each transition. Longer sample intervals were taken at the “steady state” before and after each transition.



**Figure 20. Heated Lance for  $\text{SO}_3$  Controlled Condensation and Total Hg sampling**

The second probe was used to provide a continuous stream of treated flue gas to an online mercury analyser. A Elemental Hg Analyser (Ohio Lumex RA-915+) logged mercury emissions at 1Hz and was located at a level down from the stack gantry. The second probe (shown in Figure 21) was not heated but fitted with an optional quench system to prevent condensation of acid gas and mercury components. The flue gas was optionally passed/bypassed through a  $0.1\text{M SnCl}_2 / 1\text{M HCl}$  solution, intended as a reducing agent for oxidised mercury species to provide an online “Total Hg”. The gas was then passed through a  $1\text{M Na}_2\text{CO}_3$  solution which was intended to capture oxidised Hg and  $\text{SO}_2$  (a species known to interfere with Hg spectral measurements). These solutions were iced to remove  $\text{H}_2\text{O}$  and the gas was then fed through  $\sim 15\text{ m}$  of  $\frac{1}{2}$ ” PFA tubing to the Hg analyser and vacuum pump below. Vacuum pressure was kept at  $\sim 15\text{kPa}$  with the whole gas stream passing through the analyser. The 1<sup>st</sup> (Monday) test regime utilised the switch for the  $\text{SnCl}_2$  “Total Hg” and  $\text{Na}_2\text{CO}_3$  “Elemental Hg”. The 2<sup>nd</sup> (Tuesday) test utilised the  $\text{Na}_2\text{CO}_3$  quench unit pumped with a small peristaltic pump. A comparison of the  $\text{SnCl}_2$  “Total Hg” with the heated lance interval Total Hg showed that the rate of  $\text{Hg}^{2+}$  reduction in the  $\text{SnCl}_2$  solution was unable to keep up with the shortened sampling intervals, resulting in under-measured values for Online Total Hg. Elemental Hg values are still considered valid. Photographs of sampling location, heated and non-heated lances are shown in Figure 22-24 respectively. Figure 25 shows both lance inserted in the stack.

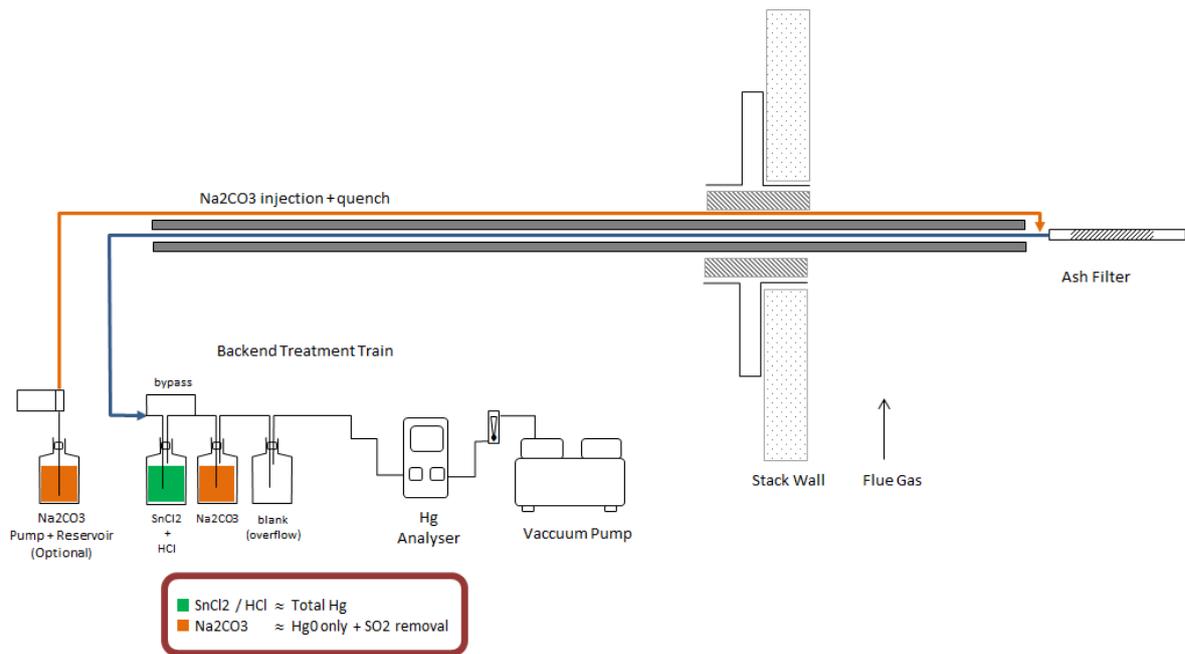
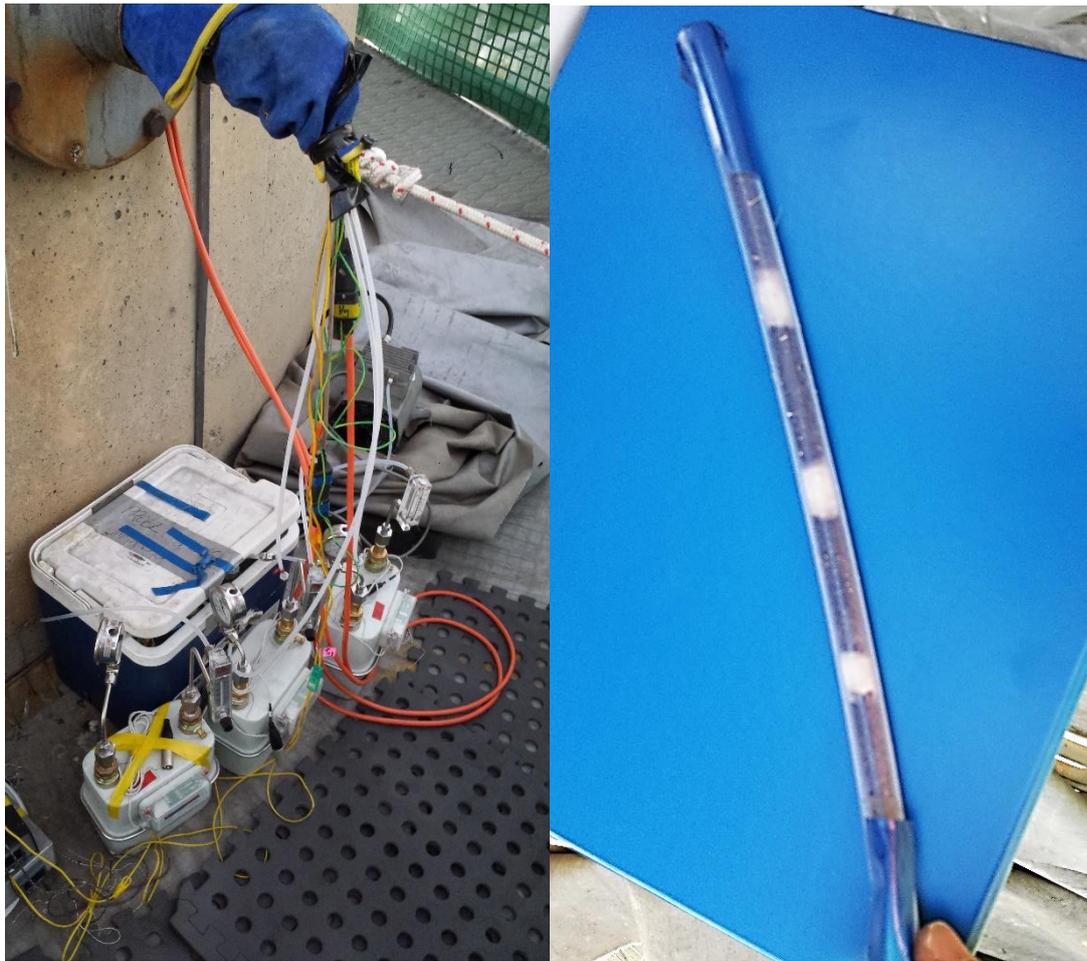


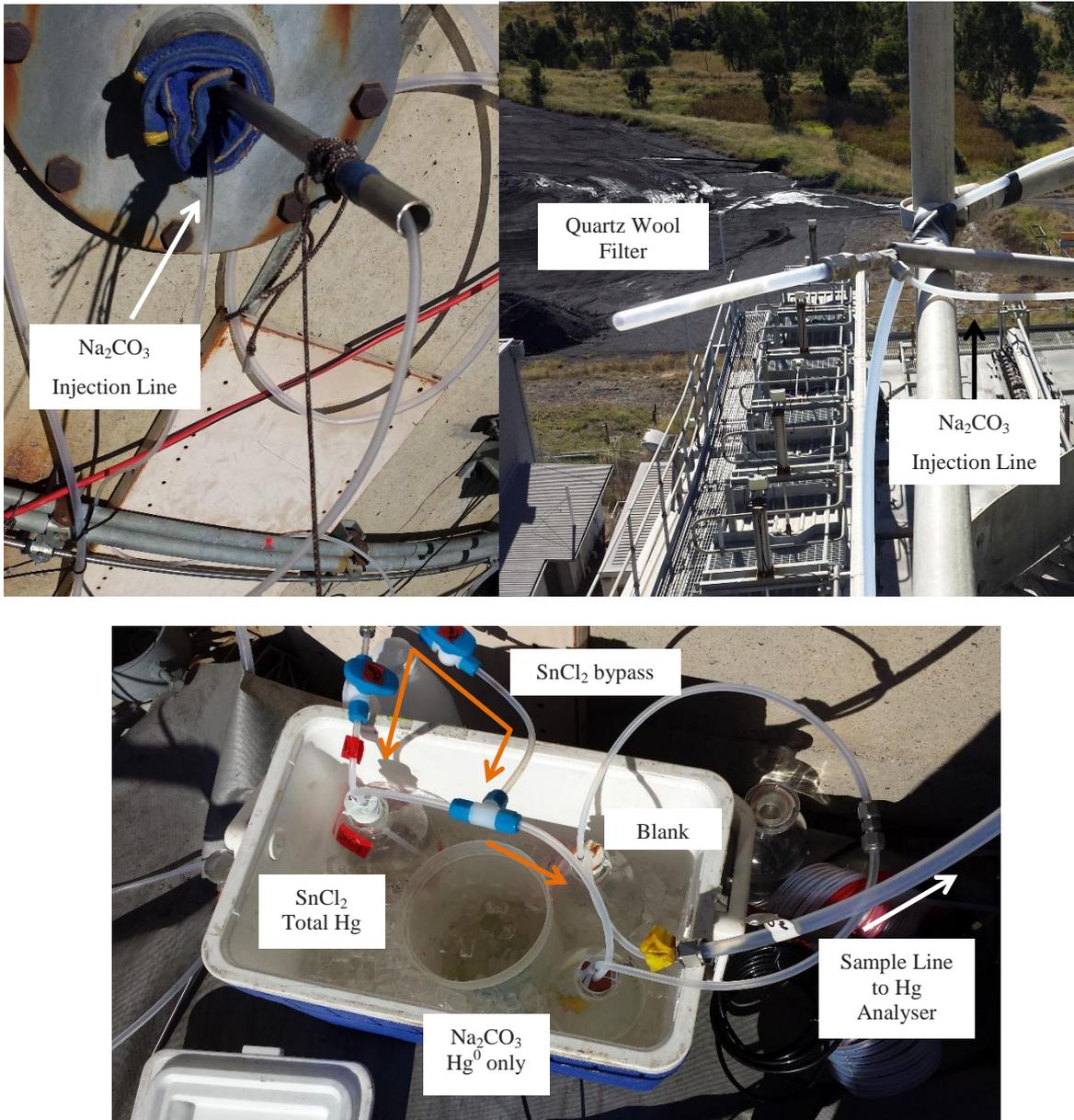
Figure 211. Non-heated lance for “Online Hg” sampling



Figure 22: Photographs of stack showing sampling locations for both heated and online lances (left) and sample lines to Ohio Lumex Hg Analyser (right and inset).



**Figure 23: Photographs of heated lance during sampling including backend treatment train for flue gas (left) and PFA activated carbon sorbent trap for Total Hg (right).**



**Figure 24: Photographs showing the Online Hg lance during sampling (top left); the lance filter and Na<sub>2</sub>CO<sub>3</sub> quench connection (top right) and backend treatment train for the flue gas prior to Hg analysis (bottom)**

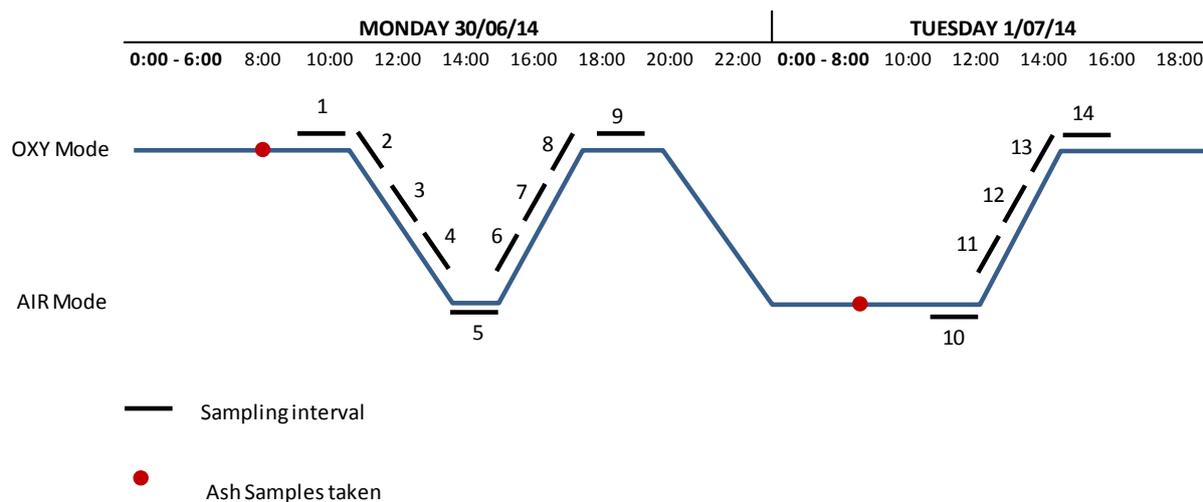


**Figure 25: Photograph of both heated and non-heated lances inserted in stack.**

#### ***4.3.3 Test Sequence***

The Callide A unit was fired with Callide coal for the tests. The testing regime was split over two days, with a double transition from oxyfuel to air firing and back to oxyfuel on Day 1 and a single transition from air to oxyfuel on Day 2. Figure 25 shows the schedule for these tests and the sample intervals taken with the heated probe. The blue line represents the change in CO<sub>2</sub> concentration. Overall, 14 sample intervals were taken over the 2 days, with a further 3 sample intervals taken a few days prior as preliminary measurements. For mercury, the duplicate samples represent a total of 28 measurements taken over 2 days and this compares favourably with the 115 measurements taken over 4 weeks during the Macquarie University December 2012 test campaign [26]. Figure 26 also shows when ash samples were taken from the fabric filter hopper, both at approximately 8-10am each morning after the ash hoppers were cleared at 4am. Samples were taken from each bag filter A-H. For this milestone report, composite samples were made for analysis using equal amounts from each hopper.

While this may not accurately reflect the true proportion of fly ash reporting to each filter hopper, it is expected that in practice no significant difference exists in particle size distribution between air firing and oxyfuel firing.



**Figure 26: Stack sampling schedule during OXY-AIR transitions indicating the 14 approximate time intervals and sample identification for SO<sub>3</sub> and Total Hg measurements. Fly ash samples were taken at 8am on both days after clearing the ash hoppers at 4am.**

#### 4.3.4 Results

The online and interval measurements for gas phase mercury concentration across the three transitions are given in Figures 27-29. Also included in each figure is the CO<sub>2</sub> concentration to clearly mark the transition. It should be noted that each transition took approximately 2¼ hours to take place with a number of stages included. In all cases, the oxyfuel conditions yield higher gas phase mercury, with a tendency to be lower in air mode. The start of Day 1 (Monday) measurements began in Oxy mode with the highest Total Hg reading of 6-7µg/m<sup>3</sup>. Comparison with the online Hg results (in Hg<sup>0</sup> mode) shows that the dominant proportion of mercury in the gas phase exists in oxidised form (eg 89.1% Hg<sup>2+</sup>). However, as the first transition progressed, the level of gas phase mercury dropped significantly, in particular the oxidised Hg level. By the end of the first transition (~12:30 on Figure 27), the Total Hg measurements aligned with the Online Hg measurements showing that the remaining portion of gas phase mercury consisted entirely of elemental Hg<sup>0</sup>. It should also be noted that such concentrations of Hg exiting a boiler are considerably lower (~0.05-0.1µg/m<sup>3</sup>) and previous measurements (ie Macquarie University Trial 2012) suggested that oxyfuel Hg levels should be 2.7-4.9 µg/m<sup>3</sup>. In that previous study, the proportion of oxidised Hg in the gas phase was ~70% and was considered to be an underestimate due to high probe temperatures.

The afternoon measurements (in Figure 28) continued to show low mercury levels, despite an increase to 0.15µg/m<sup>3</sup> as the transition from air to oxy mode completed. During this second transition, the proportion of oxidised Hg increased from 0% to 76.9%. The second day of testing (Figure 29) showed higher Hg levels but comparable trends in transition as the change from air to oxy mode

exhibited a rise in Total Hg from 0.52 to 2.0  $\mu\text{g}/\text{m}^3$ . This 3.7 factor increase is consistent with the concentration rise expected from the oxyfuel recycle. The proportion of oxidised Hg also increased from 72% to 88.8% during this final transition.

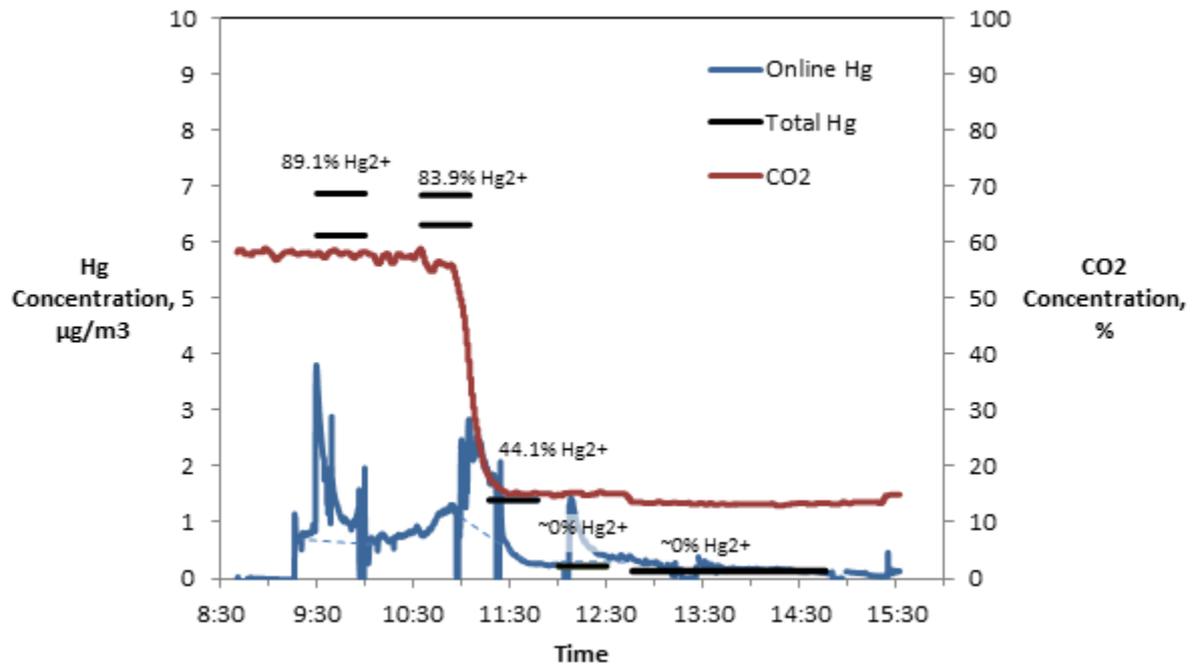


Figure 27: Mercury results for transition 1 Oxy to Air on Monday 30/06/14. The blue line represents the online results with dotted blue line indicating Total Hg by  $\text{SnCl}_2$ . Black lines indicate the Total Hg measured over a time interval.

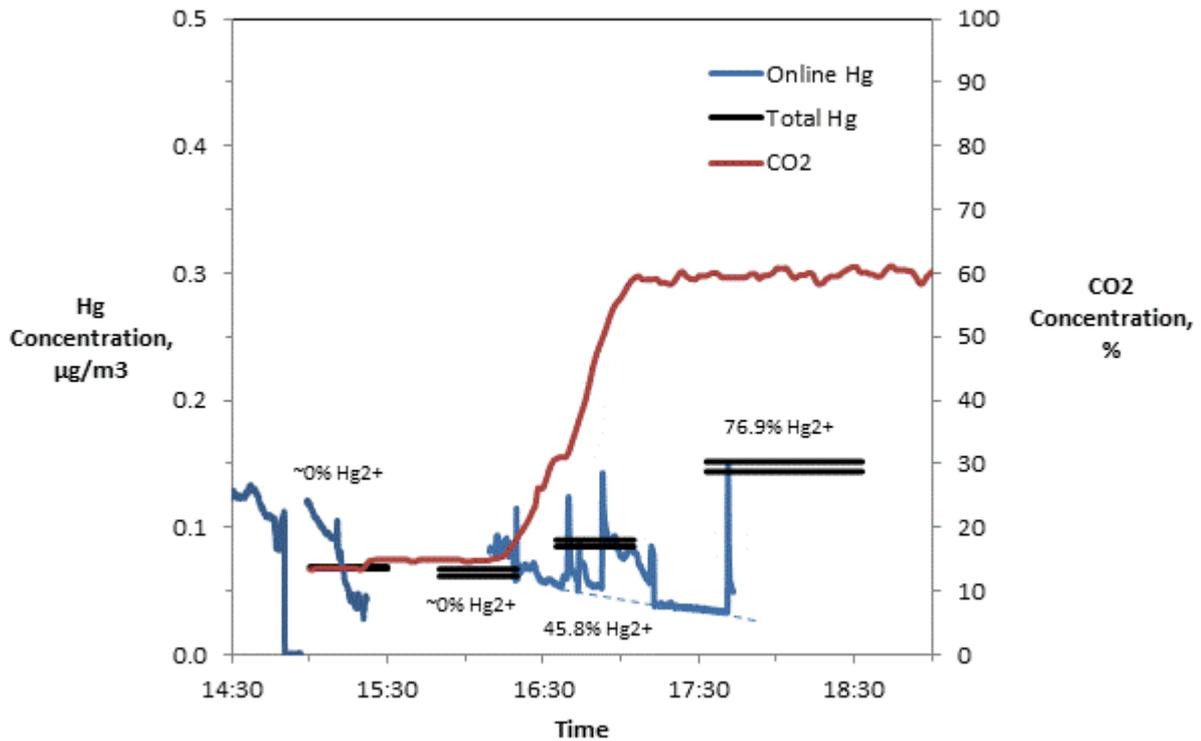


Figure 28: Mercury results for transition 2 Air to Oxy on Monday 30/06/14. The blue line represents the online results with dotted blue line indicating Total Hg by SnCl<sub>2</sub>. Black lines indicate the Total Hg measured over a time interval.

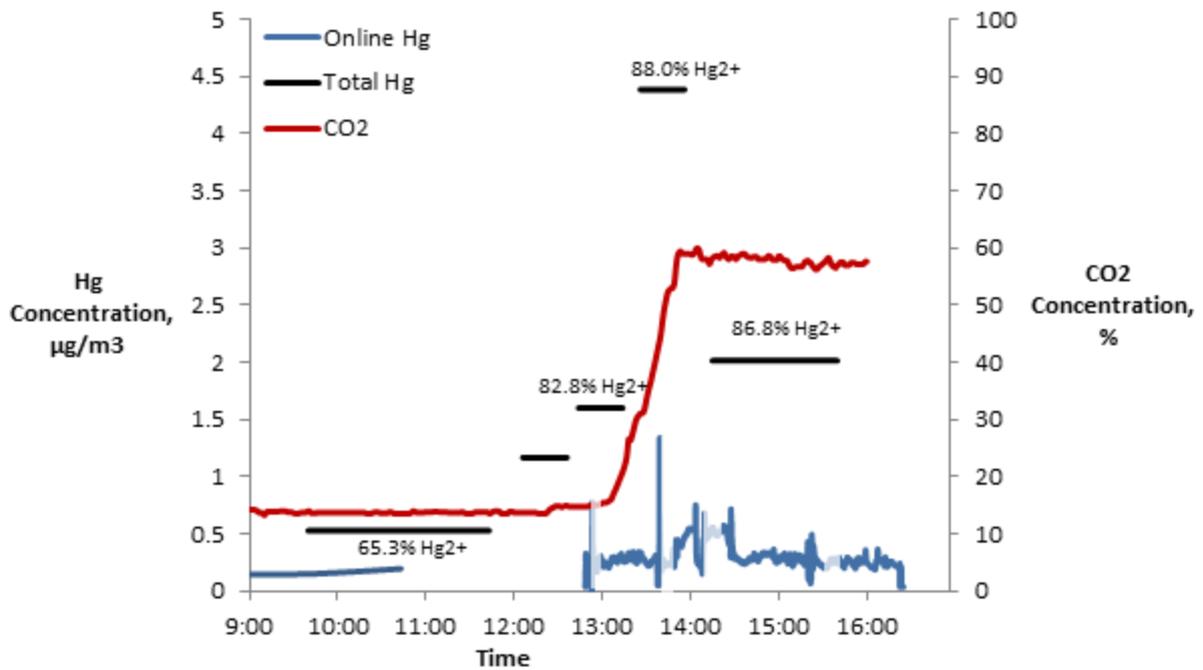
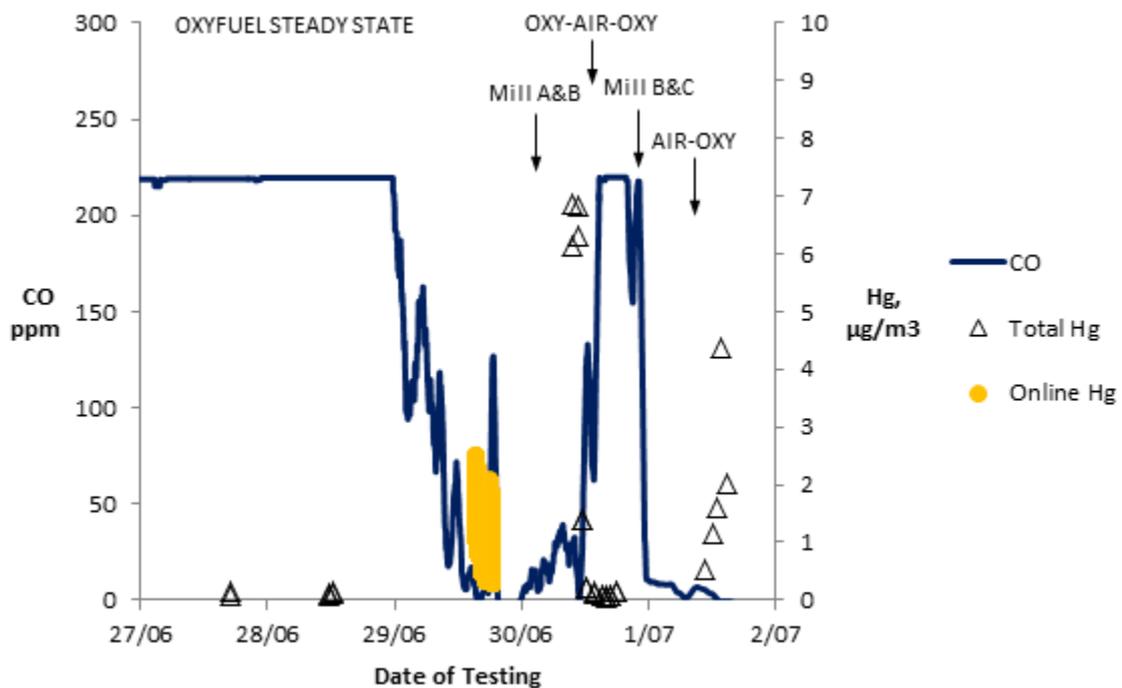


Figure 29: Mercury results for transition 3 Air to Oxy on Tuesday 01/07/14. The blue line represents the online results without SnCl<sub>2</sub> Total Hg and using the Na<sub>2</sub>CO<sub>3</sub> quench system. Black lines indicate the Total Hg measured over a time interval.

The Online and Total Hg measurements taken over the two day test program indicate that very low levels of Hg can be obtained in the flue gas. That both measurement techniques are in agreement supports a real result, rather than an artefact of sampling. However, a comparison of the two Air to Oxy transitions (Figure 28 and Figure 29) shows that the overall level of Hg in the flue gas varied by an order of magnitude in difference (eg 0.06-0.15  $\mu\text{g}/\text{m}^3$  vs 0.5-4.3  $\mu\text{g}/\text{m}^3$ ). One observation made during the testing was that the set of coal mills used during the first day of testing (Mills A&B) produced higher CO concentrations. The second day of testing used a different mill combination (Mills B&C) which resulted in lower CO levels. The most likely reason for the change in CO concentration is the use of low NO<sub>x</sub> burners fed from Mill A. Low NO<sub>x</sub> burners typically results in higher CO concentrations and tend to produce lower burnout thus producing greater amounts of carbon-in-ash. Figure 30 gives a historical trend of CO concentration across the days of testing and of those prior. It can be observed that CO levels begin to rise from the beginning of the Monday test day (30/06/14) reaching the upper instrument limit of 220ppm by approximately midday (ie the end of transition 1). The CO level remains high during transition 2 and returns to low levels after the mill change at 4am on Tuesday morning. This difference in CO is a defining characteristic between the two test days because the Total Hg measurements are clearly very low during periods of high CO and conversely return to expected higher levels when CO concentrations are lowered.



**Figure 30: Trends of CO concentration and Hg levels over the week of testing. This includes preliminary Total Hg measurements (on the 27/06/14) and Online Hg measurements (taken only on the 29/06/14, shown in red). The CO readings have been averaged over 1 hour to remove scatter.**

Also of note is that both fly ash samples were taken during periods of low CO and should be expected to contain lower carbon-in-ash levels, consistent with higher burnout than those in the high CO case (eg Monday afternoon). Due to the large number of other samples taken during the Monday tests a set of fly ash samples produced during air and oxy firing during these high CO periods was not possible. However, the measurement of CO is a good indicator for burnout and potential differences in mercury levels due to the ease of gas sampling in comparison to solid sampling.

Overall, this data suite may be split into two regimes based on the CO concentration. During periods of high CO, the effect of lower burnout and expected higher levels of carbon-in-ash produce an overwhelming response on mercury levels in the gas phase, resulting in very high levels of capture in ash. During periods of low CO, the capture rate in ash is lowered, resulting in greater mercury levels in the gas phase. This low CO regime has demonstrated that 80-90% of the gas phase mercury is present in oxidised form. Table 10 summarises the difference in capture rates of mercury under the two CO regimes. The theoretical Hg levels have been calculated by mass balance given in Table 11. In both cases the capture rate in air and oxy combustion is over 90%. Oxyfuel firing mode appears to provide similar capture rate to air mode in both high and low CO regimes.

**Table 10: Steady state measurements and calculated capture extents of the Fabric Filter for mercury at COP**

	<b>Theoretical Hg µg/m<sup>3</sup></b>	<b>Monday (high CO) µg/m<sup>3</sup></b>	<b>Capture Extent %</b>	<b>Tuesday (low CO) µg/m<sup>3</sup></b>	<b>Capture Extent %</b>
OXY	26.9	0.15	99.5	2.01	92.5
AIR	7.9	0.13	98.4	0.53	93.3

Note: The Theoretical values of gas phase Total Hg have been corrected for 15.9% dilution caused from air pulsing of Fabric Filter.

The mass balance was calculated based on the Callide coal composition given in Table 4 and has been matched on measured gas concentrations corresponding to steady state operation when the fly ash samples were taken. This balance was based on matching the gas concentrations using the coals moisture content, air ingress at the fabric filter and stoichiometric O<sub>2</sub>. Included in the table is a comparison between the theoretical and measured SO<sub>2</sub> values. The difference between the two numbers is indicative of the level of SO<sub>2</sub> captured in the fly ash through sulfation mechanisms discussed in section 4 of this report. In both air and oxy cases this SO<sub>2</sub> capture is similar in magnitude

and represents a low cost passive cleaning option for SO<sub>2</sub> removal. Measured values for SO<sub>3</sub> were below the detection limits of the water analysis for most samples. The measured SO<sub>3</sub> values are given in Table 12.

**Table 11:** Calculated mass balance and measured values

	<b>OXY</b>		<b>AIR</b>	
	<b>Theoretical</b>	<b>Measured<sup>1</sup></b>	<b>Theoretical</b>	<b>Measured<sup>2</sup></b>
<b>H<sub>2</sub>O %, wet</b>	25.8	25.8	8.1	7.4
<b>CO<sub>2</sub>, % dry</b>	56.8	57.9	14.3	13.7
<b>O<sub>2</sub>, % dry</b>	5.5	5.5	5.8	5.8
<b>N<sub>2</sub> (by diff), % dry</b>	36.8	36.5	79.7	80.4
<b>SO<sub>2</sub>, ppm dry</b>	866	724	218	176
<b>SO<sub>2</sub> Captured in ash, %</b>	16.4		19.1	
<b>SO<sub>3</sub>, ppm dry<sup>3</sup></b>	8.7		1.8	
<b>Acid Dew Point<sup>4</sup> °C</b>	141.6		115.9	

<sup>1</sup> Measured values averaged over Monday 8:30-10:30am 30/06/14, coinciding with ash collection

<sup>2</sup> Measured values averaged over Tuesday 9:00-12:00 01/07/14, coinciding with ash collection

<sup>3</sup> Estimated based on 1% conversion of theoretical SO<sub>2</sub>

<sup>4</sup> Estimated based on theoretical SO<sub>3</sub> and H<sub>2</sub>O values using ZareNezhad correlation

Where the actual amount of sulfates (in the water analysis) measured were below the detectable limit, the SO<sub>3</sub> detection limit is indicated. This minimum detection limit was based on 1mg/L SO<sub>4</sub><sup>2-</sup> and the volume of gas sampled. For the transition testing the SO<sub>3</sub> varied between 0.5-0.8ppm. Previous measurements made prior to the transition trial are also shown. These include samples taken in the days prior to the transition tests as well as those from the May 2014 Trial and all were based on steady state oxyfuel conditions. The SO<sub>3</sub> from previous UoN tests are higher than those of the transition, varying between 0.6-3.7ppm. The relative similarity of results suggests that those measurements below the detection limit are also real results. Results from the Macquarie University trial in 2012 show that SO<sub>3</sub> concentrations varied from 6-15ppm in oxyfuel; considerably higher than those measured by UoN. The main difference in testing between the two studies is the impact of steady

state. The Macquarie trial took place over 4 weeks using steady state oxyfuel conditions with long sampling intervals. The UoN trial was based on transition conditions with short sampling intervals. The sampling methods also differed, with the Macquarie trial using US EPA Method 8 (an absorption based method), while the UoN method used here is based on the controlled condensation method. The controlled condensation method was selected for the UoN trial because it favoured short sampling intervals and cannot be affected by CO<sub>2</sub>.

The reasons for such low SO<sub>3</sub> concentrations are unlikely to be technique based. With the H<sub>2</sub>SO<sub>4</sub> filter set to 90°C in the heated lance, the capture limit is based on the SO<sub>3</sub> concentration for a dew point of 90°C. For oxy mode this capture limit is 0.03ppm SO<sub>3</sub> and for air mode 0.12ppm SO<sub>3</sub>. The difference between modes is based on the higher concentration of water vapour in oxy mode, which acts to drive up the acid dew point for same concentration of SO<sub>3</sub>. Table 11 provides a SO<sub>3</sub> estimate based on a 1% conversion of the theoretical SO<sub>2</sub> concentration. The estimated SO<sub>3</sub> concentration equates to an acid dew point of 115.9 and 141.6°C respectively for air and oxy-firing.

**TABLE 12. SO<sub>3</sub> measurements at COP**

<b>Sample</b>	<b>Description</b>	<b>SO<sub>3</sub>, ppm</b>
1	OXY steady	<b>0.55</b>
2	OXY → AIR	<b>0.56</b>
3	OXY → AIR	<0.27
4	OXY → AIR	<0.23
5	AIR steady	<0.06
6	AIR → OXY	<0.25
7	AIR → OXY	<0.26
8	AIR → OXY	<b>0.82</b>
9	OXY steady	<0.14
10	AIR steady	<0.06
11	AIR → OXY	<0.28
12	AIR → OXY	<0.26
13	AIR → OXY	<0.28
14	OXY steady	<0.10
<b>Previous Measurements</b>		
31/05/2014	OXY steady	<b>3.65</b>
27/06/2014	OXY steady	<b>1.60</b>
28/06/2014	OXY steady	<b>0.58</b>

**Note:** Measurements designated with < indicate the limit of measurement based on standard water analysis (for SO<sub>4</sub><sup>2-</sup>) using the volume of gas sampled.

Process based reasons for low SO<sub>3</sub> concentrations could include fly ash capture (across the Fabric Filter) or unwanted condensation of H<sub>2</sub>SO<sub>4</sub> prior to the Fabric Filter. From the Stuttgart study, it was shown that up to 60-70% of SO<sub>3</sub> may be captured in the Fabric Filter when the inlet SO<sub>3</sub> concentrations are below 20ppm (Figure 6 in this report). If the measured SO<sub>3</sub> levels at COP are compared against the estimated SO<sub>3</sub> entering the Fabric Filter (from 1% SO<sub>2</sub>) then this removal extent is approximately 84%. The impact of this SO<sub>3</sub> capture translates to a reduction in the acid dew point from 142°C down to 123°C.

The effect of moisture level and SO<sub>3</sub> concentration on acid dew point is given in Figure 31. Included in Figure 31 are the estimated values from Table 11 which assumes no capture occurs across the Fabric Filter. Also included are results from the Stuttgart study detailed in Section 3.1 using SO<sub>2</sub> injection levels to match 0% and 20% SO<sub>2</sub> cleaning of the recycled flue gas. The 20% SO<sub>2</sub> cleaning was based on the COP configuration where the primary flue gas recirculation (nominally 20% of flow) is passed through a H<sub>2</sub>O removal stage and is partially scrubbed of SO<sub>2</sub>. The Stuttgart results include acid dew point estimates based on SO<sub>3</sub> measurements taken before and after the Fabric Filter. These results show that 2.4% of the SO<sub>2</sub> is converted to SO<sub>3</sub> (before the Fabric Filter) and that the measured capture extent of 24-69% of SO<sub>3</sub>.

Overall, the results suggest that the Stuttgart results estimate higher acid dew point because the SO<sub>2</sub> concentration was higher than measured at Callide. In part this could be partially based on the assumptions on the extent of cleaning which determined the level of SO<sub>2</sub> injected into the experiment. However, a significant finding from this work is that the measured levels of CO<sub>2</sub> at the COP during the 2 day transition testing were much lower than those measured at pilot-scale at Stuttgart. By comparison, the CO<sub>2</sub> levels at COP were approximately 58% (from Table 11) while at Stuttgart the CO<sub>2</sub> varied 95-99%. The lower CO<sub>2</sub> levels at the COP are almost certainly due to air ingress and residual N<sub>2</sub> during the transition experiments and have typically been reported as 67-71% CO<sub>2</sub> at steady state. However, this dilution effect had a positive influence by reducing the acid dew point estimates shown in Figure 30. If this dilution influence is factored in the estimated acid dew point for oxy mode at the COP would rise from 143°C to 154°C (using the Stuttgart 2.4% conversion). This increase in acid dew point temperature is small compared to initial rise between air and oxy mode (+26°C) and shows that higher moisture level in oxyfuel is the dominant driver of dew point temperature.

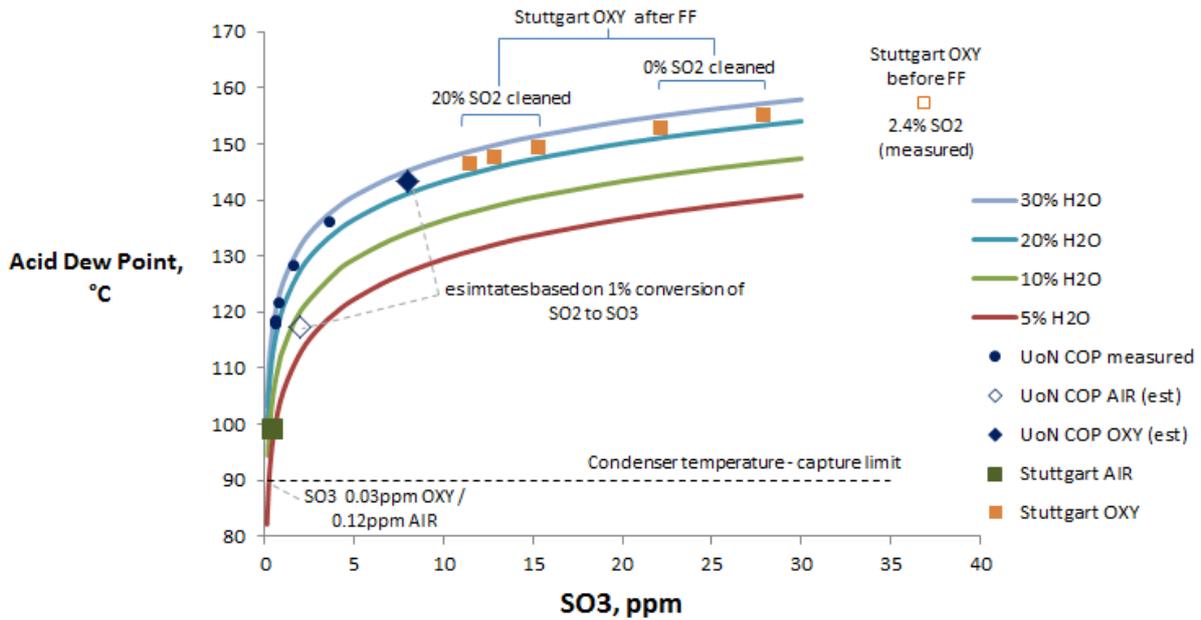
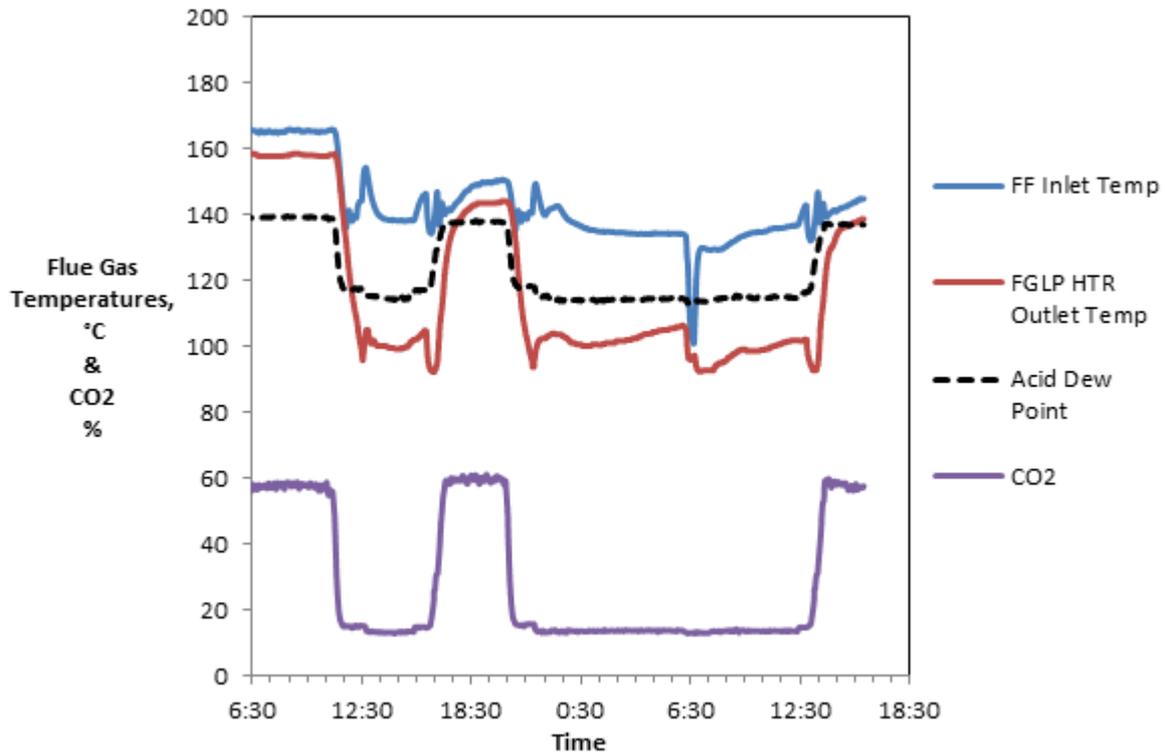


Figure 31. Acid dew point calculations for different  $\text{SO}_3$  and  $\text{H}_2\text{O}$  levels. UoN estimates of COP acid dew point are based on 1% conversion of measured  $\text{SO}_2$  (based on Table 11) and assume no  $\text{SO}_3$  capture across the Fabric Filter. Stuttgart results are taken from  $\text{SO}_2$  injection levels to match configuration cases of 0%  $\text{SO}_2$  cleaning and 20%  $\text{SO}_2$  cleaning of the recycled flue gas using measurement taken before and after the Fabric Filter. At the condenser temperature of  $90^\circ\text{C}$  used for “controlled condensation” of  $\text{H}_2\text{SO}_4$  (see Figure 20) the minimum  $\text{SO}_3$  detectable is shown to be 0.03 and 0.12 ppm respectively for oxy and air-firing.

Figure 31 indicates that if  $\text{SO}_3$  levels are less than 0.03 ppm respectively for oxy-firing then no condensation of  $\text{H}_2\text{SO}_4$  will be observed at the  $90^\circ\text{C}$  of the “controlled condensation” technique. This, then, corresponds to most “undetectable” measurements at the COP shown in Table 12. In searching for an explanation, a potential reason for the undetectable levels of  $\text{SO}_3$  may be the lower temperatures encountered in the Flue Gas Low Pressure Heater (FGLP HTR), a heat exchanger located prior to the fabric filter. This heat exchanger is designed with a controlled bypass allowing a portion of gas to be cooled and a portion to be bypassed. The combined gas then enters the fabric filter. Figure 32 shows the two measured temperatures of cooled gas exiting the FGLP HTR and the total gas entering the fabric filter. For comparison, the acid dew point has been estimated using the 1% conversion of measured  $\text{SO}_2$  concentration and the measured  $\text{H}_2\text{O}$  levels (supplied from the COP). It can be observed that only morning interval tests appear to be higher than the ADP temperature. For the other test interval, the temperature exiting the FGLP HTR is lower than the estimated ADP, suggesting that  $\text{H}_2\text{SO}_4$  may be condensing inside this heat exchanger. Under air-firing, the FGLP HTR was bypassed, while in oxy-firing the damper valves allowed 100% of the flue gas to flow through the FGLP HTR. The overall impact of acid condensation would be to reduce the  $\text{SO}_3$  levels measured after the fabric filter.



**Figure 32: Comparison of flue gas temperatures and estimated  $\text{H}_2\text{SO}_4$  acid dew points. The FGLP Heater is a heat exchanger located prior to the Fabric Filter with the controlled bypass to attenuate the gas temperature entering the Fabric Filter. The acid dew point is estimate from measured  $\text{SO}_2$  and  $\text{H}_2\text{O}$  levels.**

#### 4.3.5 Comparison of Studies

The calculated mercury capture rate in Table 10 has shown that capture of >90% of Hg is possible using a Fabric Filter. However, this method relies on measured Total Hg concentration in the flue gas to determine the “uncaptured Hg” with the Theoretical Hg concentration determined by a mass balance matching coal properties to measured gas concentrations. This “estimation by gas” allows the alignment of measured gas concentrations with measured Hg levels, providing a real time measure of capture rate. This was particularly useful in comparing the two CO regimes which occurred during the trial. The drawback of the technique is that it relies on coal properties which have been sampled at a different time period (in this case using the same coal properties as that supplied to the University of Stuttgart).

Other methodologies for estimating capture rate are based on mercury levels measured in the fly ash (eg. Estimation by ash). In this case, the measured mercury in the fly ash is compared to the mercury in the coal using an assumed proportion of coal ash reporting to each Fabric Filter hopper (ie A-H). The benefits are the ease of sampling (relative to mercury testing) with the detraction being the error

in assuming fly ash proportions reporting to each hopper and the reliance on constant coal properties. Figure 33 compares mercury capture using the “estimation by ash” method using the two fly ash samples taken during this test campaign with the previous study performed by Macquarie University in December 2012. In both test campaigns, the level of burnout in oxyfuel is higher than in air firing, leading to fly ashes in air mode containing more carbon-in-ash (in this case determined by loss on ignition, LOI). The resulting lower LOI in oxyfuel reduces the amount of Hg captured in the fly ash. However, a comparison of the two data sets shows that the fly ashes contained lower carbon-in-ash for the UoN campaign which lead to a lower overall capture rate than the previous study. One important difference between the two data sets is the higher amount of coal ash in the UoN trial (~32.5%db) compared with the earlier study (~27.5%db), highlighting the natural variability of coal supply to the Callide Oxyfuel Project. However, the higher proportion of ash to mercury would be expected to provide greater capture, rather than less. Overall, the difference is most likely due to the inherent errors in the estimation method using ash rather than gas.

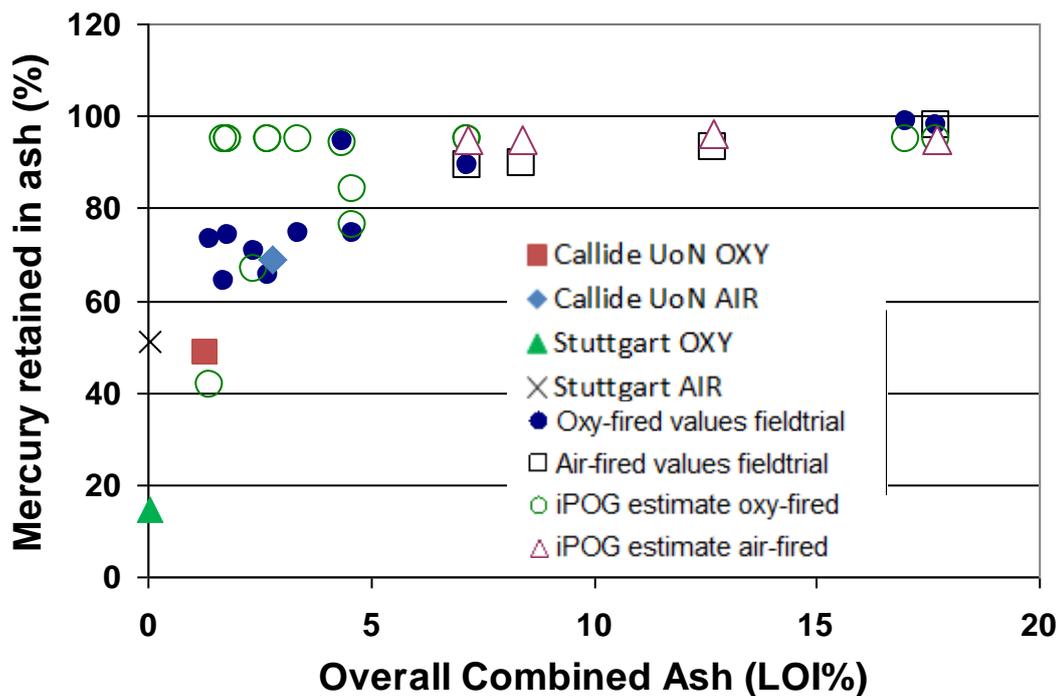


Figure 33: Comparison of Hg capture from three studies using the same Callide coal, based on an original figure by [23]. This comparison uses the “estimation by ash” method for calculating mercury removal.

Also for comparison is the data produced from the University of Stuttgart. This data set is particularly different from the two Callide studies because of the high level of burnout leading to significantly low carbon-in-ash. Under these conditions the amount of mercury captured is lower than the corresponding AIR/OXY values at Callide A. It must also be stated that the Stuttgart tests used

injected Hg levels to simulate the effect of flue gas recycle. In these tests, the amount of Hg injected was based on simulating a recycle stream with 50% Hg captured on the Fabric Filter. However, this field campaign has shown that the capture rate is relatively high (>90%). As a consequence, the Stuttgart tests use a higher level of Hg than those experienced in either field campaign, which ultimately contribute to lower Hg capture.

The “estimation by ash” method relies heavily on the accurate estimation of the proportion of ash reporting to each hopper (rear pass and fabric filter) and to the furnace bottom ash. The need for this arises because of the significant variation on Hg contained in the ash of each hopper. Figure 34 provides the Hg content of each fly ash sample. In the majority of samples the amount of Hg in the air fired ash is higher than that of oxyfuel. However, the amount of fly ash which reports to each hopper is estimated, rather than quantified, and the difference between air and oxyfuel firing is not known. This ash balance is further confounded by the split between fly ash at the fabric filter and that reporting to the rear pass and furnace bottom. The Macquarie University trial has shown that the amount of Hg contained in the these other ash samples is minimal, however the amount of ash is likely to vary between air firing and oxy-firing and this variation has yet to be quantified. It may be noted that the level of UBC in the furnace ash is much higher than in the fly ash. In addition, the temperature zones very different. This may also have a large bearing on the retention of mercury in the fly ash.

Figure 35 shows some of the variability in the use of this method of calculating Hg capture. The AIR/OXY averages have been calculated using two different average Hg contents (a linear average and proportionally weighted average). This variation is between 10-15% of the capture rate. Also shown is the capture rate calculated using the Hg content of the first Fabric Filter Hopper (A) which notionally contains the highest amount of captured fly ash. The result is a significantly reduced estimation of Hg capture by ~25%. A final comparison is made using the iPOG estimation method, which incorporates empirical effects of coal properties, firing conditions and mercury control options. The software is based on real testing but does not incorporate oxyfuel impacts. For this example the oxyfuel estimate has used an artificially increased coal sulfur, chlorine and mercury content (by a factor of 3.7) to reflect the concentration increase introduced by recycled flue gas. Under these conditions it can be observed that the LOI% is the governing factor influencing the capture of mercury with a Fabric Filter. Above 4% LOI this estimated capture rate reaches a maximum of 95% and does not increase further. The effects of higher concentrations due to recycle are minimal. It was also observed that the iPOG software considerably reduces its estimation when a ESP is selected instead a Fabric Filter- recognising the improved capture performance of a Fabric Filter in relation to mercury.

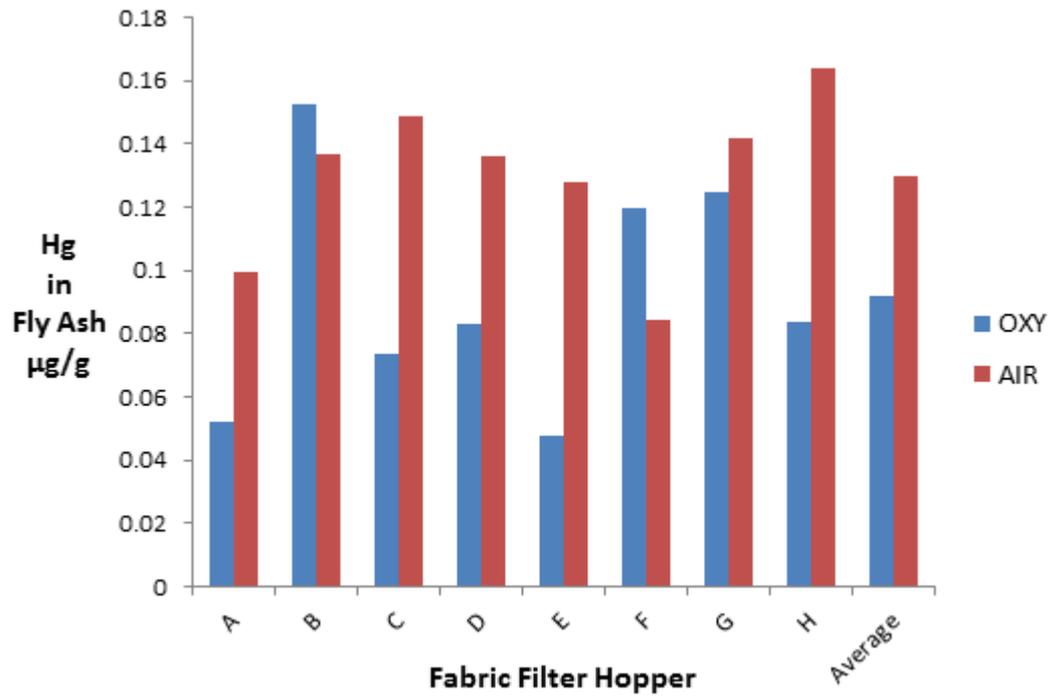


Figure 34. Variation in Hg content for fly ash samples taken during the UoN campaign.

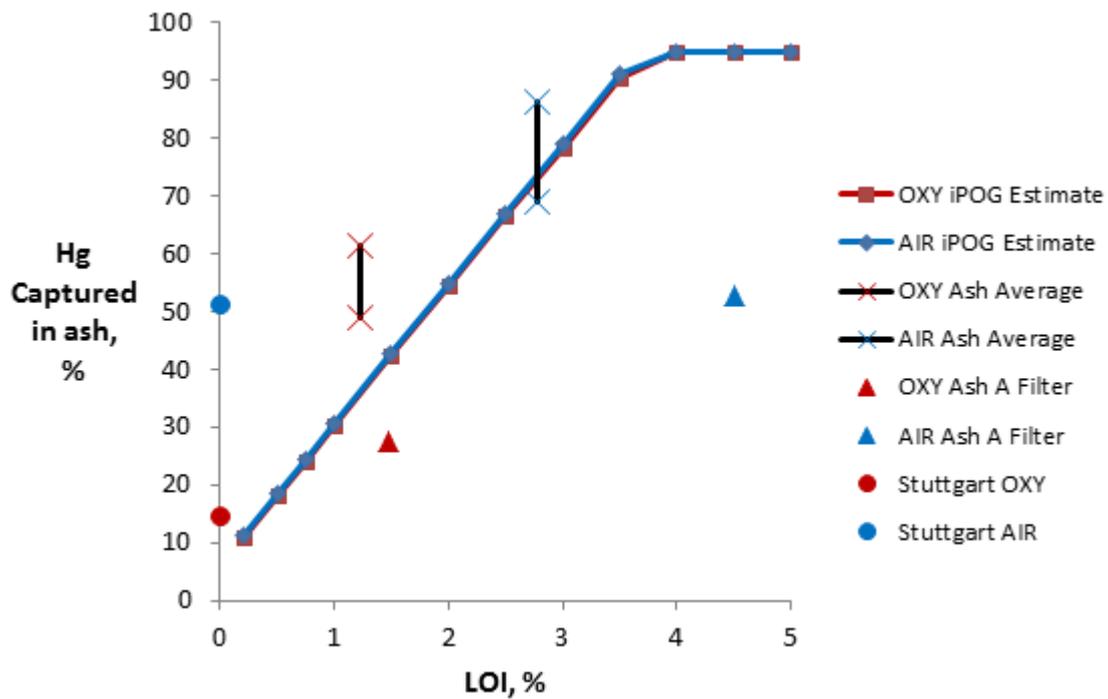
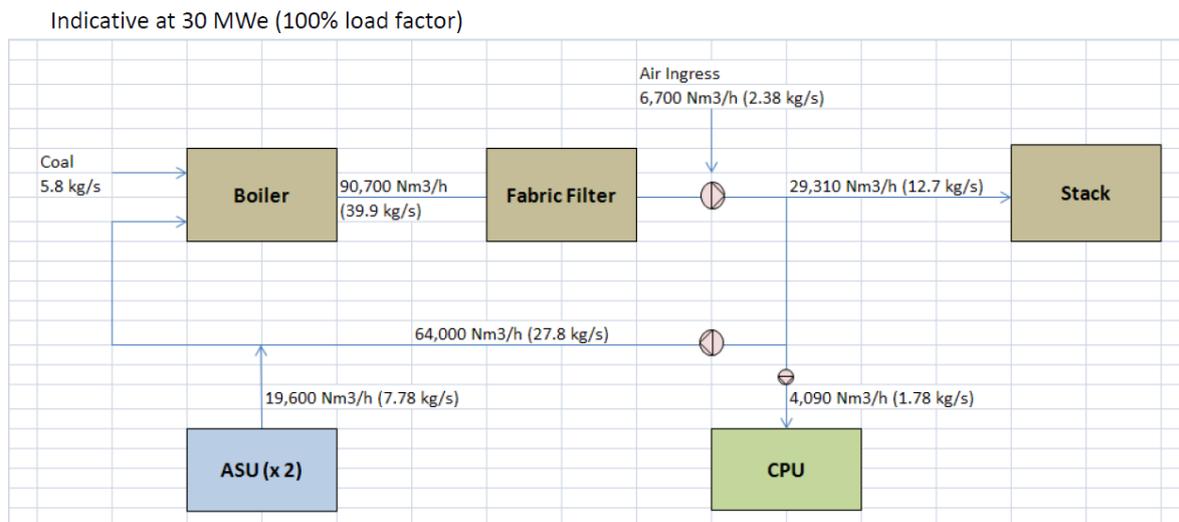


Figure 35. Variation in mercury capture estimates using different assumptions and values.

### 4.3.6 Note on comparing stack emissions between air and oxy-fuel firing conditions

An important distinction between the Air firing and Oxy-firing mode is the significant difference between the flows exiting the boiler block. Under air firing, the total flue gas is directed to the stack. However, under oxy-firing the recycled flue gas accounts for ~65% of total flow and thus only 35% of the flow is required to be processed by the CPU. As such a direct comparison between flue gas constituents from an emissions perspective must also account for this difference in flow. In a commercial oxy-fuel plant the current concept of “emissions” is made redundant due to the role of the CPU, which removes impurities during CO<sub>2</sub> compression and liquefaction. Emissions to the stack would only occur during transition between modes, during unexpected shutdowns and when operated in air mode. Emissions from the CPU are unlikely to be in the same form as those emitted under air firing and may require different regulations and reporting. The Callide Oxyfuel Project differs from most expected commercial configurations due to the smaller size of the CPU, which processes ~5% of the total flue gas. The remaining (~30%) flue gas is exhausted through the stack. Figure 36 shows an indicative mass balance with CPU slip stream and stack flow.



**Figure 36. Indicative mass balance of the Callide Oxyfuel Project, noting that the CPU processes a portion (~4%) of total flue gas and 30% of the flue gas from the boiler reports to the stack. Taken from [30]**

Consequently, the COP will have higher emissions when expressed on a ppm basis than those of commercial plant of the future.

This section is intended to provide clarity on the emissions from the COP as may be required for reporting. Table 13 shows measured gas concentrations during a transition between air and oxy-firing conditions. Importantly, it provides an example of NO<sub>x</sub> flue gas concentrations and total mass flow to the stack. It may be noted that the measured NO<sub>x</sub> *concentration* (ppm) is higher in oxy-mode, but when the total flue gas is accounted for the *amount* of NO<sub>x</sub> (g/s) is significantly lower.

**TABLE 13. Firing Sequence in transition from AIR mode to OXY mode (at 28MWe)<sup>1</sup>**

**Actual data (at 28 MWe)**

Flue Gas Composition		Air-Firing mode	O2 Sequence	RFG Mode	Oxy-mode
O2	vol %, dry	4.5	6.0	6.8	5.4
CO2	vol %, dry	15.0	16.2	59.9	72.2
CO	ppm, dry	20	20	12	12
SO2	ppm, dry	220	230	800	890
NO	ppm, dry	550	720	1195	965
NO2	ppm, dry	9	10	45	46
H2O	vol %	8	8.5	20.5	21.6
NOx	ppm, dry @ 7% O2	474	681	1223	907
NOx	ppm, dry @ 12% CO2	447	541	248	168
Flue Gas to Stack	kg/s (wet)	54	59	15.4	14.0
	Nm3/s (wet)	40.8	44.3	9.77	8.48
<b>NOx</b>	<b>g/s</b>	<b>43</b>	<b>61</b>	<b>21</b>	<b>15</b>

<sup>1</sup> Taken from [30]. RFG is an oxy mode during transition involving higher exit O<sub>2</sub>. Here, only the air and oxy mode data is used.

The previous sections of this report have reported the measured mercury concentrations without further accounting for total flow. Table 14 gives the measured steady state mercury measurement in oxy-fuel mode after transition on 1/07/2014 (taken from Table 10) and the comparable air fired mercury levels measured prior to transition. Here, the data for the low CO condition is used, which is considered to be the normal operating mode. The mercury concentration is higher in oxy-firing than during air firing. As with Table 13 above, the mercury levels of Table 14 have then been corrected for the difference in flow by calculating them at a constant CO<sub>2</sub> concentration of 12%. After these flow corrections, the two measurements appear to be quite close in values. A further calculation on the mass flow of mercury species to the stack was made using the flow rate of stack gas from Table 13 and a correction for the reduced load during the mercury measurement campaign (ie 23MWe as opposed to 28MWe in Table 13). All calculations were made using a dry gas basis to coincide with

the dry basis mercury measurements. Under these calculated conditions the actual amount of mercury emitted during operations is 34% less under oxy-fuel firing in comparison to air firing. We note that the calculation is based on the reported volumetric flow data of Table 13 rather than measurements taken during the present test campaign.

**TABLE 14. Mercury emissions from the stack at COP**

	<b>Tuesday (low CO) µg/m<sup>3</sup></b>	<b>Hg emissions (at 12% CO<sub>2</sub>) µg/m<sup>3</sup></b>	<b>Furnace Load MW</b>	<b>Flue Gas<sup>1</sup> Flow Nm<sup>3</sup>/s dry</b>	<b>Hg emissions to stack µg/s</b>
OXY	2.01	0.42	22.7	5.4	10.8
AIR	0.53	0.46	23.0	30.8	16.3

<sup>1</sup> Taken from Table 13 and corrected for dry basis and reduced load at 23MWe

For comparison, the same calculations were applied to the average NO<sub>x</sub> measurements taken during the same time period as the mercury measurements. These values are given in Table 15. These values are similar to previous NO<sub>x</sub> data given in Table 13 above. The average Total NO<sub>x</sub> during the mercury campaign measured 920 ppm in oxy-firing compared to 534 ppm in air-firing. However, when accounting for difference in stack flow rates, the mass emission to the stack is significantly reduced by 70% under oxy-firing. This compares well to previously published results given in Table 13 showing a 65% reduction in NO<sub>x</sub> under oxy-firing.

**TABLE 15. NO<sub>x</sub> emissions from the stack at COP**

	<b>NO<sub>x</sub><sup>1</sup> (low CO) ppm</b>	<b>NO<sub>x</sub> emissions (at 12% CO<sub>2</sub>) ppm</b>	<b>Furnace Load MW</b>	<b>Flue Gas<sup>2</sup> Flow Nm<sup>3</sup>/s dry</b>	<b>NO<sub>x</sub> emitted to stack g/s</b>
OXY	920	191	22.7	5.4	7.0
AIR	534	468	23.0	30.8	23.2

<sup>1</sup> Average NO<sub>x</sub> concentrations during same time period as Hg in Table 14

<sup>2</sup> Taken from Table 13 and corrected for dry basis and reduced load at 23MWe

These calculations reveal that the NO<sub>x</sub> emission levels in oxyfiring, when expressed on a mass emission basis as in Table 15 are substantially lower than in air firing, this being

expected due to the reburning (ie reduction by reaction to  $N_2$ ) of the recycled  $NO_x$  as it passes the fuel-rich regions of the flame. However, the differences given for mercury in Table 14 are difficult to explain. It is noted that the mercury removal by the bag filter is considerable and this is very sensitive to unburnt carbon rather than firing mode, and these differences were not measured with the ash sampling accuracy required for this assessment in the current study.

## 5. Conclusions

The studies at laboratory, pilot-scale and at the Callide Oxyfuel Project lead to the following conclusions:

..... *Greater capture of both mercury and sulfur gases is expected by “clean” ash with C-in-ash levels less than 0.1% in oxy-firing compared to air-firing, with the difference being coal specific.*

..... *The results emphasize that for C-in-ash > 5%, mercury capture by a fabric filter is high (>80%) with little impact on ash quality. The results indicate that competition between mercury and SO<sub>3</sub> by ash can be neglected for practical C-in-ash levels.*

.....*The results for SO<sub>3</sub> levels of the flue gas exiting the COP fabric filter are less than 0.25 ppm, being the lower limit of the “controlled condensation” technique used. This yields much lower acid dew point temperatures compared to the results at pilot-scale. A potential reason for the low levels of SO<sub>3</sub> may be the lower gas temperatures encountered in the Flue Gas Low Pressure Heater (FGLP HTR), a heat exchanger located prior to the fabric filter, in which condensation will occur.*

..... *The results emphasise that process units which may operate at temperatures below the Acid Dew Point (ADP) will be prone to acid attack, and are a practical issue in oxyfuel technology, as suggested here during transitions (and also previously during start up and shut down at the Vattenfall pilot-plant)*

..... *The sensitivity of the acid dew point temperature may be related gas composition using ZareNehzhad’s correlation, with sensitivity to increased SO<sub>3</sub> levels and a sensitivity to increased H<sub>2</sub>O levels, both being higher in oxy-firing compared to air firing.*

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