# Trace Element Speciation under Coal Fired Power Station Conditions

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*Abstract:* - Coal combustion from power stations is one of the largest contributors of potentially toxic trace elements to the environment. Some trace elements may be released in range of valencies, often with varying toxicity and bioavailability. Hence, determination of trace element speciation in coals and their combustion products is important for conducting comprehensive risk assessments of the emissions from coal-fired power stations. This study focuses on speciation of selected trace elements, As, Cr, and Se, in coal combustion products and Hg in flue gas, which were sampled at one Australian power station. Results showed that As, Cr and Se are all present in a range of valency states in coal. Concentrations of As and Se in the bottom ash as well as the more toxic hexavalent chromium were less than the detection limits. Fly ash contained the more toxic $As^{3+}$ form at 10% of total arsenic, while selenium was mainly found in $Se^{4+}$ form. Hexavalent chromium ($Cr^{6+}$) in fly ash was 2.7 % of the total fly ash chromium. Mercury speciation in flue gas was determined using the Ontario Hydro sampling train and analysis technique. Approximately 58% of the total mercury in flue gas was released in the elemental form ($Hg^0$), which has the highest residence time in the environment among all mercury species.

*Key-Words:* - Trace Elements, Speciation, Arsenic, Chromium, Selenium, Mercury, Coal Combustion

## 1 Introduction

Toxic trace elements, which occur naturally in the environment, become part of the coal structure through the coalification process [1]. Although present in only small amounts in the coal, the large quantity used result in significant emissions. Approximately 85% of electricity in Australia is generated by coal fired power stations and, consequently, 127 Mt of coal is utilised annually. Toxic trace elements from coal fired power stations are released to the environment either through leachate from ash disposal dams or in the gas or particulate phase in flue gas. Some trace elements, such as mercury, can bioaccumulate in the environment and be converted to even more toxic forms such as organic mercury. It is increasingly evident that distribution, mobility and biological availability of any chemical element not only depends on their total concentrations but, critically on their various chemical forms and oxidation states, known as speciation [2].

Globally, environmental regulators are concerned with emissions of toxic metal compounds to the environment from various anthropogenic sources. The National Pollutant Inventory (NPI) in Australia [3] has developed a list of the following toxic trace metals and their compounds as priority pollutants in consultation with the technical advisory group (TAG) and steering group (SG) for the 'Air Toxics' program:

(i)    Arsenic and compounds
(ii)   Mercury and compounds
(iii)  Lead and compounds
(iv)   Hexavalent chromium ($Cr^{6+}$) compounds
(v)    Cadmium and compounds
(vi)   Nickel and compounds

Selenium and compounds are not listed as 'air toxics' but they have the potential to impact ecosystem. For example, selenium in tissues of fish from Lake Macquarie located in the state of New South Wales, Australia were reported as 12 times higher than recommended levels for human consumptions [4]. Apart from other industrial activities such as copper zinc smelter and sewage treatment plant, two major coal fired power stations are located near Lake Macquarie and selenium contribution from these two power stations alone has been quantified as 400 kg/year. Selenium, either in vapour forms from flue gas stack or as leachate from ash disposal dams, can be deposited in aquatic

bodies through airborne and fluvial sources or, subsequently, can accumulate in fish [4].

Although NPI discriminates only in the case of highly toxic hexavalent chromium as a priority trace element compound, it has been well documented that some specific forms of trace elements i.e. arsenic, selenium, nickel, mercury etc., are more toxic than their other forms of the same elements. As an example, the $As^{3+}$ form of arsenic is 50 times more toxic than $As^{5+}$, while $Se^{4+}$ was reportedly more toxic than $Se^{6+}$ [5-6]. As discussed elsewhere [7], arsenic and selenium are antagonistic to each other in the human body, counteracting each other's toxicity. However, arsenic may also interfere with the essential role of selenium in human metabolism. Toxic effects of selenium in human body have similar effects to arsenic.

In the case of mercury, power station emissions to the environment include three forms: elemental ($Hg^0$), oxidised ($Hg^{2+}$) and particle bound ($Hg^p$). While the elemental $Hg^0$ form can travel long distances in the environment, $Hg^p$ and $Hg^{2+}$ can be deposited near the power station. Moreover, $Hg^{2+}$ and $Hg^p$ are easier to capture by conventional pollution control technologies compared to $Hg^0$ [8].

Mercury has become one of the greatest toxic trace elements of concern for the coal fired power stations. This is mainly due to the cycles of transport and distribution of atmospheric mercury in the environment. The first cycle involves emission of mercury from land sources to the atmosphere and its precipitation in the oceans [9]. The second cycle is associated with methylation of mercury in the oceans and river systems and accumulation of methylmercury in the aquatic biota, which can enter the human food chain, primarily through consumption of fish [10]. Mercury is highly volatile and large amounts are emitted annually through power station flue gas. Mercury is chemically bound in coal and during combustion it is entirely liberated in its elemental form ($Hg^0$). Depending on the coal type and reaction with other species in the flue gas, mainly compounds of chlorine, $Hg^0$ is partly converted to oxidised form ($Hg^{2+}$) and partly associated with fly ash particles in the post-combustion zone.

Total concentration of trace elements in power station coal and ash samples and their partitioning within coal fired power station have been previously extensively studied. Diverse analytical methods are available for determining the total concentration of

these trace elements, as discussed previously by Huggins [11]. Speciation of individual trace elements, however, requires more specific and very sophisticated analytical measurement techniques, which are significantly different from those applicable to total elemental concentration analysis [12-23].

Speciation of chromium in coal and combustion ash samples were determined by Huffman et al. [24] to demonstrate capability of X-Ray absorption fine structure spectrometry (XAFS) for their speciation. Chromium, in this work, was mainly found in $Cr^{3+}$ form (>95%). Modes of occurrence of chromium in sub bituminous and bituminous ranked Canadian coals were studied using sequential leaching with $H_2O$, $NH_4OAc$ and HCl and it was found that chromium in coal was entirely present as $Cr^{3+}$ [25]. Separate study in Canadian power station showed association of trivalent chromium $Cr^{3+}$ in coal with organic matter, while in bottom ash and fly ash small presence of $Cr^{6+}$ was detected [26]. XAFS was also carried out to speciate chromium in combustion ash and fine particulate $PM_{10}$ matter by Huggins et al. [27]. It was found that hexavalent chromium ($Cr^{6+}$) in the analysed ash samples was less than 5% of the total chromium.

Semi-quantitative analysis of arsenic speciation identified dominant mode of occurrences of arsenic in coal as arsenic associated with pyrite and $As^{5+}$ [24]. Arsenic in combustion ash was found to be present mainly in less toxic $As^{5+}$ with a little presence of the more toxic $As^{3+}$ form [27]. In our previous study, speciation of arsenic and selenium using XAFS was determined for selected Australian power station coals and combustion ash samples and it was found that arsenic in coal is present as arsenopyrite, $As^{3+}$ and $As^{5+}$, while in fly ash samples arsenic was mainly found as less toxic $As^{5+}$ with a low presence of toxic $As^{3+}$ which varied between 5 to 15% for analysed samples [28]. The same study showed association of selenium in coal with the organic or elemental form ($Se^0$), whereas in fly ash samples it was mainly present as $Se^{4+}$.

Speciation of trace elements in stack gas requires gas sampling prior or during the analysis. Ontario hydro sampling and analysis method for mercury speciation is an established method used previously by Lee et al. [29] who studied mercury emission and speciation from various combustion sources including coal fired power station. They found that about 85% of Hg was present as $Hg^0$ in the flue gas.

Previous studies have identified the importance to speciate, not only the hexavalent chromium, but also the other priority toxic elements in the coal combustion products and flue gas. The main objective of this paper was to determine speciation of arsenic, chromium and selenium in coal and ash from one power station located in NSW Australia. Mercury speciation in flue gas for the same power station was determined using a standard stack sampling technique. The work gives an overview of the speciation of selected trace elements, which can be further applied for assessment of the environmental impacts of a single point emission power station source.

## 2   Methodology

### 2.1   Sampling Site
Power station located in the state of New South Wales, Australia was chosen for speciation of selected trace elements. This power station operates two 660 MW generating units. Coal combustion temperature is set to approximately 1470 $^0$C. Depending on amount of ash in coal the coal flow rate ranges from 260 T/hr to 280 T/hr and at full load of 660MW ash production is ~90 T/hr, out of which ~76.5 T/hr is fly ash and ~13.5 T/hr is collected as bottom ash. The analysed power station contains fabric filters as the only pollution control device.

The ultimate and proximate analysis of a representative coal sample used in the power station at the time of sampling is given in Table 1. The coal sample was first pulverised to -50μm before undertaking these analyses. Bottom ash from each power station was collected manually from the hopper at the bottom of the boiler. Representative fly ash sample was obtained by an external contractor during the same sampling period.

### 2.2 Elemental Analysis of Trace Elements
Total chromium was determined by digesting 0.1 g of sample with HF/HNO$_3$ for 90 minutes at 110$^o$C. The resulting solution was analysed for chromium content using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

The elemental concentration of arsenic and selenium in the coal and ash samples were determined with Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) according to the Australian standard method, AS 1038.10.2. For this analysis,

coal and ash samples weighing 0.25 g were mixed with 1 g of Eschka fusion mixture and heated in a muffle furnace at 800$^o$C for 2 hours. The mixture was then extracted with 50% HCl and the analytes were determined by ICP-AES after generating their volatile hydrides.

Table 1: Ultimate and proximate analysis of coal (Air Dried Basis)

| | Property | % |
|---|---|---|
| Proximate Analysis | Air dried moisture | 2.8 |
| | Ash | 26.8 |
| | Volatile matter | 26.5 |
| | Fixed Carbon | 43.9 |
| Ultimate Analysis | C | 57.54 |
| | H | 3.68 |
| | N | 1.38 |
| | O | 37.27 |
| | S | 0.13 |

Mercury content in coal was determined by ASTM D 6722-01; direct combustion analysis in which sample was heated in the instrument and then was thermally and chemically decomposed. Halogens, nitrogen and sulphur oxides were trapped from the decomposed product and remaining part was carried to gold amalgamator to trap mercury. The gold amalgamator was rapidly heated to generate mercury vapour which was detected by atomic absorption spectrophotometer at 253.7 nm.

### 2.3 Speciation Analysis of Trace Elements
#### 2.3.1   Chromium speciation by ion chromatography combined with colorimetric detection
To determine trace element speciation in solid material, such as coal and ash, extraction or digestion of the sample is required to produce a solution containing the analyte for further separation and detection. The severity of digestion depends on the nature of the solid matrix from which the analyte is to be extracted.

In this work and for purpose of chromium speciation, the sample was digested using 0.28 M Na$_2$CO$_3$/0.5 M NaOH solution heated at 90-95 $^0$C for 60 minutes to dissolve Cr$^{6+}$ and stabilise it against reduction to Cr$^{3+}$. To suppress oxidation,

magnesium ($Mg^{2+}$) in a phosphate buffer was added. Spike recovery data for soluble and insoluble forms of $Cr^{6+}$ was used to ensure accuracy of the method.

The digestion step was followed by colorimetric detection (US EPA 7199) during which the solution prepared after digestion was filtered and pH adjusted to 9-9.5 with a buffer solution. A known quantity of sample (50-250 μL) was introduced into an ion chromatograph. A guard column removes organics to prevent rapid reduction of soluble $Cr^{6+}$ to $Cr^{3+}$. $Cr^{6+}$ was separated as $CrO_4^{-2}$ through column packed with high capacity anion exchange resin after which it was reacted with diphenylcarbazide in post-column reactor and colored complex was obtained. The colored complex formed by this post-column derivatisation process was detected at 530 nm using low-volume flow through cell visible lamp detector for colorimetric detection of $Cr^{6+}$. The detector response in terms of peak area and height against time was recorded and used for calculating $Cr^{6+}$ content in the sample (Fig. 1).
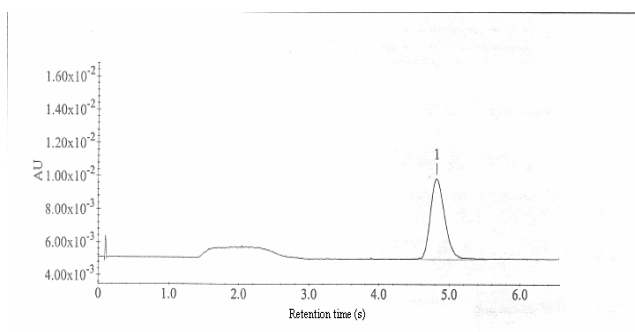


Figure 1: Calibration spectra obtained from colorimetric detection of $Cr^{6+}$

The marked peak, as shown in Figure 1, corresponds to $Cr^{6+}$. A calibration curve was obtained by analysing solutions of known $Cr^{6+}$ concentrations, where various calibration standards with different concentrations were prepared to obtain a calibration curve of peak area versus concentration (Fig. 2). Based on the peak area for unknown sample, the concentration of $Cr^{6+}$ in the sample solution was calculated using this calibration curve. Detection limit for $Cr^{6+}$ was 4 μg/kg. The concentration of $Cr^{3+}$ was determined by subtracting $Cr^{6+}$ from the total chromium determined by ICPMS.
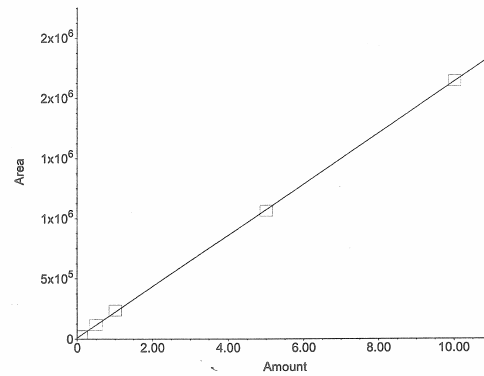


Figure 2: Calibration curve for quantifying $Cr^{6+}$ ($r^2$=0.9996)

### 2.3.2 X-Ray Absorption near Edge Structure Spectrometry (XANES)

XANES is a non destructive and direct technique for trace element speciation analysis using synchrotron radiation source. The synchrotron radiation facility at the Australian National Beamline Facility (ANBF), located at BL20, Photon Factory, Tsukuba, Japan was applied for XANES analysis in this work. Further details of the instrument, experimental setup and calibration of instrument/method were discussed elsewhere [28].

### 2.3.3 Mercury Speciation in Flue Gas- Ontario Hydro Sampling Train and Analysis

Flue gas sample was collected near stack using Ontario hydro sampling method (ASTM D 6784-02). Ontario hydro method is a standard test method to determine elemental, oxidised and particle bound mercury in flue gas where total mercury should be in the range of 0.5 - 100 μg/$Nm^3$ [30]. This method is based on forcing the flue gas through series of eight glass impingers immersed in an ice-bath. First three impingers contain 1 mol/L KCl solution where $Hg^{2+}$ present in flue gas is collected. The fourth impinger containing 5% $HNO_3$ & 10% $H_2O_2$ solution and the fifth to seventh impinger containing 4% $KMnO_4$ & 10% $H_2SO_4$ collect $Hg^0$ present in flue gas. Mercury content in all impinger solutions is determined using Cold Vapor Atomic Absorption Spectrometry (CVAAS) in which absorption of radiation at 253.7 nm by mercury vapour is carried out. The eighth impinger contains silica gel for capturing flue gas moisture.

In this work, sampling was conducted when boiler was running at power stations' full load capacity of 660MW. Flue gas sampling in this case was conducted at flue gas duct located at the entrance of

the stack. A total of 48 traverse points were selected at different locations in the duct. Sample was collected for 5 minutes at each traverse point. Laboratory glassware for solution preparation and the field impingers were thoroughly cleaned using hot soap water wash and overnight soaking in dilute nitric acid. Demineralised water was used for rinsing after hot soap water wash. All reagents and chemicals used were of analytical grade and milli-Q water was used for final washing of the glassware, impingers and during solution preparation. Solution blanks were also analysed to check contamination of mercury.

# 3. RESULTS AND DISCUSSION

Total concentrations of As, Cr and Se in coal, bottom ash and fly ash are shown in Table 2. Mercury present in coal was with the lowest quantity, while chromium had the highest levels in the coal. The concentrations of arsenic and selenium in bottom ash were below detection limit, but in case of fly ash, both concentrations were higher than in the original coal sample indicating arsenic and selenium have volatile nature in the combustion zone and they condense on the submicron fly ash particles. Mercury content was determined for coal sample only.

Table 2: Elemental concentration of selected toxic trace elements (in mg/kg)

| Trace Element | Coal | Bottom Ash | Fly ash |
|---|---|---|---|
| Arsenic | 2.5 | ND | 5.4 |
| Chromium | 10.1 | 26.3 | 31.3 |
| Selenium | 1.3 | ND | 4.1 |
| Mercury | 0.06 | - | - |

## 3.1 Speciation of Cr with hyphenated analytical techniques

Speciation analysis in coal and ash samples were at first carried out using hyphenated techniques such as ion chromatography combined with colorimetric detection for $Cr^{6+}$. The $Cr^{6+}$ spectra obtained with the hyphenated speciation technique for coal, fly ash and bottom ash are shown in Fig. 4. The peaks marked with 1, 2 and 3 were associated with $Cr^{6+}$ and the area under the corresponding peaks were proportional with the $Cr^{6+}$ concentration. Figure 4 reveals $Cr^{6+}$ in bottom ash was below detection limit. Table 3 summarises elemental and speciation

analysis of chromium for the representative coal, fly ash and bottom ash samples. $Cr^{6+}$ was calculated with integration of the corresponding $Cr^{6+}$ peaks against the calibration data, while $Cr^{3+}$ was assumed to represent the difference between total Cr and $Cr^{6+}$. Enrichment of chromium in fly ash and bottom ash indicates the non-volatile nature of chromium under power station combustion conditions. Concentration of $Cr^{6+}$ in fly ash was 0.857 mg/kg compared to 0.065 mg/kg in coal, while $Cr^{6+}$ was not detected in the bottom ash. In terms of relative percentage, $Cr^{6+}$ is present with 2.7% of total Cr in fly ash which is in agreement with the lower end of the $Cr^{6+}$ concentrations from previous studies that have reported levels of $Cr^{6+}$ between 3 and 5% in power station fly ash [28, 31, 32], with exception to an Israeli power station where $Cr^{6+}$ concentrations were up to 20% [12].
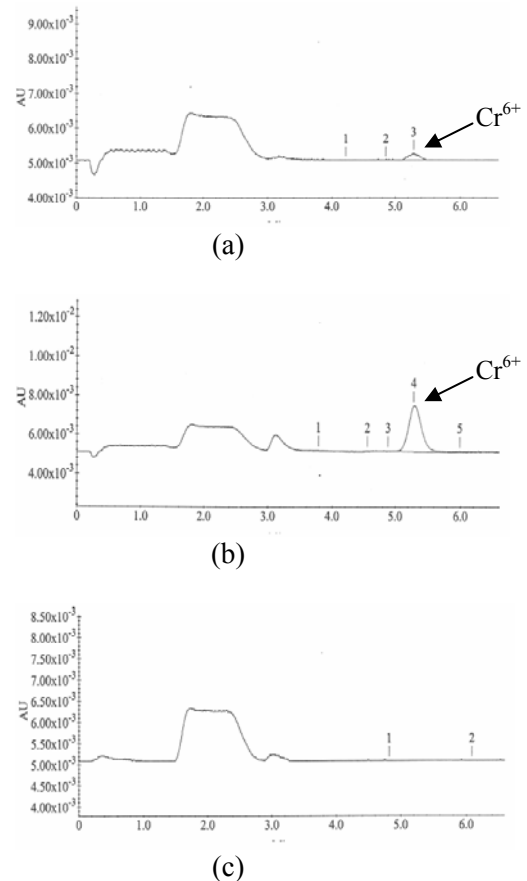


(a)



(b)



(c)

Figure 4: Spectra obtained from colorimetric detection of $Cr^{6+}$ (a) Coal (b) Fly ash (c) Bottom ash

Table 3: Speciation of chromium
(in mg/kg)

| | Total | $Cr^{6+}$ | $Cr^{3+}$ by difference | $Cr^{3+}$ % | $Cr^{6+}$ % |
|---|---|---|---|---|---|
| Coal | 10.1 | 0.065 | 10.035 | 99.4 | 0.6 |
| Bottom ash | 26.3 | ND | ~26.3 | 100 | - |
| Fly ash | 31.3 | 0.857 | 30.443 | 97.3 | 2.7 |

### 3.3 Speciation of As and Se with XANES

XANES spectra of arsenic in coal and fly ash are shown in Fig. 5. Peak locations associated with different forms of arsenic are indicated in the figure. Arsenic was found to be associated with pyrite (As/pyrite), arsenite ($As^{3+}$) and arsenate ($As^{5+}$) in coal samples which is in agreement with previous studies [24, 28]. Semi-quantitative analysis was performed on arsenic species and results are shown in Table 4. The arsenic concentration in bottom ash was found to be lower than the detection limit indicating high volatility of arsenic under combustion conditions. Speciation of arsenic in the fly ash suggested significant combustion induced conversion relative to the feed coal, as 90% of arsenic was found as the less toxic $As^{5+}$ compared to 65% in feed coal. In previous studies arsenic in fly ash was mainly associated with the less toxic $As^{5+}$ form with small presence of the more toxic $As^{3+}$ [22,24,25-28]. Arsenic present in As/pyrite form in coal was completely oxidised to its higher oxidation states.

Selenium XANES spectra for coal and fly ash are shown in Fig. 6. The results revealed that organic or elemental selenium is dominant form in feed coal and $Se^{4+}$ is dominant form in fly ash sample which is in agreement with results obtained for the previous study for a range of power stations [28]. Both arsenic and selenium are found to be volatile under combustion conditions as they are depleted in bottom ash and enriched in fly ash sample.

Table 4: Semi-quantitative
determination of arsenic species

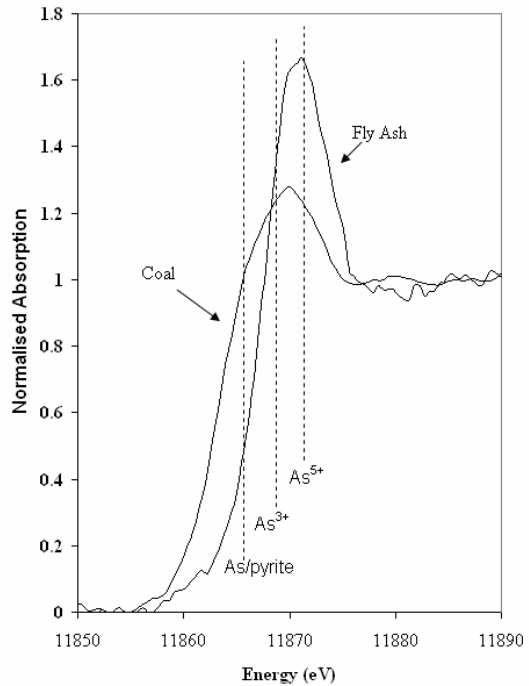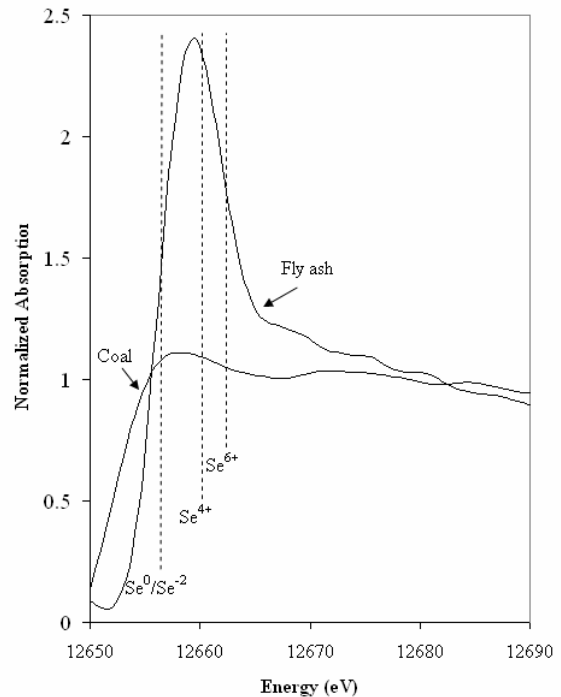| Sample | As/Pyrite (%) | $As^{3+}$ (%) | $As^{5+}$ (%) |
|---|---|---|---|
| Coal | 10 | 25 | 65 |
| Fly ash | - | 10 | 90 |
| Bottom ash | - | - | - |



Figure 5: Arsenic XANES spectra
of coal and fly ash samples



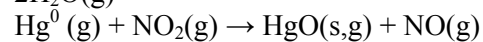Figure 6: Selenium XANES spectra
of coal and fly ash samples

### 3.4 Speciation of Hg in flue gas
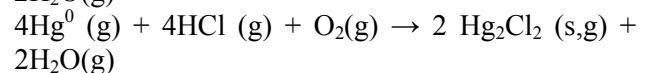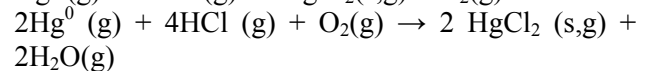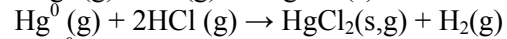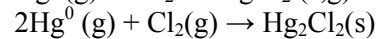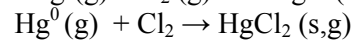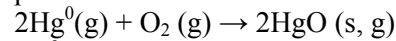
Mercury speciation in flue gas was conducted with the Ontario-hydro sampling train method. The components of Ontario hydro sampling train, such as filter, probe rinse and impinger solutions, were analysed using Cold Vapour Atomic Absorption Spectrometry (CVAAS). Table 5 summarises concentrations of various forms of mercury. It is observed that 58 % of total mercury is released as $Hg^0$. It is known that this mercury form can travel long distances in the environment as it has high residence time because of higher vapour pressure and lower solubility compared to other Hg species such as $Hg^P$ and $Hg^{2+}$ [33]. $Hg^P$ measured at 8% and $Hg^{2+}$ at 34% are more likely to deposit near the power station having mainly local environmental impacts creating local 'hotspots' of mercury pollution. Previous studies carried out at overseas power stations, have reported variable proportion of mercury species. Guo et al [34] studied mercury speciation with Ontario hydro method at 300 MW power station located in China and found that 55-69% of emitted mercury was in $Hg^{2+}$ form and 31-45% was in $Hg^0$, while total mercury was in the range of 13-21 $\mu gN^{-1}m^{-3}$. Particle bound mercury $Hg^P$ was found negligible in this case. Otero-Rey et al. [35] sampled flue gas at 1400 MW power station located in Northwest of Spain, using Ontario hydro method and found that $Hg^{2+}$ was predominant (~60%) Hg species in flue gas and the remaining was emitted as $Hg^0$. Total mercury was measured 19.1-21.8 $\mu gN^{-1}m^{-3}$ and $Hg^P$ was found in negligible amount. Lee et al. [36] studied mercury speciation in flue gas at 500 MW power station located in South Korea. This power station was equipped with electrostatic precipitator (ESP) and flue gas desulphurisation unit (FGD) as air pollution control devices. Mercury speciation in flue gas was conducted at locations before and after the existing pollution control devices. Many tests were conducted and it was observed that large amount of $Hg^P$, above 50% of Hg, could be removed by cold-side ESP. FGD unit was successful in removing the $Hg^{2+}$ form of mercury from flue gas but the $Hg^0$ form could not be captured by neither of the two pollution control devices. Lei et al. [14] studied mercury speciation in flue gas at different locations of power station and at six different power stations located in China. Speciation was conducted before and after pollution control devices and it was observed that total gaseous mercury was in the range of 0 to 48.07 $\mu gN^{-1}m^{-3}$. More than 99% of $Hg^P$ was removed by ESP or fabric filters and hence $Hg^P$ was in negligible amount after these particulate capture devices.
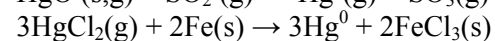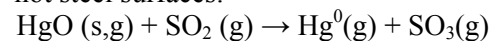
Table 5: Mercury speciation in flue gas

|  | Concentration ($\mu g/Nm^3$) | % of total |
|---|---|---|
| Particle Bound Mercury ($Hg^P$) | 0.04 | 8 |
| Oxidised Mercury ($Hg^{2+}$) | 0.17 | 34 |
| Elemental Mercury ($Hg^0$) | 0.29 | 58 |
| Total Mercury | 0.5 | - |

Mercury speciation in flue gas is largely dependent on the availability of certain gas species which have affinity to react, oxidise or reduce the flue gas Hg compounds. Galbreath and Zygrlicke [33] have discussed chemistry of Hg in flue gas where $Hg^0$ emitted during coal combustion can react with flue gas components such as $O_2$, HCL, $Cl_2$, $SO_2$, $NO_2$, $N_2O$, NO, $NH_3$, $H_2S$ at a temperature range of 20 to $900^oC$. The following range of reactions might be possible under combustion conditions:

$2Hg^0(g) + O_2 (g) \rightarrow 2HgO (s, g)$

$Hg^0(g) + Cl_2 \rightarrow HgCl_2 (s,g)$

$2Hg^0(g) + Cl_2(g) \rightarrow Hg_2Cl_2(s)$

$Hg^0(g) + 2HCl (g) \rightarrow HgCl_2(s,g) + H_2(g)$

$2Hg^0(g) + 4HCl (g) + O_2(g) \rightarrow 2 HgCl_2 (s,g) + 2H_2O(g)$

$4Hg^0(g) + 4HCl (g) + O_2(g) \rightarrow 2 Hg_2Cl_2 (s,g) + 2H_2O(g)$

$Hg^0(g) + NO_2(g) \rightarrow HgO(s,g) + NO(g)$

It was also reported that the rate of reaction of $Hg^0$ (g) with $Cl_2(g)$ is about 3 times higher than the rate of reaction of $Hg^0$ (g) with HCl (g) which makes $Cl_2(g)$ as one of the determining flue gas components for final mercury speciation.

$Hg^{2+}$ compounds such as HgO(s) and $HgCl_2(g)$ formed through the above oxidation reactions may reduce to $Hg^0$ (g) by $SO_2(g)$ present in flue gas or hot steel surfaces.

$HgO (s,g) + SO_2 (g) \rightarrow Hg^0(g) + SO_3(g)$

$3HgCl_2(g) + 2Fe(s) \rightarrow 3Hg^0 + 2FeCl_3(s)$

HgO (g) can also be reduced by CO(g) present in flue gas by following reaction:

$HgO(s) + CO (g) \rightarrow Hg^0(g) + CO_2(g).$
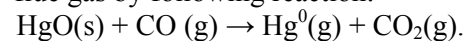
Previous work also showed that final mercury speciation in flue gas varies and depends on factors

such as coal type, chlorine content, operating condition of the power station including presence of existing pollution control devices [13,14,16,36-39]. In this work, total mercury emitted is lower compared to many overseas power stations. Also, speciation of Hg observed here shows elemental form $Hg^0$ as dominant form form of mercury in the flue gas.

# 4. CONCLUSIONS

The aim of the work was to determine speciation of chromium, arsenic, selenium and mercury in ash samples and flue gas collected from an Australian power station. The results show that arsenic, chromium and selenium in coal are present in range of their forms. Approximately, 25% of arsenic in coal was present as the more toxic $As^{3+}$ form, while organic or elemental form of selenium was dominant in coal. Concentrations of As and Se were below detection limit in bottom ash. The toxic $Cr^{6+}$ was also not detected in the bottom ash. In case of fly ash, 10% of total As was found to be in the more toxic $As^{3+}$ form. Majority of arsenic in fly ash was present in the less toxic $As^{5+}$ form. Selenium was mainly found as $Se^{4+}$, while 0.857 mg/kg of $Cr^{6+}$ was found in fly ash compared to 0.065 mg/kg in feed coal. The results showed that, during the course of sampling, 0.5 $\mu g/Nm^3$ of total mercury was emitted through flue gas while 58 % of total mercury was released as $Hg^0$.

# 5. ACKNOWLEDGEMENTS

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