

# **Impacts of trace components on Oxy-combustion for the Callide Oxy-fuel Project – Results from Callide fieldtrials, December, 2012**

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## SUMMARY

It is recognised that the behaviour of trace metals and the related characteristics of the formation of fine particles may have important implications for process options, gas cleaning, environmental risk and resultant cost in oxy-fuel combustion. In spite of its potential importance to oxy-fuel combustion, the effects of firing in O<sub>2</sub>/CO<sub>2</sub> mixtures on trace metal department, speciation, and behaviour in flue gas cleaning systems have not been extensively studied. Environmental and operational risk will be determined by a range of inter-related factors including:

- The concentrations of trace metals in the gas produced from the overall process;
- Capture efficiencies of the trace species in the various air pollution control devices used in the process; including gas and particulate control devices, and specialised systems for the removal of specific species such as mercury;
- Gas quality required to avoid operational issues such as corrosion, and to enable sequestration in a variety of storage media without creating unacceptable environmental risks; the required quality for CO<sub>2</sub> transport will be defined by (future and awaited) regulation but may be at the standards currently required of food or beverage grade CO<sub>2</sub>; and
- Speciation of some trace elements

The last issue is particularly important as it is widely recognised that distribution, mobility and bioavailability of any element not only depends on the total concentration but, critically on the chemical forms and oxidation states of these elements. For example, the toxicity of Cr varies dramatically depending on whether it is present as Cr<sup>6+</sup> or Cr<sup>3+</sup>.

Macquarie University was engaged by the Australian National Low Emissions Coal Research and Development Ltd (ANLEC R&D) to undertake a research program to investigate the behaviour of trace elements during oxy-firing and CO<sub>2</sub> capture and processing. In December 2012, a test program was undertaken over a three week period on the retrofitted Callide A power plant with capability for both oxy and air-firing. During this period four coal feeds (including mixtures of two coal types, sub-bituminous and semi-anthracite, from three mining locations) were combusted under both air-fired and oxy-fired conditions.

Gaseous and particulate sampling was undertaken in the process exhaust gas stream after fabric filtration at the stack and at various stages of the CO<sub>2</sub> compression and purification process. These measurements provide detailed information on trace components of oxy-fired combustion gases and comparative measurements under air fired conditions, including:

- Trace metal and particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>) emission rates from oxy-combustion compared to air-fired systems - this will provide information for environmental risk assessment of stack emissions from the Callide Oxy-Fuel Plant. In fully commercial plants there are not expected to be any stack emissions during oxy-firing, but plants would be expected to operate in both

air and oxy-firing modes and to meet emission standards in both circumstances;

- Trace element speciation in oxy-combustion products (gas, bottom and fly ash) - speciation determines the toxicity, environmental transport behaviour and hence the risk associated with these products; and
- Trace metal capture and transformation rates in the flue gas cleaning system and CO<sub>2</sub> processing plant;
- Ultimate trace component concentrations in product CO<sub>2</sub>,

In the project the target list of species to be characterised was based on the list of reportable substances included in the Australian National Pollutant Inventory (see <http://www.npi.gov.au/substances/list-of-subst.html>).

Mercury was particularly targeted, given its importance from both a health and operational perspective. Measurements of mercury concentrations were made at the exhaust stack of the power plant and throughout the CPU using the activated carbon sorbent tube method and in the CPU also using continuous measurement techniques.

### **Outcomes:**

A field campaign was held during the period 3<sup>rd</sup> – 20<sup>th</sup> December, 2012 with a focus on establishing the fate and possible operational impacts of trace elements in the Callide Oxyfuel processing plant. During this time four coal feeds, including mixtures of two coal types, sub-bituminous and semi-anthracite, from three mines were combusted under both air-fired and oxy-fired conditions. The feed coals are characterised as two medium volatile bituminous coals (CL and BL), a semi-anthracite coal (MN), Blend 1 (was a mixture of CL and BL coals), Blend 2 (a mixture of CL and MN coals), along with feeds of unblended CL and MN coals. Sampling was carried out for solids inputs and outputs (coal and ash), gases at the stack exhaust (under both air and oxy-fired conditions) and at various points in the CO<sub>2</sub> Processing Unit (CPU).

The results show that the trace element content of the feed coals used in the program is very similar for most elements. Average unburnt carbon levels (UBC%) in the residual ash varied considerably during the trial period, even for the same coal and firing conditions on different days. Under air-firing conditions UBC% levels were generally higher than for oxy-firing of the same coal.

Mercury was more likely to report to ash under air-firing conditions and under these conditions 87-95% of the mercury partitioned to the ashes, while during oxy-firing this reduced to 67-74%. This is most likely a result of generally higher UBC (%) in flyash when in air-firing mode. Approximately 80% of mercury in CPU process gas was removed by the initial low pressure scrubber; with the final CPU process gas mercury concentrations approaching the levels measured in ambient air, (<2 ng/m<sup>3</sup>).

No consistent relationship in the stack gas halide (HBr, HCl and HF) concentrations between coal type and/or firing mode (oxy or air-fired) was apparent. Elemental halogens, Br, Cl and F were at or below detection limits for the sampling techniques in both the stack and CPU.

Stack gas trace metal concentrations during both oxy and air-firing were low compared to allowable emission standards for stack gases and should have minimal environmental impact. Some differences in partitioning to the gas phase are apparent with three distinct groups of elements; low level partitioning (<5%) for most metals studied (As, Be, Co, Cu, Pb, Mn), a second group where retention in the gas phase is consistently higher; Sb (5.5 – 8.8%), B (16.2 – 40.4%), Cd (9.1 – 40.7%), Se (8.1 – 55%) and Hg (5 – 33%). For a third group of three elements Cr, Ni and Zn there is a lack of consistency in the outcomes which are being further investigated.

From these initial results it did not appear that partitioning of trace metals to the gas phase at the stack was a function of either firing condition (oxy or air-firing) or coal type. Further analysis for trace metals in the ash samples produced during the field trial will be carried out to provide further information of the metals partitioning and will be included in the final report.

Process gas concentrations of most metals in the CPU were at or around the method detection limits (MDL) beyond the first low pressure scrubber.

Under oxy-firing conditions SO<sub>2</sub> concentrations in the stack gases ranged from 1325 – 4059 mg/dscm, these levels were three to four times lower (300 -720 mg/dscm) during air-firing reflecting the increased mass flows of gas. The influence of feed coal sulfur on the concentrations observed in the tests is apparent in the results, where as might be expected higher sulfur coals result in higher stack gas SO<sub>x</sub> concentrations. Under air-firing conditions SO<sub>3</sub> was not detected, while under oxy-firing concentrations of 23 – 48 mg/dscm were determined.

Sulfur in the gas stream is removed effectively from the CPU process gas by the initial quench low pressure scrubber column and levels of SO<sub>x</sub> in the later stages of the CPU are at or below the MDLs, for both SO<sub>2</sub> and for SO<sub>3</sub>.

Overall the project objectives were achieved and the results suggest that oxy-firing does not pose significantly higher environmental or operational risks than conventional air-firing. The levels of trace metals in the “purified” CO<sub>2</sub> gas stream should not pose operational issues within the CPU.

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## INTRODUCTION and CONTEXT

Carbon dioxide capture and sequestration and storage (CCS) has been proposed as a mechanism to reduce carbon dioxide emissions from the industrial use of fossil fuels to produce electricity and other services. Oxy-combustion is a candidate technology for CCS, and a demonstration of this technology is being undertaken through the Callide Oxy-fuel Project.

(<http://www.callideoxyfuel.com/What/CallideOxyfuelProject.aspx>).

A potential component of the overall risk associated with oxy-combustion will be due to residual trace species in the CO<sub>2</sub> stream as these trace species will determine the need for and costs associated with gas-cleaning protocols for oxy-combustion to avoid emissions issues, and corrosion problems. It is recognised that the behaviour of trace metals and the related characteristics of the formation of fine particles may have important implications for process options and resultant cost (Toftegaard *et al.* 2010).

Environmental and operational risk of trace elements in oxyfuel processing will be determined by a range of inter-related considerations including:

- The emission flux (mass/time) of trace metals from the overall process;
- Capture efficiencies of the trace species in the various air pollution control devices used in the process; these may include gas and particulate control devices, and specialised systems for the removal of specific species such as mercury;
- Gas quality required to avoid operational issues such as corrosion, and to enable sequestration in a variety of storage media without creating unacceptable environmental risk; and
- Speciation of the trace species

A detailed review of the possible impacts of trace elements from coal combustion on the oxyfuel process has been prepared for ANLEC R&D as an initial part of this project (Nelson 2013). Wall *et al* (2013) also identified gas quality as an early research and regulatory issue, as the gas produced from oxy-fuel has higher levels of inert gases, sulfur and nitrogen gases, and other trace impurities. A detailed knowledge of the impacts of gas quality on power plants and materials, on transport systems, and on the regulations imposed on gas quality for storage, is thus required to reduce the risk of this CCS technology, as the costs of gas cleaning is likely to be higher for oxy-fuel (Wall et al. 2013).

Based on the earlier work outlined above it is clear that a significant component of the risk associated with oxy-combustion may be due to trace species in the CO<sub>2</sub> stream. These trace species will have an impact on costs associated with gas-cleaning requirements for oxy-combustion to avoid emissions and operational issues, such as corrosion. In the current project a combination of laboratory experiments, modelling and computational studies, and field measurements were proposed (this report covers the field work component), to obtain detailed information on trace components of oxy-fired combustion gases, including:

- Trace metal, gas and fine particulate matter (PM) emission rates from oxy-combustion compared to air-fired systems; to provide information for environmental risk assessment of stack emissions from the Callide Oxy-Fuel Plant; in fully commercial plants there are not expected to be any stack emissions (although plants would be expected to be able to operate and be compliant in both firing modes);
- Trace metal speciation in oxy-combustion products (gas, bottom and fly ash); speciation determines the toxicity, environmental transport behaviour and hence the risk associated with these products;
- Trace metal capture and transformation rates in the flue gas cleaning system and CO<sub>2</sub> processing plant;
- Ultimate trace component concentrations in product CO<sub>2</sub>, and an assessment of the suitability of the CO<sub>2</sub> for various uses (eg, pipeline quality for transport and storage; comparison with food grade CO<sub>2</sub> and required additional cleaning required to meet food grade standards); and
- Physical modelling and computational studies to assess flue gas composition effects on CO<sub>2</sub> capture, and to support, through predictive capability, the next stage of commercialisation.

### ***Target Species***

There are a number of accepted listings of trace metals and elements of environmental and/or human health concern. These include priority lists developed by the USEPA and by the Commonwealth for its Air Toxics Program. In the present work the target list of species to be characterised was based on the list of reportable substances included in the Australian National Pollutant Inventory (see <http://www.npi.gov.au/substances/list-of-subst.html>).

The target element list for the project was:

- Antimony (Sb)
- Arsenic (As)
- Beryllium (Be)
- Boron (B)
- Cadmium (Cd)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Lead (Pb)
- Manganese (Mn)
- Mercury (Hg)
- Nickel (Ni)
- Selenium (Se)
- Zinc (Zn)

## **WORK PROGRAM**

A series of measurements of trace element concentrations at the 25 MW Callide A Oxy-fuel plant were undertaken in the period 3<sup>rd</sup> – 20<sup>th</sup> December, 2012. Although the program had originally been planned to take place as two field campaigns in May,

2012 and April, 2013 these were compressed into one extended campaign by agreement with Callide Oxyfuel Services Pty Ltd (COSPL) and ANLEC R&D.

The field campaign involved personnel from Macquarie and Newcastle Universities, Malfroy Environmental Strategies and a contracted four person, specialist stack testing team (ECS Pty Ltd).

This component of the overall ANLEC R&D project 6-0411-0130 examines trace element transformations in the flue gas of the retrofitted Callide A power plant and CO<sub>2</sub> Processing Unit (CPU) during oxy and air-firing, to examine reactions between gas and particulate phases, and to determine trace element capture efficiencies in air pollution control devices. Details of the plant can be found on the Callide Oxyfuel website: <http://www.callideoxyfuel.com/What/CallideOxyfuelProject.aspx>

During the three week period of the test program; four coal feeds, including mixtures of two coal types, two which were sub-bituminous (CL and BL) and one semi-anthracite (MN), from three mining localities were combusted under both air-fired and oxy-fired conditions. These were CL, Blend 1 (CL+BL), Blend 2 (CL+MN) and MN. Sampling was carried out for solids inputs and outputs (coal and ash), gases at the stack exhaust (under both air and oxy-fired conditions) and at various points within the CPU.

Three detailed summary tables of furnace conditions, input parameters etc were provided by COSPL and are appended to this report:

- Test Results - Overall
- Test Results – Fly Ash
- Test Results – Flue Gas

The data gathered on the Callide plant during the December, 2012 field campaign will be integrated with laboratory experiments of coal combustion in oxy-fired systems for a final project report to be submitted to ANLEC R&D in 2014.

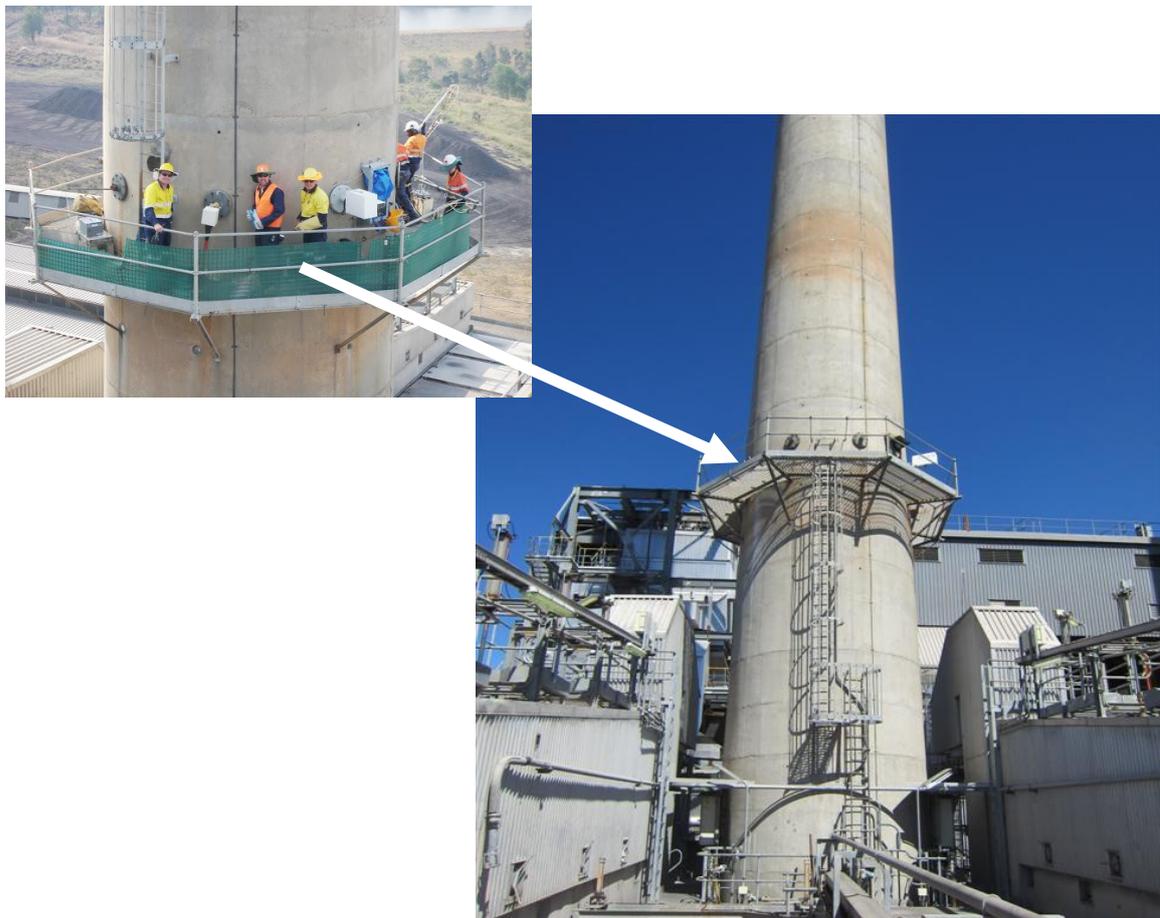
# SAMPLING AND ANALYSIS

## *Mercury Sampling*

During the field trials sampling for mercury was undertaken across the Callide A plant at both the stack outlet and at various points within the CO2 Processing Unit (CPU), these locations are listed in Table 1 and shown in Figures 1, 2 and 3.

**Table 1. Field trial sampling locations within the Callide A plant and CPU**

Sampling site	Abbreviation	Location Identification Code
Stack	Stack	Callide A exhaust stack
Blower Outlet	Blower	AP 370B-1
CPU Compressor Outlet	Compressor	AP 2404B
Drier Outlet/Cold Box Inlet	Drier Outlet	AP 4057B
Cold Box Outlet	Coldbox Outlet	AP 5316A



**Figure 1 Stack sampling locations used on the Callide A plant.**

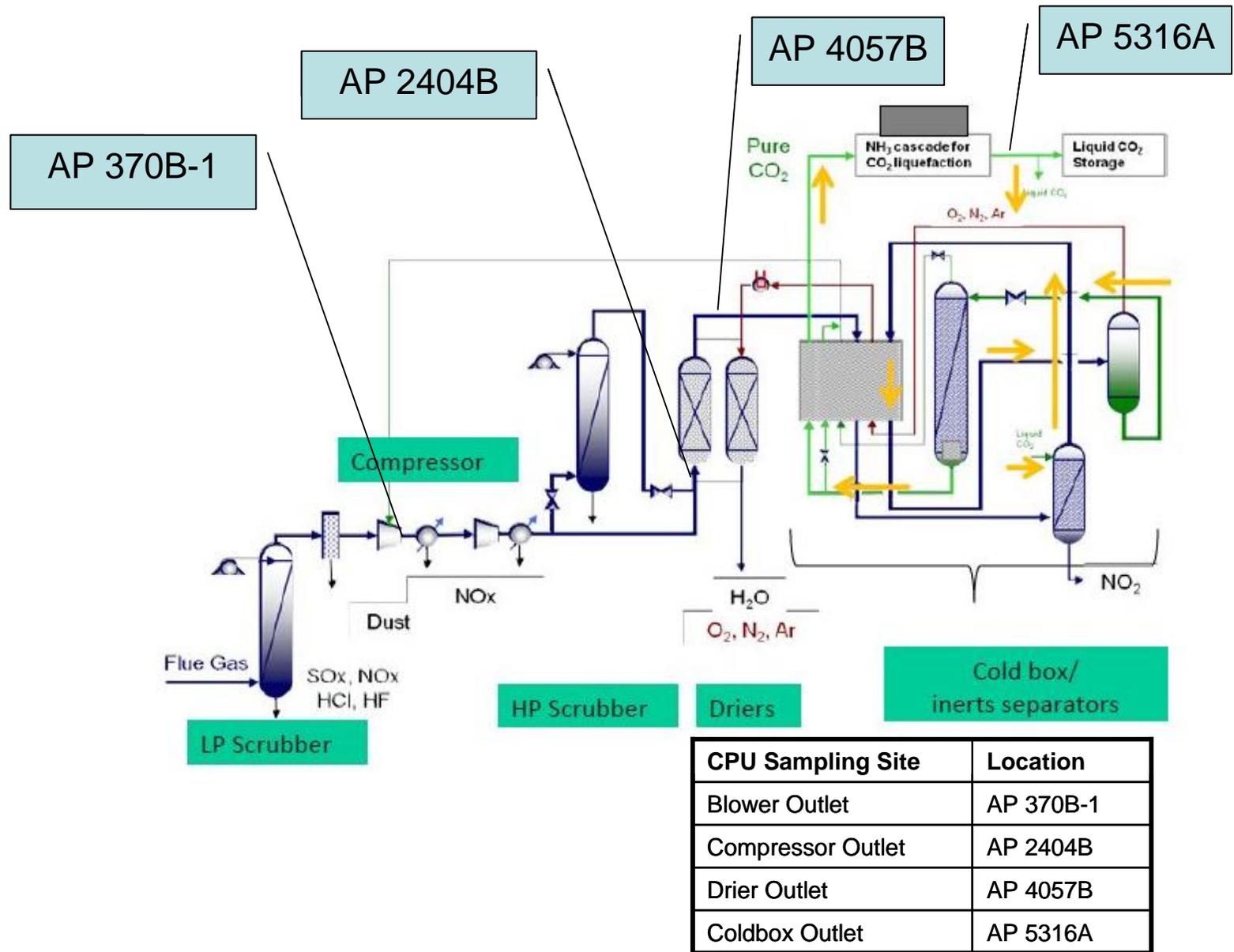
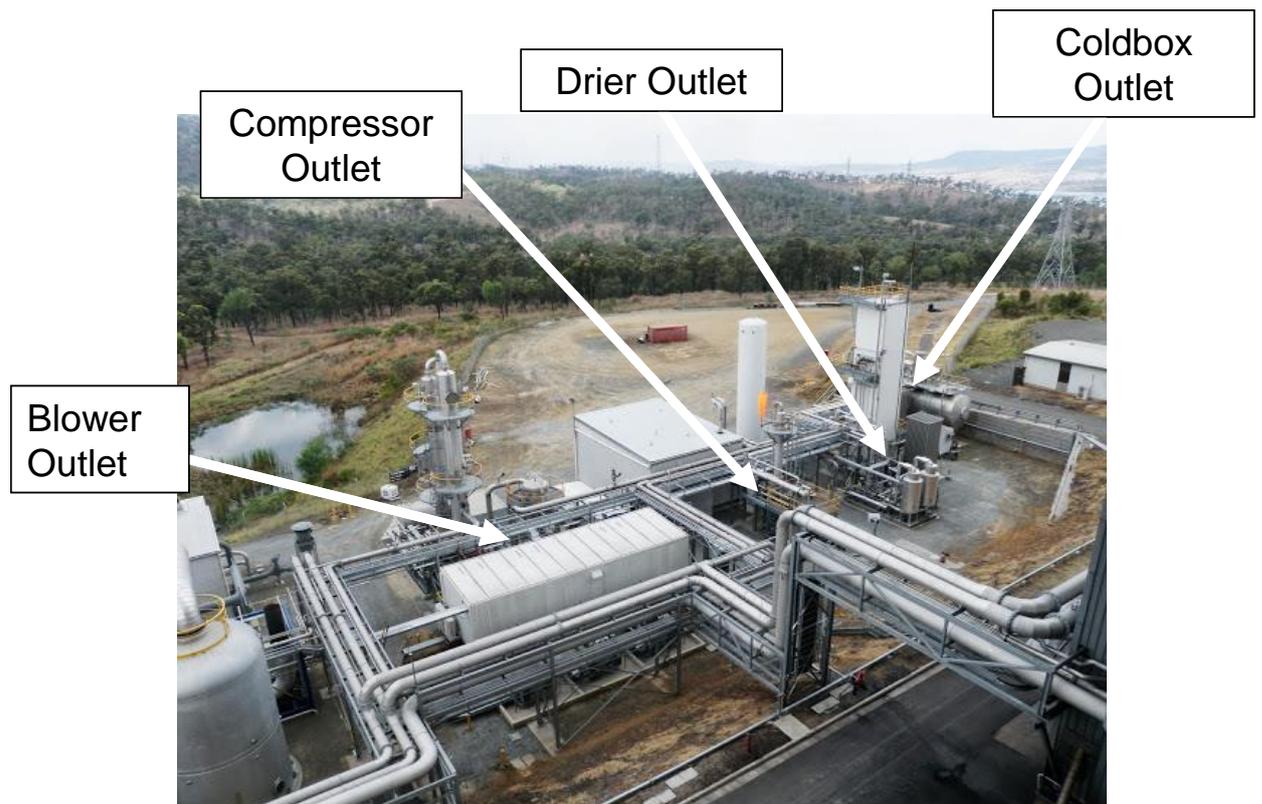


Figure 2 Schematic diagram of the CPU showing sampling locations (original diagram Air Liquide)



**Figure 3 Sampling locations used on the CPU.**

Flue gas sampling was carried out on seventy three occasions by ECS Pty Ltd; of these, sampling was at the stack on fifty occasions and on the CPU on a further twenty three. This sampling is broken down into combustion gases (14), halogens and halides (21), metals (17), particulates (10) and sulfur oxides (11).

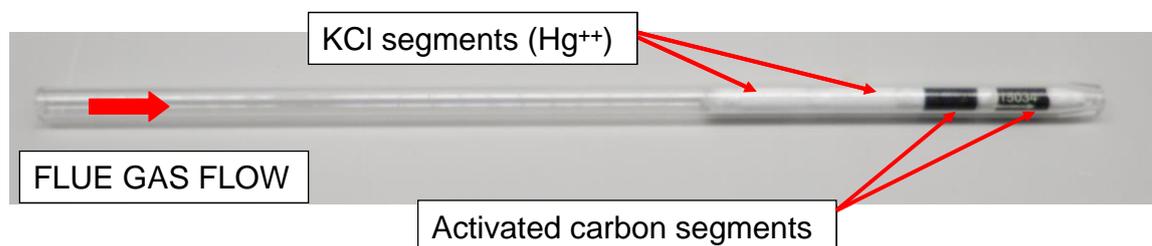
Mercury sampling was undertaken by the Macquarie University team on eighty three occasions throughout the field trials. Sorbent sampling techniques (Schmid and DeRosier 2011) were used for mercury measurement in both stack and CPU locations. Sorbent samples were generally taken in duplicate, although single sorbent samples were taken during periods at the CPU Blower Outlet when a Tekran<sup>1</sup> continuous mercury analyser was run in parallel to sorbent tube collection .

### **Sorbent Tube Collection**

Sorbent tube collection methods generally followed the sample collection protocols set out in USEPA Method 30B (USEPA 2013d). However, because of the research nature of the project the sorbent tubes were constructed containing two initial segments of potassium chloride (KCl) followed by two segments of iodated activated charcoal (Figure 4). The use of the KCl segments allows an estimate of Hg<sup>2+</sup> concentration in the stack gases to be made, although breakthrough of mercury into the second KCl trap, even when probe flow was lowered, suggests that the levels

<sup>1</sup> <http://www.tekran.com/files/Tekran-2537B-Unique-Features.r103.pdf>

estimated should be seen as a lower limit rather than as absolute concentrations. The inaccuracies in  $\text{Hg}^{2+}$  estimation are not reflected in the total mercury results as levels of mercury in the second iodated charcoal trap were universally low, indicating that all available mercury was retained in the sorbent trap.



**Figure 4 Sorbent tube showing two initial KCl segments for  $\text{Hg}^{2+}$  collection**

Based on field and analysis blanks taken during the field trial period, inherent levels of mercury in the sorbent tubes were estimated to be 0.14 ng for the KCl traps and 0.33 ng for the iodated carbon traps. The results obtained have been corrected using these blank values. The blank correction was generally small compared to the overall mercury captured in the segment.

Analysis of spiked segments of sorbent traps returned values of 98% recovery, which is well within the accepted range of  $\pm 10\%$  of the analytical spike target (USEPA 2013d).

### **Sorbent Tube Analysis**

Sorbent tube analysis was undertaken both onsite during the trials using a Milestone Direct Mercury Analyser (DMA)<sup>2</sup> and by Ohio-Lumex in the USA, using their proprietary analyser<sup>3</sup>, following the trials. The DMA thermally releases mercury from the samples by combustion and the Ohio-Lumex analysis method uses thermal desorption of the samples. In both instruments this is followed by detection of evolved mercury using atomic absorption spectrophotometry. Both analysis techniques are recognised as appropriate under USEPA Method 30B for measurement of mercury in flue gases (USEPA 2013d).

Initially it was proposed to carry out all the analysis on site using the DMA during the December trial. Operational difficulties with the interaction of the samples with the catalyst in the equipment made this impractical and it was necessary to have most of the samples analysed after the trials by Ohio-Lumex.

In total 110 sorbent tubes were exposed and analysed during the December trial. In addition a further 10 spiked samples or field blanks were also analysed using the same techniques for the purpose of QA/QC.

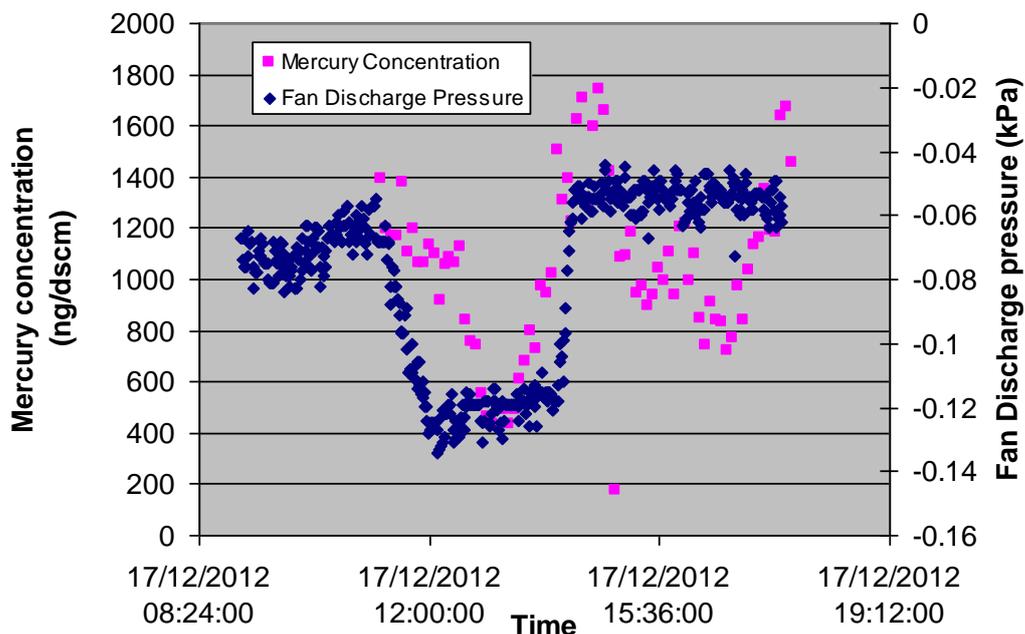
<sup>2</sup> <http://www.milestonesci.com/product-menu/mercury/dma80-overview/mercury-tech-specs.html>

<sup>3</sup> [http://www.ohiolumex.com/products/ra915\\_mercury\\_analyzer.php](http://www.ohiolumex.com/products/ra915_mercury_analyzer.php)

## Continuous Mercury Measurements

Continuous measurements of total mercury in the gas stream were made within the CPU using an ambient mercury Tekran 2537B analyser. The analyser uses gold preconcentration combined with atomic fluorescence detection. The manufacturers stated minimum detection limit for the analyser is less than  $0.1 \text{ ng/m}^3$ . An internal mercury permeation source allows routine calibrations to be automatically or manually initiated. The calibration unit generates concentrations of mercury by using a National Institute of Standards and Technology-traceable temperature-controlled saturated mercury vapour source. Precision mass flow controllers are used to dilute the output of this source to the desired value.

Total mercury levels could be measured directly from the process gas downstream of the compression stage of the CPU i.e. where total mercury levels were relatively low. The Tekran could be left for extended periods in these locations to automatically measure and log mercury levels. At the blower outlet, where mercury concentrations at times had short term peaks of up to  $5 \text{ } \mu\text{g/m}^3$ , it was necessary to dilute the process gas stream to bring the concentration within the range of the instrument. This was achieved by using a rotameter to provide  $\sim 0.4 \text{ L/min}$  of process gas and then using an electronic mass flowmeter to provide an approximately 40:1 dilution of the process gas stream with  $20 \text{ L/min}$  of dry instrument air. A pre-dilution mercury concentration was then calculated from the Tekran output data.



**Figure 5 Pressure and concentration trace for the blower outlet 17th December, 2012.**

Because of pressure fluctuations in the system which affected the rotameter flow it was not possible to leave the system running unsupervised as it required ongoing adjustment of the rotameter flows. As a result only those periods when the flow system was “supervised” are reported although much longer periods were logged. Even with supervision it is probable that some of the variation in measured mercury concentration is due to system variations in pressure and/or flow. As an example,

Figure 5 shows the pressure and mercury concentration trace for the blower outlet for an extended period on the 17<sup>th</sup> December, 2012, where a drop in the output pressure is followed by a drop in the apparent measured mercury concentration. This data suggests that a more sensitive dilution system maybe required if accurate continuous measurements of mercury are to be made at the blower outlet using the existing Tekran measurement system.

Comparison of a series of five sorbent tubes which were collected from the blower outlet contemporaneously with periods of well controlled continuous mercury analysis shows a high degree of correlation (0.8) and linearity ( $r^2=0.9$ ), but there is an unexplained and significant concentration offset ( $\sim 0.6 \mu\text{g/dscm}$ ) (Figure 6). This offset in the may be a result of the dilution system, although because this hypothesis cannot be tested, a conservative approach has been taken and the Tekran results have not been corrected for the offset. Therefore the Tekran mercury results reported at the Blower Outlet (where dilution was required) remain higher than those that were obtained using the sorbent collection technique. Results from the sampling points further downstream from the blower outlet (high pressure scrubber, dryer outlet, coldbox outlet) are unaffected as no dilution was required.

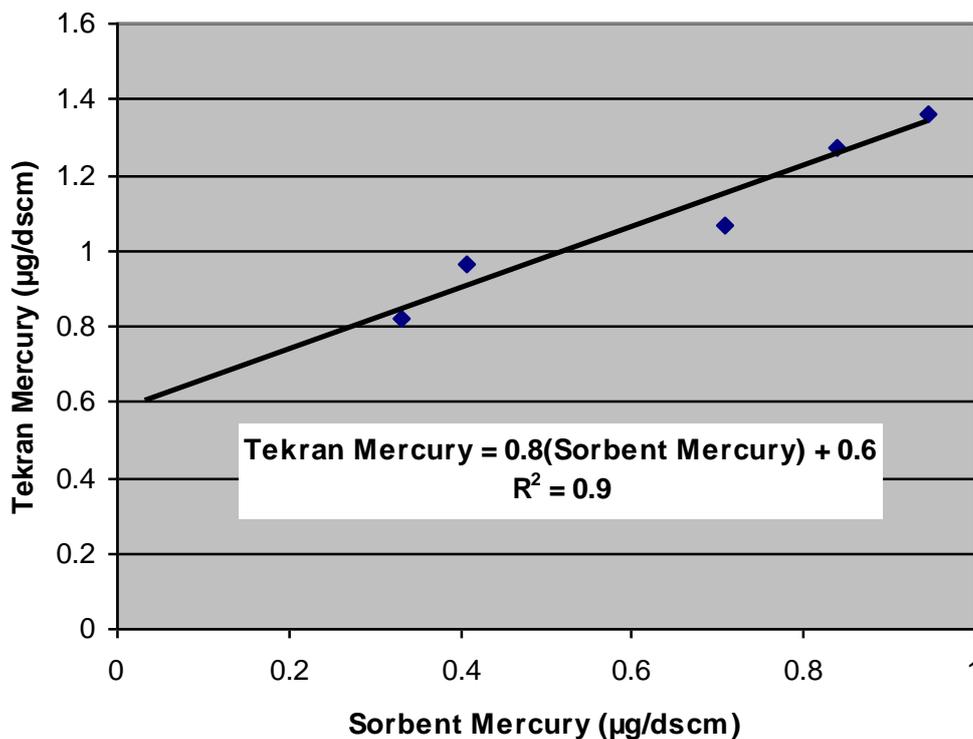


Figure 6 Correlation between continuous measurements and sorbent tube analysis for mercury concentration

### ***Halogen and Halide sampling***

The halogen and halide species Br, Cl, F, HBr, HCl and HF were determined using USEPA Method 26A (USEPA 2013b) at the stack. On the CPU sampling could not be performed isokinetically (following USEPA 26A) in the pressurised environment and the sampling train was modified to allow constant rate sampling. Sampling was undertaken on eleven occasions at the CPU [blower outlet (5), compressor outlet (4), dryer outlet (1), coldbox outlet (1)]. At the stack, sampling was undertaken on ten occasions by ECS Stack Pty Ltd. .

### ***Metals sampling***

Multi-metal emissions (Sb, As, Be, B, Cd, Cr, Ca, Cu, Pb, Mn, Ni, Se, Zn) were determined using USEPA Method 29 (USEPA 2013c) at the stack. In common with the halide sampling on the CPU, sampling could not be performed isokinetically (following USEPA 29) in the high pressure environment and the sampling train was modified to allow constant rate sampling. Sampling was undertaken on seven occasions at the CPU [blower outlet (3), compressor outlet (3), dryer outlet (1)]. At the stack, sampling was undertaken on ten occasions by ECS Stack Pty Ltd.

### ***Detection limits for sampled elements***

Minimum detection limit ranges for the elements sampled in the stack and CPU gases are given in Table 2.

### ***Combustion gas concentrations***

Combustion gas concentrations (SO<sub>2</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub> and O<sub>2</sub>) were determined during the program using portable gas analysers. In addition, sulfur concentrations (as SO<sub>2</sub>, and SO<sub>3</sub>) were also determined at the stack on six occasions and in the CPU at all four sampling locations using USEPA Method 8 (USEPA 2013a).

### ***Ash and Coal Sampling***

Ash and coal samples were collected for chemical analysis by COSPL on a daily basis, with the ash collected at 13 locations within the ash handling train (Figure 8 and

Figure 7, Table 3).

**Table 2 Range of minimum detection limits (MDLs) for elements and gases sampled during the fieldwork program.**

Element	MDL Range (mg/dscm) STACK	MDL Range (mg/dscm) CPU
Antimony	0.0017- 0.0043	0.00055-0.00082
Arsenic	0.0042 – 0.0110	0.0014-0.0021
Beryllium	0.0017- 0.0043	0.00055-0.00082
Boron	0.0042 – 0.0110	0.0014-0.0021
Cadmium	0.0017- 0.0043	0.00055-0.00082
Chromium	0.0017- 0.0043	0.00055-0.00082
Cobalt	0.0017- 0.0043	0.00055-0.00082
Copper	0.0017- 0.0043	0.00055-0.00082
Lead	0.0017- 0.0043	0.00055-0.00082
Manganese	0.0017- 0.0043	0.00055-0.00082
Nickel	0.0017- 0.0043	0.00055-0.00082
Selenium	0.0043 – 0.0110	0.0014-0.0021
Zinc	0.0042 – 0.0110	0.0014-0.0021
Bromine	0.031 – 0.077	0.016 – 0.033
Chlorine	0.150 – 0.390	0.031 – 0.170
Fluorine	0.031 – 0.077	0.022 – 0.160
HBr	0.038 – 0.077	0.016 – 0.130
HCl	0.190 – 0.390	0.031 – 0.170
HF	0.190 – 0.390	0.082 – 0.170
SO <sub>2</sub> (USEPA 6c)	2.90	N/A
SO <sub>2</sub> (USEPA 8)	0.93 -2.10	0.36 – 0.95
SO <sub>3</sub> (USEPA 8)	0.72 – 1.30	0.44 – 0.79
Element	MDL Range (ng/dscm)*	MDL Range (ng/dscm)*
Mercury	0.1 – 1.2	0.1 – 1.2

\* Note change of units





**Figure 8 Collection of flyash from hoppers at the base of fabric filters**

A standardised collection distribution for the ash handling train based on previous work was provided by COSPL (C. Spero *pers comm.*). This collection distribution is shown in Table 3 and was used in subsequent mass balance calculations.

**Table 3 Standardised collection distribution for ash samples in ash collection train (provided by COSPL)**

Ash Collection Position	Collection distribution (Wt % of total ash)
Fabric Filter A	20.0
Fabric Filter B	16.5
Fabric Filter C	12.5
Fabric Filter D	10.0
Fabric Filter E	7.5
Fabric Filter F	5.5
Fabric Filter G	3.5
Fabric Filter H	2.0
Rear Pass A	2.5
Rear Pass B	2.5
Air Heater A	1.25
Air Heater B	1.25
Furnace Ash	15.0
<b>TOTAL</b>	<b>100</b>

Individual coal and ash samples were analysed for Hg and UBC content and a daily reconstituted ash sample (based on the assumed retained percentages in Table 3) was analysed for some trace metals and oxides. Mercury analyses were carried out in triplicate and the averaged results reported.

## RESULTS AND DISCUSSION

### ***Coal and ash analyses***

Coal and ash samples collected during the trials were analysed by Bureau Veritas and the results supplied by COSPL appear in Table 4, Table 5 and Table 6. The results show that the trace element contents of the two coals (CN, MN) and the two blended coal feeds (Blend 1, a mixture of CL and BL coals, Blend 2, a mixture of CL and MN coals) are very similar for most elements determined, with the exception of Ba, B and Mn. The MN coal had a Ba level of 790 mg/kg which is ~12 times the average levels of the CL coal (~67 mg/kg) and ~3-4 times that of the blends (190 – 270 mg/kg).. Levels of B in the MN coal (58.4 mg/kg) are around twice that of CL (~28 mg/kg) and this is reflected in a slight elevation in the levels of Blend 2 (~36 mg/kg). Levels of Mn are lower in the MN coal (100 mg/kg) compared to an average of 325 mg/kg in the CL and blended coals.

Total sulfur for the MN coal (0.43%, as received) are approximately double that of the CL coal (0.21%, as received) and this is reflected in slightly elevated values (0.26%, as received) for Blend 2. The Blend 1 coal also has higher sulfur levels (0.28%, as received) suggesting that the BL coal (not tested separately) also has higher sulfur levels.

Table 6 includes the major oxides determined for the ash samples, the trace metals in the ash will be discussed in a subsequent section. No differences of note are apparent in the major oxides between the samples.

### ***Mercury in coal and ash***

Table 7 shows the averaged results of mercury analyses obtained for the coal and ash samples obtained during the trial period. Results are the average of three analyses undertaken by Ohio-Lumex. For some samples where the result appeared anomalous (**bold** in the Table) the analysis was replicated a further three times. These repeated results were not significantly different and as an outcome the average of all analysed values was reported.

Reproducibility and repeatability of mercury analyses was excellent. As an indication, the homogenised CL coal was sampled and analysed on seven occasions, the averaged values (of triplicate analysis) ranged from 31.2 – 39.4 (ng/g), with the average of all analyses (n=21) being 33.6 (ng/g) with a standard deviation (SD) equal to 3.5 (ng/g). The lower accuracy mercury results provided in Table 4 are generally in accordance with these, ranging from 0.03 – 0.04 mg/kg, with the exception of the analyses on two days, where higher levels (0.06, 0.07 mg/kg) were determined. Based on the single available sample, the MN coal appears have a mercury content (22.9 ng/g), which is lower than the mercury content of the CL coal used in most firings.

Mercury contents in the ash varied widely with the highest concentrations reporting in the flyash (43 – 270 ng/g), whilst the other ash repositories, in the higher temperature regions of the process (Rear Pass, Air Heater, Furnace Ash) contain significantly

lower mercury levels (1.7 – 24 ng/g). A detailed discussion of the distribution and partitioning of mercury in the process appears later in this report.

### ***Unburnt carbon in ash samples (UBC)***

Residual carbon in the ash (UBC) produced from coal combustion is believed to have a significant effect on the capture efficiency of mercury in air pollution control devices (Senior and Johnson 2005; Chen et al. 2007; Hudson 2008). As a consequence, analyses for UBC% of all ash fractions were undertaken and these results appear in Table 8. The UBC% was estimated from the loss on ignition of the ash samples at 1000°C and the estimation assumes that all other volatiles have been previously removed during the ignition process.

The UBC% values vary considerably from run to run and even from day to day with the same coal. The results show that under air-firing conditions UBC% levels were generally higher than for oxyfiring of the same coal. It is expected that the UBC% in oxy-firing for the same %O<sub>2</sub> in the flue gas will be lower due to the greater time for combustion and also the higher O<sub>2</sub> during combustion (i.e. O<sub>2</sub> through the burners of 27% rather than 21%). For air-firing the UBC% ranged from 7.2 – 17.7%, whilst for oxy-firing it was 1.4 – 17.0%.

Due to the lower gas flowrates during oxy-firing it is recognised that contact times between the exhaust gases and the UBC is likely to be increased over that occurring during air-firing providing greater opportunity for mercury capture on the surface of residual carbon particles.

Very high UBC% in ash values (up to ~30% for some ash fractions)) from the firing of MN coal on the 19<sup>th</sup> and 20<sup>th</sup> December (averaging ~17%) are likely to be sub-optimal due to the failure of a coal swirler in the burner during the testing period.

**Table 4 Analysis of trace elements in coal feed (dry basis) (mg/kg) (data provided by COSPL)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+ BL	CL+ BL	CL+MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND1	BLEND2	BLEND2								
Antimony	0.2		0.4	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.4	
Arsenic	0.8		1.4	1.5	1.5	1.4	1.5	1.0	1.1	1.3	0.9	1.0	1.0	1.5	
Barium	55		270	190	190	210	190	81	70	56	73	71	59	790	
Beryllium	1		1	1	1	1	1	1	1	1	1	1	1	2	
Boron	27.8		23.7	23.0	23.0	34.4	37.4	29.2	28.7	26.8	27.2	27.0	28.0	58.4	
Bromine	<25		<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	
Cadmium	0.14		0.14	0.12	0.12	0.11	0.13	0.12	0.10	0.14	0.11	0.1	0.11	0.07	
Chromium	13		13	11	11	13	16	14	13	16	18	15	14	16	
Cobalt	8		8	7	7	10	11	8	8	10	9	9	8	16	
Copper	23		23	20	20	20	21	27	29	26	29	29	25	17	
Lead	12		12	11	11	13	12	13	13	15	13	13	13	9.9	
Manganese	300		300	270	270	280	350	330	350	380	360	380	340	100	
Mercury	0.03		0.03	0.03	0.03	0.04	0.04	0.04	0.06	0.07	0.03	0.04	0.03	0.02	
Nickel	17		17	10	10	15	16	18	17	16	19	20	15	20	
Selenium	0.3		0.3	0.3	0.3	0.4	0.4	0.3	0.3	0.4	0.3	0.3	0.4	0.6	
Silver	0.16		0.16	0.18	0.18	0.19	0.16	0.18	0.18	0.19	0.21	0.19	0.19	0.15	
Thallium	<1		<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Thorium	5		5	4.6	4.6	5.5	5.2	5.5	5.1	5.5	5.4	5.3	5.4	5.3	
Tin	<2		<2	<2	<2	<2	<2	2	<2	nd	<2	<2	<2	<2	
Vanadium	41		41	38	38	37	39	48	45	43	45	47	44	37	
Zinc	18		18	15	15	20	21	17	14	23	16	15	15	22	

**Table 5 Coal analyses (Data provided by COSPL)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+ BL	CL+ BL	CL+MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND1	BLEND2	BLEND2								
Total Moisture (%) <sup>1</sup>	13.0		11.5	12.7	12.7	11.8	12.5	13.5	12.8	12.2	13.3	16	17.1	5.8	
Ash (%) <sup>1</sup>	22.6		18.9	20.8	20.8	24.8	23.7	25.6	24.2	25.8	22.8	22.2	23.4	23.9	
Volatile Matter (%) <sup>1</sup>	21.9		18.6	17.2	17.2	21.6	21.9	20.4	21.5	21.8	21.7	20.9	20.6	27.9	
Fixed Carbon (%) <sup>1</sup>	42.5		51	49.3	49.3	41.8	41.9	40.6	41.5	40.2	42.2	40.9	38.9	42.4	
Fuel Ratio (FC/VM) <sup>1</sup>	1.94		2.74	2.86	2.86	1.93	1.91	1.99	1.93	1.84	1.94	1.96	1.89	1.52	
Total Sulfur (%) <sup>1</sup>	0.2		0.27	0.28	0.28	0.26	0.26	0.22	0.22	0.2	0.24	0.2	0.21	0.43	
Chlorine (%) <sup>1</sup>	0.02		0.04	0.04	0.04	0.04	0.04	0.02	0.01	0.02	0.01	n.a.	n.a.	0.02	
Gross Calorific Value (MJ/kg) <sup>1</sup>	18.91		21.91	20.59	20.59	19.04	19.04	17.75	17.97	18.05	18.63	18.03	17.28	23.43	
HGI <sup>2</sup>	81		80	85	85	77	73	80	80	76	82	74	86	50	
Carbon (%) <sup>3</sup>	77.89		81.17	81.49	81.49	77.76	77.93	75.28	75.83	75.59	76.01	75.79	75.24	n.a.	
Hydrogen (%) <sup>3</sup>	3.92		4.04	4.04	4.04	4.31	4.3	3.73	3.65	3.69	3.48	3.56	3.78	5.59	
Nitrogen (%) <sup>3</sup>	1.07		1.38	1.4	1.4	1.45	1.44	1.11	1.1	1.14	1.1	1.1	1.1	2.76	
Sulfur (%) <sup>3</sup>	0.31		0.38	0.42	0.42	0.42	0.41	0.43	0.35	0.32	0.37	0.33	0.35	0.65	
Oxygen (%) <sup>3</sup>	16.81		13.03	12.65	12.65	16.06	15.92	19.45	19.07	19.26	19.04	19.22	19.52	4.09	

<sup>1</sup> as received

<sup>2</sup> Hardgrove Grindability Index

<sup>3</sup> dry ash free

**Table 6 Composite ash analysis as major oxides (% , dry basis)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2								
SiO <sub>2</sub>	55.9	55.3	52.5	49.1	51.1	53.8	56.2	55.6		56.3	56.5	53.5	46.6	52.3
Al <sub>2</sub> O <sub>3</sub>	28.6	30.2	28.6	25.2	25.9	28	30.9	29.6		29.5	29	27.8	20.8	19.3
Fe <sub>2</sub> O <sub>3</sub>	8.2	8.2	8.1	7.1	8.6	8.1	7.2	8.2		7.8	7.3	7.3	6.3	5.9
CaO	0.7	0.98	0.89	0.7	0.65	0.77	0.94	0.93		0.82	0.75	0.7	0.68	0.51
MgO	0.5	0.71	0.7	0.5	0.5	0.6	0.73	0.7		0.62	0.57	0.53	0.66	0.73
Na <sub>2</sub> O	0.1	0.16	0.2	0.2	0.3	0.2	0.17	0.15		0.18	0.14	0.15	0.16	0.25
K <sub>2</sub> O	0.18	0.19	0.64	1.13	0.55	0.66	0.2	0.23		0.22	0.19	0.18	1.01	1.86
TiO <sub>2</sub>	1.7	1.78	1.6	1.3	1.3	1.5	1.83	1.74		1.68	1.64	1.55	1.05	0.79
Mn <sub>3</sub> O <sub>4</sub>	0.17	0.18	0.18	0.14	0.17	0.16	0.18	0.19		0.18	0.17	0.16	0.12	0.10
P <sub>2</sub> O <sub>5</sub>	0.04	0.05	0.11	0.17	0.17	0.24	0.04	0.06		0.05	0.05	0.05	0.33	0.59
SO <sub>3</sub>	0.10	0.10	0.13	0.17	0.15	0.17	1.06	0.13		0.12	0.12	0.1	0.26	0.33
SrO	nd	nd	0.02	nd	0.04	0.05	ND	nd		nd	nd	nd	0.07	0.11
BaO	nd	nd	0.04	0.06	0.05	0.08	0.03	0.03		0.03	0.02	nd	0.12	0.24
ZnO	nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd
V <sub>2</sub> O <sub>5</sub>	nd	0.03	nd	nd	nd	nd	0.03	0.02		0.02	0.02	nd	nd	0.02

n.d. not detected

**Table 7 Results of averaged\* ash and coal analyses for mercury (values are ng/g)**

SAMPLE DATE	5/12/2012	6/12/2012	7/12/2012	8/12/2012	10/12/2012	11/12/2012	12/12/2012	13/12/2012	16/12/2012	17/12/2012	18/12/2012	19/12/2012	20/12/2012
FIRING CONDITION	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	MN	MN
			BLEND 1	BLEND 1	BLEND 2	BLEND 2							
Coal	31.4		29.4	32.6	34.0	28.4	32.9	34.7	31.8	31.2	33.9	22.9	
Fabric Filter A	101.3	240.8	116.5	89.8	94.1	270.3	<b>61.1</b>	273.6	127.7	<b>44.4</b>	129.3	151.1	<b>42.8</b>
Fabric Filter B	193.2	100.0	179.8	71.3	129.8	226.4	117.1	153.9	185.9	148.8	169.2	<b>52.3</b>	182.3
Fabric Filter C	154.3	204.0	247.1	90.9	102.0	219.5	145.6	193.6	116.4	141.9	122.5	192.1	180.5
Fabric Filter D	145.0	154.0	134.6	93.6	167.4	204.5	121.4	204.3	149.5	158.5	207.1	158.3	110.0
Fabric Filter E	172.2	129.0	215.8	115.7	189.4	219.9	246.0	160.2	136.3	149.2	247.4	171.2	119.6
Fabric Filter F	216.9	148.9	217.1	107.5	205.3	190.6	189.6	159.8	135.5	159.5	194.4	<b>93.7</b>	186.1
Fabric Filter G	179.3	190.5	162.9	145.8	217.0	219.1	236.6	188.7	168.2	132.4	254.2	180.0	186.1
Fabric Filter H	211.0	166.9	181.9	138.0	235.8	269.7	177.8	203.3	<b>87.3</b>	162.4	256.0	265.5	198.0
Rear Pass A	1.7	1.5	1.3	1.5	1.7	1.2	1.4	1.8	1.0	1.5	2.1	0.9	0.8
Rear Pass B	1.8	1.7	2.0	1.2	1.4	1.1	1.1	1.4	1.3	3.1	1.8	1.6	0.8
Air Heater A	10.9	7.9	5.6	24.0	20.1	11.6	5.5	5.5	4.7	4.3	10.7	20.8	15.6
Air Heater B	12.6	5.7	7.4	15.6	6.2	11.6	7.5	6.1	3.3	3.3	8.1	9.0	8.3
Furnace Ash	7.4	3.5	2.8	4.5	3.5	3.1	3.3	3.7	3.1	3.8	1.8	2.8	2.4
Overall Combined (ng/g)	123	134	135	74	108	180	103	157	112	96	134	109	103
Weighted average FF (ng/g)	156	172	174	94	139	231	132	202	143	122	172	140	131

\* individual samples were analysed in triplicate, all three analyses of results in bold were repeated, and result reported is the average for all six analyses

## **Mercury in stack and CPU process gas**

### **Sorbent tube sampling**

Table 9 shows averaged results of sorbent trap sampling for mercury ( $\text{Hg}$  (total),  $\text{Hg}^\circ$  and  $\text{Hg}^{2+}$ ) at both the stack sampling position and at the blower outlet (APF 370B-1). Although some tests were undertaken in the CPU further downstream of the blower (compressor outlet, dryer outlet, coldbox outlet) these results were all at or below the MDLs for this technique and are therefore not reported, although results from the Tekran continuous analyser are available for these sampling positions.

Mercury concentrations measured at the stack ranged from 0.08 – 4.86  $\mu\text{g}/\text{dscm}$  during the test period. With the exception of the run on the 20<sup>th</sup> December (with exceptionally high UBC% due to a burner swirler failure) the mercury concentration levels in the oxy mode process gas are significantly higher than those under air-firing mode. The anomalous result on the 20<sup>th</sup> December also appears to have lower concentrations of mercury at the stack than at the first sampling point in the CPU (Blower Outlet) which is difficult to explain. Discounting this anomalous result, total measured mercury concentrations at the stack during oxy-firing averaged  $\sim 3 \mu\text{g}/\text{dscm}$  during the trial, while the average concentration during air-firing was  $\sim 0.3 \mu\text{g}/\text{dscm}$ . Some of this concentration difference can be accounted for by the lower gas mass flows for oxy-firing rather than air-firing (a factor of around 3) but the residual amount is the decrease in partitioning of mercury to the ash phase during oxy-firing.

The averaged  $\text{Hg}^{2+}/\text{Hg}_{\text{total}}$  ratio calculated for both stack gas and CPU process gas sampled at the blower outlet can be found in Table 9. The results in the stack gas range from 0.48 – 0.80. Given the limited number of firing conditions no discernable pattern is evident resulting from oxy or air-firing mode. Notwithstanding this, the highest ratios occurred under oxy-firing mode and the lowest under air-firing mode.

In the CPU process gas the absorption of large quantities of mercury (particularly  $\text{Hg}^{2+}$ ) by the two initial wet low pressure scrubbers in the CPU (Figure 2) can be clearly seen and the residual gas has a much reduced overall mercury concentration ranging from 0.34 – 0.91  $\mu\text{g}/\text{dscm}$ . As a result total measured mercury concentration at the blower outlet using the sorbent tubes averaged  $\sim 0.6 \mu\text{g}/\text{dscm}$  during the trial period.

**Table 8 Ash% and UBC% for coal and ash samples**

SAMPLE DATE	5/12/2012	6/12/2012	7/12/2012	8/12/2012	10/12/2012	11/12/2012	12/12/2012	13/12/2012	16/12/2012	17/12/2012	18/12/2012	19/12/2012 <sup>2</sup>	20/12/2012 <sup>2</sup>
FIRING CONDITION	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	MN	MN
			BLEND 1	BLEND 1	BLEND 2	BLEND 2							
<b>Ash (%)</b>													
Coal Ash (%)	22.6		18.9	20.8	24.8	23.7	25.6	24.2	22.8	22.2	23.4	23.9	
Produced Ash (%) <sup>1</sup>	23.1	22.9	19.8	23.8	27.1	24.8	26.5	24.6	23.2	22.8	25.2	29.0	28.8
<b>UBC (%)</b>													
Fabric Filter A	2.5	1.3	8.6	13.8	7.0	3.2	6.1	1.5	1.6	3.9	8.0	8.3	15.5
Fabric Filter B	3.8	1.9	5.7	14.2	12.7	5.8	2.1	2.1	1.2	1.8	6.2	27.9	19.4
Fabric Filter C	3.3	0.9	4.8	13.2	7.9	4.2	1.8	1.5	1.5	3.0	6.7	7.7	12.5
Fabric Filter D	1.8	0.9	3.9	13.2	6.8	5.2	3.6	1.3	1.1	3.2	4.6	11.9	19.4
Fabric Filter E	1.1	1.2	2.4	13.3	5.9	5.1	2.4	1.3	1.2	1.6	2.4	12.0	17.4
Fabric Filter F	1.4	1.0	2.4	14.4	3.8	5.3	3.0	1.4	1.0	1.3	3.7	23.4	14.8
Fabric Filter G	1.0	1.3	1.4	11.7	4.5	3.9	2.8	1.3	0.9	1.0	2.3	9.6	11.5
Fabric Filter H	1.1	0.8	1.1	14.7	3.4	2.9	1.8	1.8	0.7	0.9	2.1	3.4	10.4
Rear Pass A	3.0	2.1	1.8	7.4	7.0	6.0	2.5	2.9	2.7	3.7	6.7	17.9	21.6
Rear Pass B	4.2	3.4	2.4	8.1	8.7	7.8	4.1	4.5	2.9	6.9	7.9	25.2	19.6
Air Heater A	3.7	2.4	2.3	6.6	14.5	6.8	4.3	1.8	2.2	3.1	6.4	24.9	26.0
Air Heater B	5.4	4.4	3.7	11.1	8.5	1.2	2.9	3.0	2.8	5.5	11.2	30.4	19.1
Furnace Ash	0.9	1.5	2.4	10.0	11.3	2.7	3.3	1.9	3.5	1.9	14.5	32.7	19.4
Overall Combined Ash (UBC%)	2.4	1.4	4.6	12.7	8.4	4.4	3.4	1.8	1.7	2.7	7.2	17.7	17.0
Weighted Average FF (UBC%)	2.5	1.3	5.2	13.6	7.8	4.5	3.4	1.6	1.3	2.6	5.7	14.2	16.2

<sup>1</sup> Produced Ash includes ash and unburnt carbon in that ash <sup>2</sup>Results may be suboptimal due to failure of burner swirler during test period

**Table 9 Averaged results of sorbent trap testing for mercury in both stack and CPU process gas ( $\mu\text{g}/\text{dscm}$ )**

SAMPLE DATE	5/12/12	6/12/12	7/12/12	8/12/12	8/12/12	10/12/12	11/12/12	12/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
FIRING CONDITION	OXY	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND1	BLEND2	BLEND2	(AM sample)								
Total Hg (STACK)	3.65	3.41	2.75	4.42	0.13	0.40	0.76	0.93	3.53	4.09	4.06	4.86	4.01	0.48	0.08	0.10
Hg <sup>2+</sup> (STACK)	n.d.	n.d.	n.d.	0.51	0.09	0.19	0.53	0.67	2.84	2.58	2.57	3.19	2.67	0.25	0.06	0.09
Hg <sup>o</sup> (STACK)	n.d.	n.d.	n.d.	3.90	0.04	0.21	0.23	0.27	0.69	1.51	1.49	1.67	1.34	0.23	0.02	0.01
Hg <sup>2+</sup> / Hg <sup>total</sup> RATIO (STACK)	n.d.	n.d.	n.d.	n.d.	0.65	0.48	0.68	0.70	0.80	0.63	0.63	0.65	0.66	0.50	0.62	0.72
Total Hg (CPU BLOWER OUTLET)	0.89	0.91	0.61				0.34		0.51	0.58		0.55	0.69			0.35
Hg <sup>2+</sup> (CPU BLOWER OUTLET)	n.d.	n.d.	n.d.				0.02		0.08	0.09		0.02	0.02			0.01
Hg <sup>o</sup> (CPU BLOWER OUTLET)	n.d.	n.d.	n.d.				0.32		0.43	0.49		0.53	0.66			0.35
Hg <sup>2+</sup> / Hg <sup>total</sup> RATIO (BLOWER)	n.d.	n.d.	n.d.				0.07		0.15	0.17		0.05	0.04			0.05

n.d. not determined (results removed due to inaccuracies in the collection method)

## Continuous mercury analysis

Results taken with the sorbent tube mercury measurements show that 75-80% of the mercury entering the CPU in the process gas is effectively removed in the first low pressure scrubber. Under normal operating conditions residual mercury is only evident at very low levels at process units beyond the compressor and high pressure scrubber. Averaged results for Tekran mercury concentration measurements in the CPU over extended time periods are shown in Table 10. The levels measured using the Tekran analyser in these parts of the CPU were generally at or below the levels which might be measured in ambient air (~1-2 ng/dscm). Figure 9 shows a schematic diagram indicating the level of loss of mercury from the flue gas as it travels through the CPU unit processes.

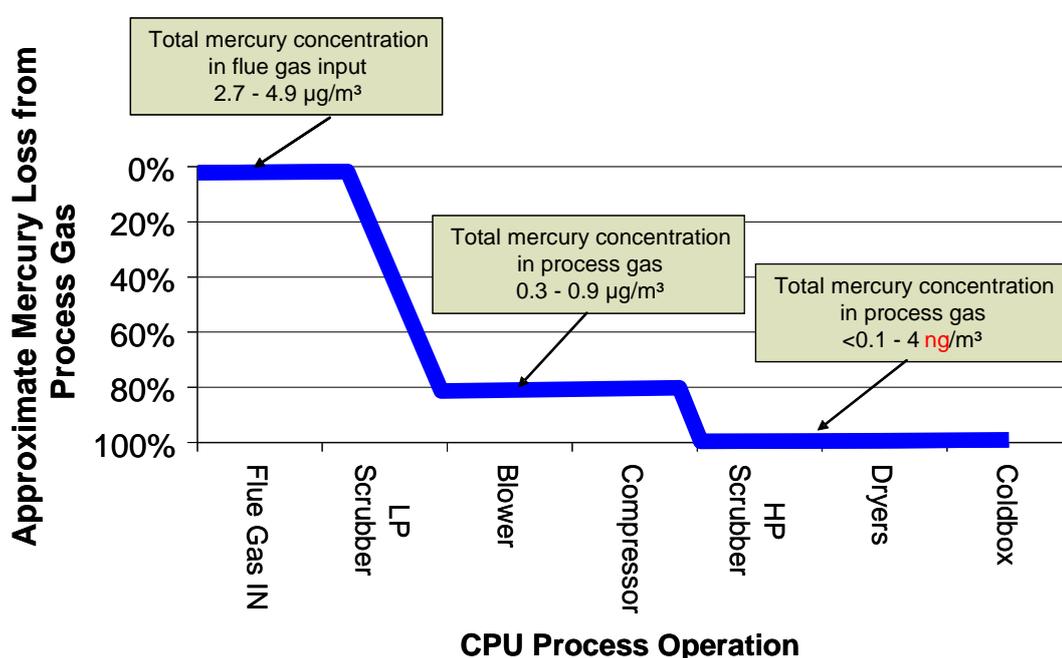


Figure 9 Schematic diagram indicating approximate mercury losses (%) from flue gas in CPU unit processes

The continuous mercury analyser output shows that even during “stable” periods of operation there is some variation in mercury concentration measured in the process gas at the compressor outlet. The mercury concentration determinations for a period from December 11 (18:00 hours) to December 12 (04:00 hours) is shown as an example in Figure 10.

**Table 10 Averages of mercury concentration in the CPU measured for extended periods by the Tekran continuous analyser**

Date -time	Coal	Blower Outlet ( $\mu\text{g/dscm}$ )	Compressor Outlet ( $\text{ng/dscm}$ )	Dryer Outlet ( $\text{ng/dscm}$ )	Coldbox Outlet ( $\text{ng/dscm}$ )
4/12/2013 18:30 – 24:00	CL				0.46
5/12/2013 00:00 – 10:00	CL				0.38
6/12/2013 00:00 – 18:00	CL				<0.10 (MDL)
6/12/2013 18:00 – 24:00	CL				0.18
7/12/2013 00:00 – 10:00	CL				0.35
7/12/2013 16:40 – 24:00	BLEND 1				<0.10 (MDL)
8/12/2013 00:00 – 07:00	BLEND 1				<0.10 (MDL)
8/12/2013 08:30 – 09:40	BLEND 1			3.92	
11/12/2013 09:20 – 12:20	BLEND 2			2.40	
11/12/2013 12:30 – 15:10	BLEND 2		0.69		
11/12/2013 15:25 – 17:20	BLEND 2			1.31	
11/12/2013 17:30 – 24:00	BLEND 2		0.54		
12/12/2013 16:30 – 24:00	CL			0.31	
13/12/2013 00:00 – 10:00	CL			0.67	
13/12/2013 18:00 – 24:00	CL				<0.10 (MDL)
14/12/2013 00:00 – 08:50	CL				0.38
16/12/2013 14:00 – 18:00	CL	1.1 $\mu\text{g/dscm}$			
17/12/2013 10:40 – 17:40	CL	1.1 $\mu\text{g/dscm}$			
20/12/2013 10:15 – 14:15	MN	1.3 $\mu\text{g/dscm}$			

\* NOTE change of units for concentrations (to  $\mu\text{g/dscm}$ ) at the blower outlet (grey)

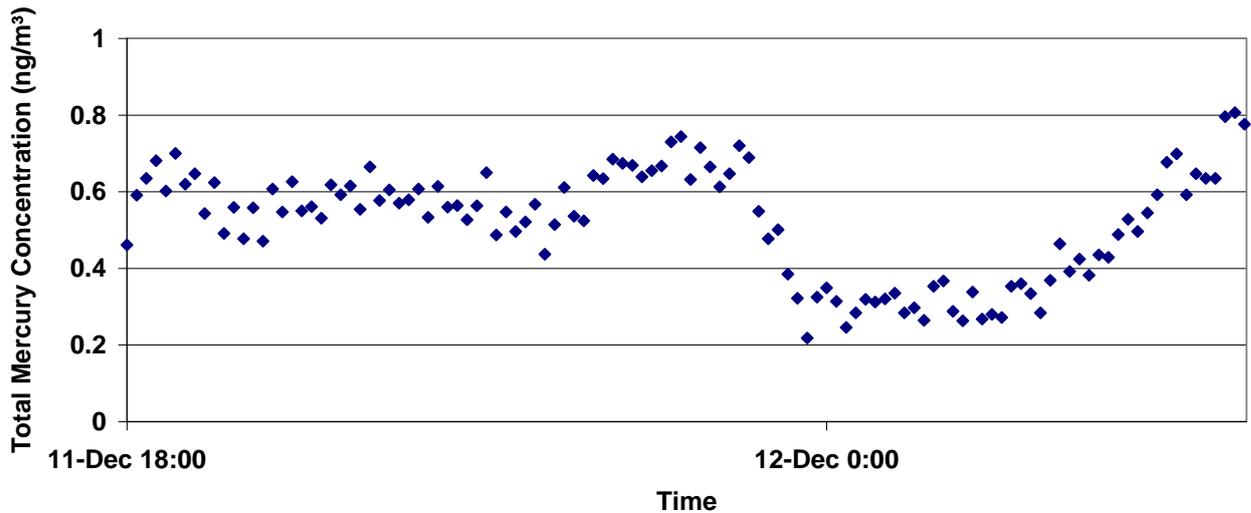


Figure 10 Mercury concentration at the compressor outlet under stable operating conditions 11-12<sup>th</sup> December 2012 (ng/dscm<sup>3</sup>)

### Observations of mercury re-emission

Use of the Tekran analyser over extended periods included several occasions when unintended shutdown (trips) of the CPU occurred. During these periods it was observed that mercury levels in the system beyond the high pressure compression stage rose rapidly and then once the system pressure was re-established mercury levels fell sharply back to the previous low levels measured routinely during stable plant operations. Figure 11 shows an example of the effect of such a plant outage on December 12<sup>th</sup> on mercury concentration at the compressor outlet sampling location.

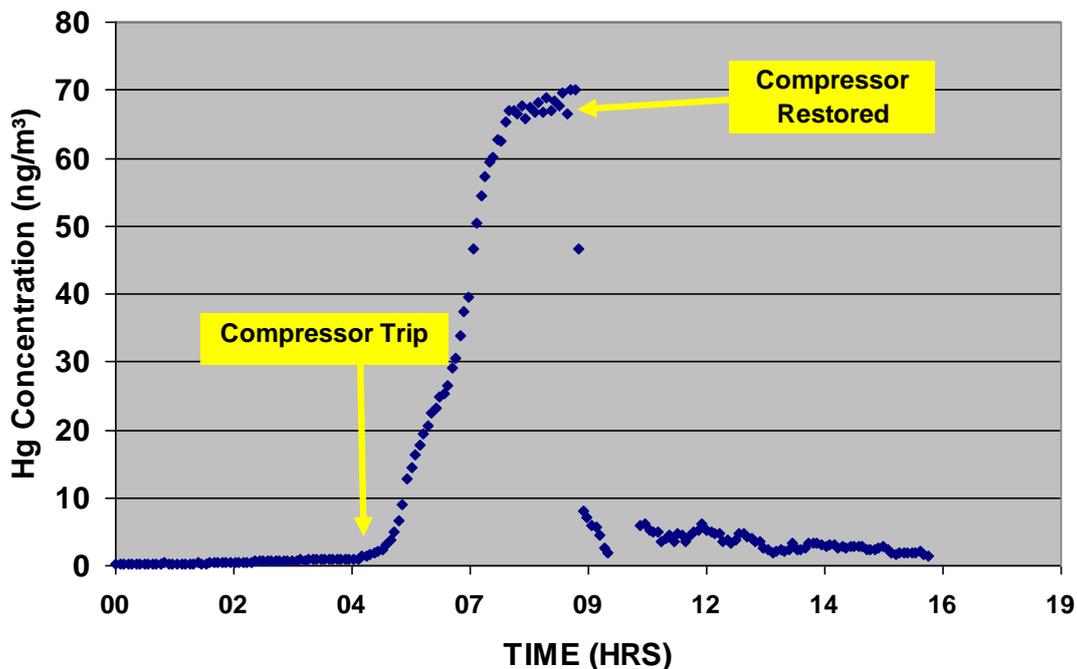


Figure 11 Mercury concentration at the compressor outlet sampling location during a plant outage on Dec 12<sup>th</sup> (ng/dscm<sup>3</sup>)

The observations give some credence to the hypothesis postulated (Ting et al. 2013) that in the CPU high pressure reactions of mercury with nitric acid may produce

soluble  $\text{Hg}(\text{NO}_3)$ . Ting et al. (2013) also believed that once the pressure in the system is reduced, the mercury will revaporise, although the form of the revaporised mercury is unknown. These observations will be followed up by more detailed laboratory experimentation as part of the ongoing project.

### ***Mercury mass balance calculations and mercury distribution in the process***

Calculations of the distribution of mercury to the process gas and solids phases have been made using the analysed mercury and UBC% values given in Table 8 and Table 9. For the calculation additional process parameters such as gas flowrates at the stack ( $F_{\text{stack}}$ ) and CPU ( $F_{\text{CPU}}$ ), particle loadings ( $\text{Conc}_{\text{part}}$ ) and coal burn rates ( $\text{Coal}_{\text{burn}}$ ) are required and these have been provided by both COSPL and from the measurements undertaken by ECS. The data set used for the mass balance calculations is given in Table 11 and the outcomes from the calculations appear in Table 12. A sample calculation showing the method used for determining the mass balance and distribution is shown in Appendix A.

Results of the mass balance calculation show that with the exception of the runs on Blends 1 and 2 in air-firing mode (8<sup>th</sup> and 10<sup>th</sup> December), all other mass balances overestimated the mercury outputs ( $\text{Hg}_{\text{coal}}$  should equal  $\text{Hg}_{\text{ash}} + \text{Hg}_{\text{stack}} + \text{Hg}_{\text{CPU}}$ ). The output estimations range from 57% (Blend 1 Air Mode) – 166% (Blend 2 Oxy Mode). In an endeavour to produce a consistent picture of the results these have been normalised to 100% based on the estimated total output mercury.

The normalised results in Table 12 show a relatively consistent picture with mercury retained in the ash being consistently lower (65-75%) under oxy-firing conditions when compared to the air fired condition (90-98%). The notable exceptions to this are the runs undertaken with Blend 2 (11<sup>th</sup> December) and MN coal (20<sup>th</sup> December), in both cases it is believed that operational issues may have influenced these results. In the former (11<sup>th</sup> December), the experiment followed a sustained period of air-firing mode and it is possible that because of constraints on feed coal availability insufficient time was allowed for the system to stabilise and equilibrate before on the samples were taken. In the latter (20<sup>th</sup> December), the outcome is without doubt influenced by the failure of a swirler in the coal burner (C. Spero *pers comm.*) which resulted in a very high UBC% level of 17% in the ash fraction. As stated previously, residual carbon is known to be a highly influential factor in mercury retention in the ash fraction (Senior and Johnson 2005; Chen et al. 2007; Hudson 2008).

Comparison of the results of the mercury distribution (Table 12) with the overall UBC% results in (Table 8) are consistent with research findings from other airfired combustion plants, that higher levels of UBC% results in higher levels of mercury capture to the solids (flyash and furnace ash) fractions and lower emissions via the gas phase. The results from the anomalous run on the 20<sup>th</sup> of December, when very high UBC% levels occurred suggest that were higher UBC% levels routinely maintained under stable oxy-firing conditions that the retention rate of mercury in the ash fraction may well increase. Conversely, if it were practicable to control the air-firing mode to produce a lower level of residual carbon in the ash it is possible that mercury levels in the flue gas under those circumstances may increase.

**Table 11 Data set used for mercury mass balance calculations**

SAMPLE DATE	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
FIRING CONDITION	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2							
<b>Hg<sub>coal</sub> (ng/g)</b>	31.4	<b>31.4</b>	29.4	32.6	34.0	28.4	32.9	34.7	31.8	31.2	33.9	22.9	<b>22.9</b>
<b>Hg<sub>ash</sub> (ng/g)</b>	123	134	135	74	108	180	103	157	112	96	134	109	103
<b>Hg<sub>FF</sub> (ng/g)</b>	156	172	174	94	139	231	132	202	143	122	172	140	131
<b>UBC<sub>ash</sub> (%)</b>	2.4	1.4	4.6	12.7	8.4	4.4	3.4	1.8	1.7	2.7	7.2	17.7	17.0
<b>Conc<sub>part</sub> (mg/dscm)</b>	456	<b>456</b>	463	390	529	425	486	512	488	<b>488</b>	605	619	<b>488</b>
<b>F<sub>stack</sub> (dscm/s)<sup>1</sup></b>	15.4	<b>15.4</b>	15.8	46.7	42.3	15.8	11.5	15.1	14.0	<b>14.0</b>	43.0	42.0	<b>14.0</b>
<b>F<sub>CPU</sub> (dscm/s)<sup>2</sup></b>	1.3	1.3	1.4	n.a.	n.a.	1.2	1.3	1.2	1.2	1.2	n.a.	n.a.	1.3
<b>Coal<sub>burn</sub> (kg/s)</b>	5.23	5.07	5.15	4.74	4.99	4.88	4.85	4.96	5.1	5.33	5.2	4.56	5.01
<b>Coal<sub>ash</sub> (%)</b>	22.6	<b>22.6</b>	18.9	20.8	24.8	23.7	25.6	24.2	22.8	22.2	23.4	23.9	<b>23.9</b>
<b>Hg<sub>stack conc</sub> (µg/dscm)</b>	3.65	3.41	2.75	0.13	0.40	0.76	3.53	4.09	4.86	4.01	0.48	0.08	0.10

n.a. not applicable

Data in **bold** was not available so was assumed from data from the same firing condition (oxy or air) and coal when available.

<sup>1</sup> ECS measurements at stack

<sup>2</sup> COSPL data

**Table 12 Calculated mercury mass balance and % distribution to solid and gas phases**

SAMPLE DATE	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
FIRING CONDITION	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2							
Input mercury ( $\mu\text{g/s}$ )	164.0	159.0	151.6	154.6	169.5	138.5	159.7	172.1	162.4	166.4	176.2	104.5	114.8
Output mercury ( $\mu\text{g/s}$ )													
Stack mercury ( $\text{Hg}_{\text{g stack}} + \text{Hg}_{\text{p stack}}$ )( $\mu\text{g/s}$ )	57.3	53.7	44.8	7.8	20.0	13.6	41.3	63.1	68.9	57.0	25.1	6.9	2.3
CPU mercury ( $\text{Hg}_{\text{g CPU}} + \text{Hg}_{\text{p CPU}}$ ) ( $\mu\text{g/s}$ )	4.8	4.5	3.9	n.a.	n.a.	1.0	4.5	5.2	6.0	5.1	n.a.	n.a.	0.2
Mercury retained in ash ( $\mu\text{g/s}$ )	147.5	154.8	136.9	82.0	143.5	216.3	132.0	190.2	131.1	115.5	170.8	140.9	147.2
Total estimated mercury outputs ( $\mu\text{g/s}$ )	209.6	213.0	185.5	89.8	163.4	230.9	177.9	258.5	206.1	177.5	195.9	147.8	149.6
<b>Mercury Distribution (as % Input mercury)</b>													
Stack mercury ( $\text{Hg}_{\text{g stack}} + \text{Hg}_{\text{p stack}}$ ) (%)	34.9	33.0	28.7	3.9	10.0	8.7	25.4	35.7	41.8	33.7	11.7	3.1	1.2
CPU mercury ( $\text{Hg}_{\text{g CPU}} + \text{Hg}_{\text{p CPU}}$ ) (%)	2.9	2.8	2.5	n.a.	n.a.	0.8	2.8	3.0	3.7	3.0	n.a.	n.a.	0.2
Mercury retained in ash (%)	89.9	97.3	90.3	53.0	84.6	156.1	82.7	110.5	80.8	69.4	96.9	134.8	128.2
Total estimated mercury outputs (%)	127.8	133.2	121.6	57.0	94.6	165.6	110.9	149.3	126.3	106.2	108.6	138.0	129.6
<b>Normalised mercury distribution (%)</b>													
Stack mercury ( $\text{Hg}_{\text{g stack}} + \text{Hg}_{\text{p stack}}$ ) (%)	27.3	24.8	23.6	6.9	10.5	5.2	22.9	23.9	33.1	31.8	10.8	2.3	0.9
CPU mercury ( $\text{Hg}_{\text{g CPU}} + \text{Hg}_{\text{p CPU}}$ ) (%)	2.3	2.1	2.1	n.a.	n.a.	0.5	2.6	2.0	2.9	2.9	n.a.	n.a.	0.1
Mercury retained in ash (%)	70.4	73.1	74.3	93.1	89.5	94.3	74.5	74.0	63.9	65.4	89.2	97.7	98.9
Total estimated mercury outputs (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

\* based on input data in Table 11, a sample calculation can be found in Appendix A

## ***Halogens and Halides***

A summary of results of the concentration of halogens and halides determined during the field trials are shown in Table 13 and Table 14. Halides were measurable in all but one instance in the stack, but the concentrations of halogens were below the MDLs in both the stack and CPU process gases. Halide concentrations in the CPU were all below the MDLs for all samples.

In the stack, results for halides were all of similar magnitude with the exception of a single anomalous result for the 7<sup>th</sup> December, where results of all halide species were three or more times higher than for the other runs. Given that there is little difference in the Cl and Br levels in the input coals, which were 0.02 – 0.04% for Cl and <25 mg/kg for Br, a lack variation in the flue gas is consistent with the coal analysis.

Excluding the anomalous result, the ranges of results for halides in the stack gas for the other runs were HBr (0.039 – 0.152 mg/dscm), HCl (6.9 – 23.3 mg/dscm) and HF (6.6 – 20.3 mg/dscm). There appears to be no consistent trend in the halide results between either coal type or firing mode (oxy or air-fired). No explanation for the anomalous result on the 7<sup>th</sup> of December is apparent.

In the CPU levels of halides were all low (below detection limits) and should not present any processing difficulties.

## ***Metals (other than mercury)***

### **Metal concentrations in stack and CPU process gas**

Trace metal concentrations measured at the stack are shown in Table 15. Samples were collected on eleven occasions during both oxy and air-firing and for all four coal types. For a number of elements (Sb, As, Be, Cd, Se) the results obtained are generally at or below the MDLs for the collection and analytical method.

In the CPU all metal concentrations in the process gas were at or around MDL values beyond the first low pressure scrubber (Blower sampling location APF 370B-1).

Overall the trace metal concentration levels are low.

### **Metal concentration in flyash and furnace ash**

Analysis of trace metal content was carried out by AMDEL on a reconstituted flyash and furnace (bottom) ash sample based on the percentage allocations in Table 3. The results of the analyses of these samples are found in Table 16. Except for Th and Sn (in some samples) all other metals analysed were above the MDLs for the analytical technique used. During the trial period ash samples were collected on thirteen days, covering all four coal feed types during periods of both oxy and air-firing.

**Table 13 Concentrations of halides and halogens in the stack gases measured using USEPA Method 26A (mg/dscm corrected to 7%O<sub>2</sub>)**

SAMPLE DATE	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
FIRING CONDITION	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2								
Br	<0.050		<0.050	<0.038	<0.039	0.078	<0.064	<0.062		<0.069		<0.034	<0.039	
Cl	<0.25		<0.25	<0.19	<0.20	<0.39	<0.32	<0.31		<0.34		<0.17	<0.19	
F	<0.050		<0.050	<0.038	<0.039	<0.077	<0.064	<0.062		<0.069		<0.034	<0.039	
HBr	0.110		0.609	0.097	0.033	0.152	<0.064	0.056		0.061		0.039	0.039	
HCl	14.3		67.0	18.5	13.5	23.3	10.2	9.9		8.5		6.9	13.7	
HF	10.6		36.6	8.0	8.4	20.3	11.0	10.8		8.9		6.6	8.3	

Note: greyed areas indicate results based on MDLs as these species were not detected

**Table 14 Results of measurement of halides and halogens in the CPU (mg/dscm)**

SAMPLE DATE	5/12/12	6/12/12	7/12/12	7/12/12	11/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12
FIRING CONDITION	OXY	OXY	OXY	OXY	OXY	OXY	OXY	OXY	OXY	OXY	OXY
Coal Type	CL	CL	CL	CL	CL	CL	CL	CL	CL	CL	CL
LOCATION	Blower Outlet	Compressor Outlet	Dryer Outlet	Blower Outlet	Coldbox Outlet						
Br	<0.024	<0.033	<0.024	<0.028	<0.023	<0.022	<0.022	<0.022	<0.025	<0.016	<0.031
Cl	<0.120	<0.170	<0.120	<0.140	<0.120	<0.110	<0.110	<0.110	<0.130	<0.082	<0.160
F	<0.024	<0.033	<0.024	<0.028	<0.023	<0.022	<0.022	<0.022	<0.130	<0.016	<0.031
HBr	<0.024	<0.033	<0.024	<0.028	<0.022	<0.022	<0.022	<0.022	<0.025	<0.016	<0.031
HCl	<0.120	<0.170	<0.120	<0.140	<0.120	<0.110	<0.110	<0.110	<0.130	<0.082	<0.160
HF	<0.120	<0.170	<0.120	<0.140	<0.120	<0.110	<0.110	<0.110	<0.130	<0.082	<0.160

Note: greyed areas indicate results based on MDLs as these species were not detected

**Table 15 Concentration of trace metals in the stack gases measured by USEPA Method 29 (mg/dscm corrected to 7% O2)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL + BL	CL + BL	CL + BL	CL + MN	CL + MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND1	BLEND2	BLEND2								
Antimony	<0.0034	<0.0034		<0.0031	<0.0019	<0.0017	<0.0043	<0.0039		<0.0039		<0.0031	<0.0022	<0.0029	
Arsenic	<0.0034	<0.0034		<0.0031	<0.0019	<0.0017	<0.0043	<0.0039		<0.0039		<0.0031	<0.0022	<0.0029	
Beryllium	<0.0034	<0.0034		<0.0031	<0.0019	<0.0017	<0.0043	<0.0039		<0.0039		<0.0031	<0.0022	<0.0029	
Boron	1.32	1.22		1.44	0.71	1.14	2.03	1.61		1.42		1.46	0.60	1.11	
Cadmium	<0.0034	<0.0034		0.0043	<0.0019	<0.0017	0.0047	<0.0039		0.0059		0.0031	<0.0022	<0.0029	
Chromium	0.017	0.016		0.061	0.660	0.857	1.217	0.153		0.012		0.004	0.341	0.401	
Cobalt	0.0040	0.0037		0.0073	0.0167	0.0096	0.0132	0.0053		0.0044		0.0030	0.0046	0.0076	
Copper	0.0265	0.0243		0.0251	0.0968	0.0385	0.0649	0.0441		0.0180		0.0137	0.0520	0.0410	
Lead	0.013	0.012		0.017	0.018	0.011	0.022	0.013		0.010		0.009	0.010	0.008	
Manganese	0.106	0.097		0.275	0.343	0.192	0.375	0.263		0.170		0.091	0.128	0.085	
Nickel	0.036	0.033		0.071	1.496	0.560	0.649	0.161		0.029		0.009	0.205	0.264	
Selenium	<0.0086	<0.0086		<0.0078	0.013	0.008	0.043	0.010		<0.0098		<0.0078	0.014	<0.0073	
Zinc	0.121	0.112		0.156	0.361	0.083	0.172	0.093		0.047		0.051	0.078	0.073	

Note: greyed areas indicate results based on MDLs as these elements were not detected

**Table 16 Concentration trace metals in the reconstituted ash samples (mg/kg, dry basis)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+ MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2								
Antimony	0.6	0.7	0.7	0.5	0.5	0.7	0.6	0.7		0.7	0.5	0.5	0.6	0.7
Arsenic	3.3	3.4	3.0	1.8	2.3	3.8	3.1	3.4		2.9	2.4	2.6	2.7	3.4
Barium	210	220	440	670	560	780	520	270		220	270	220	1100	2000
Beryllium	4	4	4	2	3	4	4	4		4	4	3	4	4
Boron	55.4	60.3	56.1	41.4	57.2	71	60.4	64.7		59.3	53.8	54.7	86.5	110
Cadmium	0.29	0.32	0.27	0.12	0.17	0.30	0.25	0.31		0.28	0.21	0.23	0.16	0.10
Chromium	57	52	59	40	49	68	60	70		60	61	54	51	56
Cobalt	40	38	35	22	30	41	36	37		34	34	33	34	42
Copper	68	72	63	42	47	66	60	90		86	89	64	56	44
Lead	36	45	38	18	25	39	36	45		39	32	31	28	24
Manganese	1300	1300	1200	1000	1200	1200	1100	1200		1200	1200	1200	880	630
Nickel	60	65	53	28	45	58	58	75		64	59	58	51	52
Selenium	0.9	0.9	0.9	0.6	0.8	1.2	0.9	0.9		0.7	0.7	0.9	1	1.2
Silver	0.37	0.41	0.39	0.33	0.61	0.65	0.42	0.42		0.38	0.35	0.34	0.30	0.44
Thallium	<1	<1	<1	<1	<1	<1	<1	<1		<1	<1	<1	<1	<1
Thorium	15.5	17	16.5	11.4	12.7	17.1	15.1	18.9		15.6	14	13.6	15.4	15.8
Tin	<2	<2	8	<2	5	6	6	<2		10	5	4	3	4
Vanadium	140	150	130	97	110	130	130	150		140	140	130	120	110
Zinc	64	56	53	25	40	70	56	56		46	42	50	45	57

Note: greyed areas indicate results based on MDLs as these elements were not detected

## Partitioning between gas and solids

Models of partitioning of metals within combustion systems have been well established over many years (Meij 1994; Meij and te Winkel 2007). These models involve physico-chemical phenomena which control partitioning and their final physical form and these phenomena are suggested to include the following:

- (i) Heterogeneous condensation on the existing fly ash particles and heat exchange surfaces.
- (ii) Physical/chemical adsorption on fly ash particles.
- (iii) Homogeneous condensation (nucleation) and coalescence as submicron aerosols if local supersaturation condition exists.
- (iv) Homogeneous and heterogeneous chemical reaction among trace elements, fly ash and flue gas constituents.
- (v) Residence in the vapor phase for species with high vapor pressure at typical boiler exit temperatures. (Ratafia-Brown 1994)

Meij (1994) and Meij & te Winkel (2007) proposed a classification of elements suggested by their likely occurrence in the solid or gas phase following combustion based in part on elemental volatility and this model is summarised in Table 17.

Calculations of partitioning to the gas and solids phases have been made based on the concentrations measured in the stack gas and in the ash (Table 18 and Table 19). From the results it does not appear that partitioning is consistently influenced by either firing condition (oxy or air-firing) or the coal types/blends used in the current field trials. Table 20 shows the closure of the partitioning mass balance calculations where results for metals reporting to both the gas and solids phases are available, where “perfect” closure would be a value of 100%.

Table 20 shows that for many of the tests there is significant variation from ideality, both between runs and for individual elements within runs, with closure levels varying in individual instances from 47% (Pb) - 263% (Ni). These deviations can be can result from both sampling and analytical error. Given that most of the elements are likely to report to the solids it suggests that errors in these solids samples are likely to have the most profound effect. Of the possible error the creation of a representative reconstituted ash sample probably holds the greatest potential for skewing the result.

Based on the gas and solid phase metal concentrations, the results in Table 18 and Table 19 suggest that consistently low level partitioning to the gas phase occurs for most metals studied (As, Be, Co, Cu, Pb, Mn,). For Cr, Ni, Zn the results are less consistent but also suggest low levels partitioning to the gas phase. For a small group of elements (Sb, B, Cd and Se) the retention in the gas phase is consistently higher, as was Hg in the work described earlier in this report. Overall the results are generally in agreement with the proposed partitioning model of Meij (1994) and Meij and te Winkel (2007)

Table 17 Categorisation of trace elements based on volatility behaviour (after Meij, 1994, 2007)



Class	Element	Description	Outcome
I	<b>Al, Ca</b> , Ce, Cs, Eu, <b>Fe</b> , Hf, K, La, <b>Mg</b> , Sc, Sm, <b>Si</b> , Sr, <b>Th</b> , Ti	Not volatile	Distributed between bottom ash and flyash
IIa	<b>Be, Co, Cu, Ni</b> , P, U, V and W	Volatile in boiler, significant condensation in particle collection device (PCD) on flyash	Enriched in flyash and depleted in bottom ash when compared to input coal.
IIb	<b>Ba, Cr</b> , Mn, Na and Rb		
IIc	<b>As, Cd</b> , Ge, Mo, <b>Pb, Sb</b> , Tl and <b>Zn</b>		
III	<b>B</b> , Br, C, Cl, F, <b>Hg</b> , I, N, S and <b>Se</b>	Volatile: some to hardly any condensation on ash particles in PCD	Lowest boiling point elements emitted fully in vapour phase and not enriched in flyash

Note: Elements in **bold** in current analytical suite

**Table 18 Estimations of trace metal partitioning to stack gas, based on input coal and stack gas metal concentrations (%)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+BL	CL+MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND1	BLEND2	BLEND2								
Antimony	6.4	6.7		4.0	7.0	6.1	8.0	7.4		6.5		5.5	7.4	7.1	
Arsenic	1.6	1.7		0.8	1.4	1.3	1.1	1.5		1.0		1.1	2.2	1.9	
Beryllium	1.3	1.3		1.2	2.1	1.8	1.6	1.5		1.3		1.1	2.2	1.4	
Boron	16.2	17.0		20.3	38.7	40.4	20.0	24.8		18.6		20.9	25.3	21.9	
Cadmium	9.1	9.5		11.7	17.4	16.5	13.2	12.4		14.7		11.3	20.3	40.7	
Chromium	0.4	0.5		1.8	75.0	80.6	28.0	4.9		0.3		0.1	28.9	28.8	
Cobalt	0.2	0.2		0.3	3.0	1.2	0.4	0.3		0.2		0.1	0.7	0.5	
Copper	0.4	0.4		0.4	6.0	2.4	1.1	0.7		0.2		0.2	2.5	2.8	
Lead	0.4	0.4		0.5	2.1	1.1	0.7	0.4		0.2		0.3	0.9	1.0	
Manganese	0.1	0.1		0.3	1.6	0.8	0.4	0.4		0.2		0.1	0.4	1.0	
Nickel	0.7	0.8		2.3	186.9	45.6	14.9	4.0		0.6		0.2	16.2	15.2	
Selenium	10.8	11.3		10.1	55.0	23.0	39.2	15.2		8.1		9.2	40.5	11.9	
Zinc	2.3	2.4		3.4	30.1	5.1	3.0	2.5		0.7		1.3	6.2	3.8	

Note: Greyed areas indicate results based on MDLs as these species were below detection limits in the stack gases  
Data calculated for 6<sup>th</sup> December based on coal analysis for previous day

**Table 19 Estimations of trace metal partitioning to ash, based on input coal and reconstituted ash metal concentrations (%)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2								
Antimony	80	92	39	45	51	99	92	99		94	68	51	46	54
Arsenic	110	112	48	33	50	72	95	87		86	65	79	55	69
Barium	102	105	36	96	82	116	197	109		81	103	113	43	77
Beryllium	106	105	90	55	92	113	123	113		107	109	91	62	61
Boron	53	57	53	49	51	54	63	64		58	54	59	46	58
Cadmium	55	60	43	27	47	65	64	88		68	57	64	70	44
Chromium	117	105	102	99	116	120	131	152		89	110	117	98	107
Cobalt	133	125	98	86	92	106	138	131		101	103	125	65	80
Copper	79	82	61	57	72	89	68	88		79	83	78	102	79
Lead	80	99	71	45	59	92	85	98		80	67	73	87	74
Manganese	115	114	90	101	132	97	102	97		89	86	107	271	193
Nickel	94	101	70	76	92	103	99	125		90	80	118	79	80
Selenium	80	79	67	55	61	85	92	85		62	63	68	51	61
Silver	62	68	55	50	99	115	71	66		48	50	54	62	90
Thallium	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.
Thorium	82	90	74	68	71	93	84	105		77	72	77	90	91
Tin	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.
Vanadium	91	96	71	70	91	94	83	94		83	81	90	100	91
Zinc	95	82	66	45	61	94	101	113		77	76	101	63	79

Note: greyed areas indicate results based on coal analysis from previous day

**Table 20 Mass balance closure of partitioning to gas and solid phases, where metal concentrations in ash and stack gas are both available (%)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	AIR	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2								
Antimony	86	99		52	57	107	99	99		94	73	58	53	
Arsenic	111	114		34	52	73	96	87		86	66	81	57	
Beryllium	108	107		57	94	115	124	113		107	110	93	63	
Boron	69	74		88	91	74	88	64		58	75	85	68	
Cadmium	64	70		45	64	79	76	88		68	68	84	111	
Chromium	117	106		174	196	148	136	152		89	111	146	127	
Cobalt	133	125		89	93	106	138	131		101	103	126	66	
Copper	79	83		63	74	90	69	88		79	84	80	104	
Lead	80	99		47	60	93	85	98		80	67	73	88	
Manganese	115	114		103	132	97	102	97		89	86	108	272	
Nickel	95	102		263	138	118	103	125		90	80	134	94	
Selenium	91	90		110	84	124	107	85		62	73	109	63	
Zinc	97	84		76	66	97	103	113		77	77	108	67	

Note 1: for perfect closure, value equals 100

Note 2: based on results from Tables 18 and 19

Greyed results for 6/12/12 based on coal analysis from previous day

For two elements Cr and Ni there is a lack of consistency in the outcomes and some results are very high.. Of particular note, Ni, for 8 – 13<sup>th</sup> December where during this period some of the predicted results are clearly incorrect (Ni, 8<sup>th</sup> December), when a partitioning rate to the gas phase of 187% is calculated. For the Cr results are some of these inconsistencies maybe the result of analytical or sampling imprecision (or possible contamination from the stainless steel sampling probe). It can also be seen from Table 4 that some of the reported results from coal analysis during this period were much lower than the average for coals over most of the field trial. These inconsistent results are being further investigated and may be revised in the final report.

### **Sulfuric acid mist/ sulfur trioxide and sulfur dioxide emissions**

Determinations of SO<sub>2</sub> were carried out using portable analysers (Testo 335 and Horiba PG350) which comply with USEPA Method 6c. Additional specific testing for sulfuric acid mist/sulfur trioxide (reported as SO<sub>3</sub>) and sulfur dioxide (SO<sub>2</sub>) were made using USEPA Method 8. The results of the analyses in the stack gases appear in Table 21. A comparison of the results from the two techniques shows them to be generally comparable with the SO<sub>2</sub> results for both methods within around ±10% of each other.

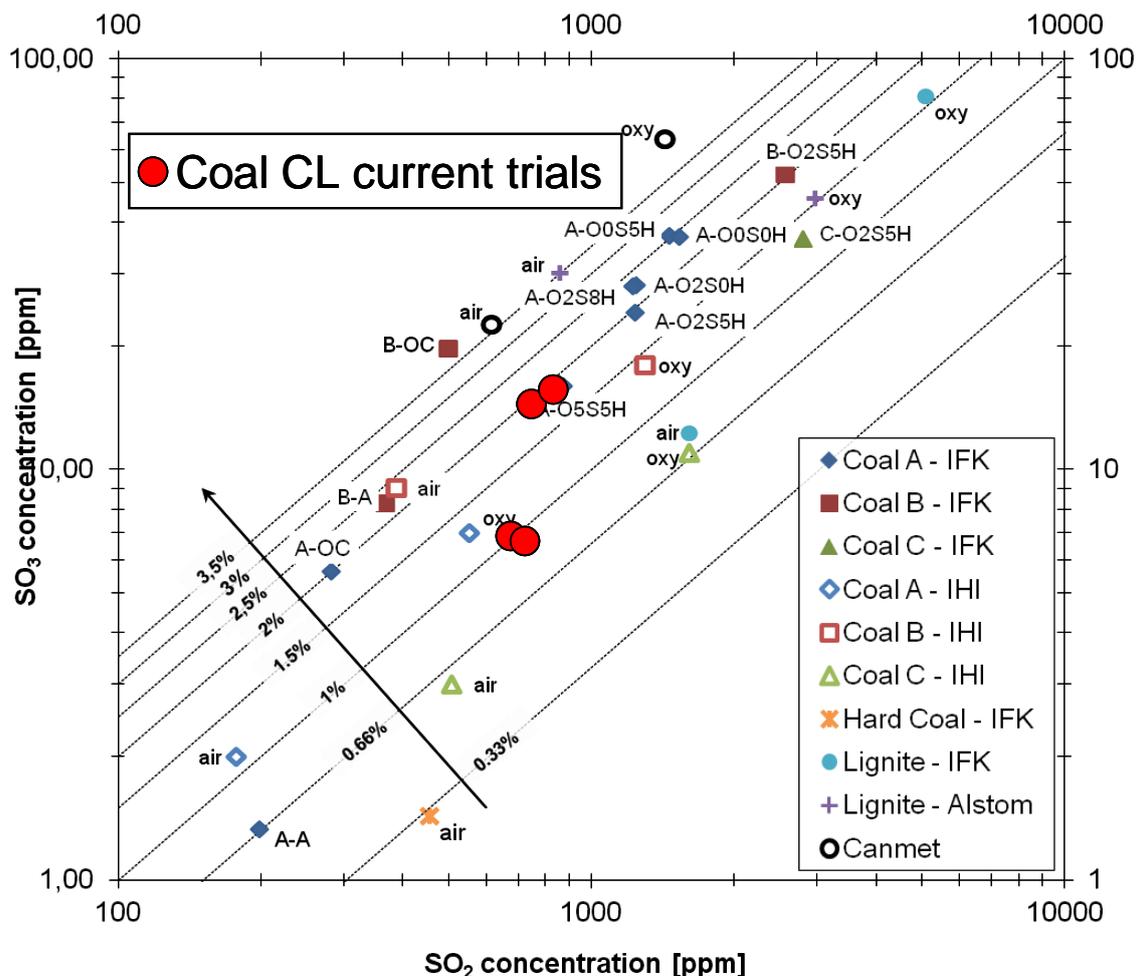


Figure 12 SO<sub>2</sub> vs SO<sub>3</sub> concentrations for current fieldwork oxyfuel trials imposed on results from other technical scale oxy and air fired experiments [diagram based on Fig 22 (Spörl and Jörg 2013)] Note units and logarithmic scale on graph.

The results in Table 21 show that under oxy-firing conditions SO<sub>2</sub> concentrations in the stack gases ranged from 1325 – 4059 mg/dscm, whilst under air-firing conditions the SO<sub>2</sub> levels were three to four times lower (300 -720 mg/dscm) reflecting the increased mass flows of gas during air-firing. It is probable that there is some influence of feed coal sulfur and the runs using CL coal had lower sulfur concentrations than those with either of the coal blends, reflecting the slight increase in sulfur in the coal blends. Under air-firing conditions SO<sub>3</sub> was not detected (results are reported as <MDL), while under oxy-firing concentrations of 23 – 48 mg/dscm were determined.

A comparison of the SO<sub>2</sub> and SO<sub>3</sub> outcomes under oxyfiring conditions with results achieved previously in technical scale experiments is shown in Figure 12. This figure shows the results for Coal CL in the current program plot in similar areas of the diagram to Coal A (an Australian coal of very similar composition and properties to Coal CL) from the work of Spörl and Jörg (2013). Results for SO<sub>2</sub> and SO<sub>3</sub> outcomes of Coal CL under air-firing conditions in the current field trials however, are significantly different and plot off the diagram, below and towards the left. It has been suggested Wall (*pers comm.*) that this apparent low rate of conversion of less than 0.15% may be an experimental artefact due to the difficulties of making these measurements under the constraints of industrial conditions. Possible causes could be the cooling and condensation in longer sampling lines, reaction with ash on filters prior to analysis, as ash catalysis will increase SO<sub>2</sub> over SO<sub>3</sub> and measurements of values close to the MDLs for the experimental method.

Testing at all four sampling locations in the CPU using USEPA Method 8 found levels of SO<sub>x</sub> at or below the MDLs, which were 0.6 – 1.0 mg/dscm for SO<sub>2</sub> and 0.4 – 0.7 for SO<sub>3</sub>. These results demonstrate that the sulfur in the process gas stream has been removed effectively from the CPU process gas by the initial low pressure scrubber.

**Table 21 Averaged SO<sub>2</sub> and SO<sub>3</sub> concentrations in stack gases determined using USEPA Methods 6c and 8 (mg/dscm corrected to 7% O<sub>2</sub>)**

Sample Date	5/12/12	6/12/12	7/12/12	8/12/12	10/12/12	11/12/12	12/12/12	13/12/12	14/12/12	16/12/12	17/12/12	18/12/12	19/12/12	20/12/12
Firing Condition	OXY	OXY	OXY	OXY	AIR	OXY	OXY	OXY	OXY	OXY	OXY	AIR	AIR	OXY
Coal Type	CL	CL	CL+ BL	CL+BL	CL+MN	CL+MN	CL	CL	CL	CL	CL	CL	MN	MN
			BLEND1	BLEND1	BLEND2	BLEND2								
SO <sub>2</sub>														
Method 8		1928			603			2225		2077	2317	551		
Method 6c		2364	3290	3477	720	4059	2043		1428	1797	1325	300		
SO <sub>3</sub>														
Method 8		25			<0.7			48		23	53	<0.9		

## LEARNINGS FROM THE FIELD TRIALS

Following the fieldwork and the analysis of the results some lessons for improvements for future trials are apparent and these are summarised below.

- Allow a longer period of combustion of the coal type/ combustion condition prior to sampling to ensure stable conditions are achieved.
- The collection of a series of results over an extended period rather than collection of a single sample over the same time period would result in improved precision and allow the errors in outcomes to be determined.
- The better control of firing conditions - CO/CO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub> control would result in greater stability in combustion parameters and contribute to increased confidence in the results.
- More information might be gained by undertaking testing with coals which exhibit greater variation in key parameters, than occurred with the coals used during the current project.
- During the current project sampling was undertaken 0600 – 1800 hours. Consideration could be given to increasing the number of samples collected during the sampling campaign by taking measures which would enable sampling to occur over a continuous 24 hour cycle. Although it is acknowledged that this would need to be examined to determine both cost and work health and safety implications.

## FURTHER WORK

- Further analysis of the existing ash samples for speciation of trace metals.
- Use of these analysis results to check the gas and solids phase partitioning results achieved.
- Comparison of the results achieved for mercury partitioning against the mercury predictive model.

Outcomes of this work will be reported in the final report for the project.

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## CONCLUSIONS

The following conclusions can be drawn from the examination of data developed during the December 2012 Callide oxyfuel fieldtrials:

1. The project was successful in meeting its scope and objectives.
2. The health and environmental outcomes under oxy-firing conditions are likely to be similar to those achieved when using conventional air-firing.
3. Levels of metals, acid gases and mercury in particular, are below the level of operational concern in the CPU beyond the first low pressure scrubber.
4. The results show that the trace element content of the feed coals used in the program are very similar for most elements determined with the exception of Ba, B and Mn.
5. Mercury contents in the produced ash varied widely, with most deposited in the flyash fraction where concentrations ranged from 43 – 270 ng/g.
6. UBC% levels varied considerably (1.4 – 17.7%) during the trial period, even for the same coal and firing conditions on different days. Under air-firing conditions UBC% levels were generally higher than for oxyfiring of the same coal. Very high UBC% levels (~17% average) experienced when feeding MN coal are likely to be due to the failure of a coal swirler in the burner during this period.
7. Higher concentrations of mercury in the stack gas occurred during oxy-firing (~3 µg/dscm) than air-firing (~0.3 µg/dscm). This being due to the lower mass gas flows during oxy-firing along with decreased partitioning to the ash phase.
8. Mercury was more likely to report to the ash under air-firing conditions. For air-firing 87-95% of the mercury partitioned to the ash, while during oxy-firing this reduced to 67-74%. This is most likely a result of generally higher UBC (%) in flyash when in air-firing mode.
9. Ratios of  $Hg^{2+}/Hg_{total}$  in the stack gas ranged from 0.48 – 0.72 and seem relatively unaffected by firing condition (air or oxy-firing).
10. Approximately 80% of mercury in CPU process gas was removed by the initial low pressure scrubber; with the final CPU process gas mercury concentration approaching the concentrations measured in ambient air (<2 ng/m<sup>3</sup>).
11. Halogens (Br, Cl and F) were at or below detection limits for the sampling techniques in both the stack and CPU. Halides (HBr, HCl and HF) were detectable in the stack (but not in the CPU), although no consistent trend in the results between coal type or firing mode (oxy or air fired) was apparent.
12. Samples were collected on eleven occasions from the stack gases for trace metal analysis, during both oxy and air-firing. Overall the trace metal concentration are low and should have minimal environmental impact.

13. Some differences in partitioning to the gas phase are apparent with three groups of elements:
  - low level partitioning (<5%) for most metals studied ( As, Be, Co, Cu, Pb, Mn);
  - a group where retention in the gas phase is consistently higher; Sb (5.5 – 8.8%), B (16.2 – 40.4%), Cd (9.1 – 40.7%) and Se (8.1 – 55%);
  - for three elements Cr, Ni and Zn there is a lack of consistency in the outcomes which may have resulted from analytical imprecision and/or sampling errors.
14. From these results it did not appear that partitioning of trace metals to the gas phase at the stack is a function of either firing condition (oxy or air-firing) or coal type.
15. Most metals analysed predominately partition to the solids phases (flyash and furnace (bottom) ash). A small group of metals, Sb, B, Cd and Se (along with Hg), report at higher levels to the gas phase. These results are consistent with partitioning behaviour during combustion found by other researchers.
16. Further analysis of the trace metals in the ash samples produced during the field trial will be carried out to provide further confirmation of the metals partitioning.
17. Concentrations of metals measured in the CPU process gas beyond the first lower pressure scrubber were at or around MDL values.
18. Under oxy-firing conditions SO<sub>2</sub> concentrations in the stack gases ranged from 1325 – 4059 mg/dscm, whilst under air-firing conditions the SO<sub>2</sub> levels were three to four times lower (300 -720 mg/dscm) reflecting the increased mass flows of gas during air-firing. Under air-firing conditions SO<sub>3</sub> was not detected, while under oxy-firing concentrations of 23 – 48 mg/dscm were determined. The probable influence of feed coal sulfur on concentrations was observed.
19. Testing at all four sampling locations in the CPU found levels of SO<sub>x</sub> at or below the MDLs, for both SO<sub>2</sub> and for SO<sub>3</sub>. These results demonstrate that the sulfur in the process gas stream has been removed effectively from the CPU process gas by the initial low pressure scrubber.

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## APPENDIX A

### Sample calculation of mercury distribution

#### Assumptions:

- All combustible material in the coal has been removed (except that represented by UBC%) for material in the ash
- Particulates in the exhaust gas carry mercury levels at the weighted average of those from the fabric filters (FF)
- Concentration of mercury in gas and particulates going to CPU is the same as that emitted from stack

#### Input Data:

Date 5/12/2012

Coal: CL

Firing condition: Oxy-firing

Mercury in coal (as received) ( $Hg_{coal}$ ): 31.4 ng/g

Weighted ash mercury ( $Hg_{ash}$ ): 123 ng/g

Weighted FF mercury ( $Hg_{FF}$ ): 156 ng/g

Weighted ash UBC ( $UBC_{ash}$ ): 2.4%

Particulate Concentration stack ( $Conc_{part}$ ): 456 (mg/dscm)

Flowrate stack ( $F_{stack}$ ): 15.4 (dscm/s) (ECS measurements)

Flowrate CPU ( $F_{CPU}$ ): 1.3 (dscm/s) (CS Energy)

Coal burn rate (kg/s) (as-received)( $Coal_{burn}$ ): 5.23 kg/s

Coal ash ( $Coal_{ash}$ ): 22.6%

Stack mercury concentration (sorber tube)( $Hg_{stack conc}$ ): 3.65  $\mu$ g/dscm

#### Calculated Outputs

$$\begin{aligned} \text{Input Mercury} &= 1000 (Hg_{coal} \times Coal_{burn}) \\ &= 1000 * 31.4 * 5.23 \\ &= 164222 \text{ ng/s} \\ &= 164.2 \text{ } \mu\text{g/s} \end{aligned}$$

$$\begin{aligned} \text{Gaseous mercury at stack} &= Hg_{stack conc} \times F_{stack} \\ Hg_{g stack} &= 3.65 * 15.4 \\ &= 56.2 \text{ } \mu\text{g/s} \end{aligned}$$

$$\begin{aligned} \text{Particulate mercury at stack} &= (Conc_{part}/1000) \times F_{stack} \times Hg_{FF} \\ Hg_{p stack} &= (456/1000) * 15.4 * 156 \\ &= 1095 \text{ ng/s} \\ &= 1.1 \text{ } \mu\text{g/s} \end{aligned}$$

$$\begin{aligned} \text{Gaseous mercury at CPU} &= Hg_{stack conc} \times F_{CPU} \\ Hg_{g CPU} &= 3.65 * 1.3 \\ &= 4.7 \text{ } \mu\text{g/s} \end{aligned}$$

$$\begin{aligned}
 \text{CPU particulate mercury CPU} &= (\text{Conc}_{\text{part}}/1000) \times F_{\text{CPU}} \times \text{Hg}_{\text{FF}} \\
 \mathbf{Hg_{p \text{ CPU}}} &= (456/1000) * 1.3 * 156 \\
 &= 92 \text{ ng/s} \\
 &= 0.1 \text{ } \mu\text{g/s}
 \end{aligned}$$

$$\begin{aligned}
 \text{Produced ash (including UBC) (Ash}_{\text{prod}}) &= \text{Coal}_{\text{ash}} \times (1 + (\text{UBC}_{\text{ash}} / (100 - \text{UBC}_{\text{ash}}))) \\
 (\% \text{ of input coal}) &= 22.6 * (1 + (2.4 / (100 - 2.4))) \\
 &= 23.1\%
 \end{aligned}$$

$$\begin{aligned}
 \text{Mercury in ash} &= \{(1000 \times \text{Coal}_{\text{burn}}) \times (\text{Ash}_{\text{prod}} / 100) \times \text{Hg}_{\text{ash}}\} - \{\text{Hg}_{\text{p stack}} + \text{Hg}_{\text{p CPU}}\} \\
 &= \{(1000 * 5.23) * (23.1 / 100) * 123\} - \{1095 + 92\} \\
 &= 147412 \text{ ng/s} \\
 &= 147.4 \text{ } \mu\text{g/s}
 \end{aligned}$$

### Output Hg as percentage of input mercury

	( $\mu\text{g/s}$ )	% Input	Normalised distribution (%)
Input mercury	164.2	100	
Stack mercury ( $\text{Hg}_{\text{g stack}} + \text{Hg}_{\text{p stack}}$ )	57.3	34.9	27.3
CPU mercury ( $\text{Hg}_{\text{g CPU}} + \text{Hg}_{\text{p CPU}}$ )	4.8	2.9	2.3
Mercury retained in ash	147.4	89.9	70.4
Total Outputs	209.5	127.7	100.0



## **APPENDIX B**

### COSPL Tables

Comb & Env Testing Dec 2012 - Test Results - Overall Rev 0

Testing Dec 2012 - Test Results - Flue Gas Rev 0

Comb & Env Testing Dec 2012 - Test Results - Fly Ash Rev 0