

Impacts of trace components on Oxy-combustion for the Callide Oxy-fuel Project – Literature Review

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EXECUTIVE SUMMARY

Carbon dioxide capture and sequestration or 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 planned through the Callide Oxy-fuel Project.

A potentially significant component of the risk associated with oxy-combustion will be due to trace species in the CO₂ stream. 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.

This report reviews previous research on trace inorganic species in oxy-combustion with a focus on the following questions:

1. What is the effect of combustion in CO₂/O₂ mixtures, compared to combustion in air, on the release, speciation and deportment of trace metals?
2. What is the effect of combustion in CO₂/O₂ mixtures, compared to combustion in air, on the absolute amounts of fine particles, and on the particle size distributions?
3. Given the importance of mercury to environmental and operating issues, what is the effect of combustion in CO₂/O₂ mixtures, compared to combustion in air, on the capture and speciation of mercury in the post combustion regime, and in the CO₂ processing plant?

A small number of studies have shown that there is a decrease in the number of sub-micron (or ultrafine) particles for combustion in O₂/CO₂ mixtures compared to combustion in air. It is believed that this effect is due in part to the higher bulk gas concentrations of CO₂ in oxy-combustion which shift the more volatile suboxides formation equilibria toward the oxide, hence reducing vaporization, and also to the reduced particle temperatures. The reduced enrichment of key species such as Fe, Ca and Si in the sub-micron fraction supports this postulate.

There have been even fewer studies of the effects on the toxic trace metals potentially released in the fine particles. In the most relevant study, researchers from the Energy & Environmental Research Center at the University of North Dakota reported results for the transformation and speciation of hazardous air pollutants (HAPs), including SO₂/SO₃; NO_x; particulate matter; mercury and other trace elements. These showed that while the flue gas has higher concentrations of the HAPs, the actual emissions of HAPs per unit of energy produced were much less than those for air combustion. In addition most non-volatile trace elements were less enriched in fly ash from oxy-combustion than from air-firing due to lower temperatures in the oxy-combustion case.

The potential environmental and operational impacts of mercury, particularly its ability to form an amalgam with aluminium which may lead to corrosion of heat exchanger elements in the CO₂ processing units of oxy-combustion plants, make measurement and management of mercury a high

priority for oxy-combustion. Extant research reports variable observations for the impact of oxy-combustion on mercury concentrations and speciation. The somewhat variable observations for mercury speciation in oxy-combustion probably reflect the complexity in the homogeneous and heterogeneous reactive pathways for this species in combustion and post combustion environments. Interactions and competitive reactions of mercury with other flue gas species determine ultimate mercury department. For this reason observations at full scale supported by carefully controlled laboratory experiments are essential for enhancing understanding of this key species during oxy-combustion.

The specific design of the CO₂ processing plant used in an oxy-fuel combustion system will have a large influence on the relevant research on trace species removal, capture and behaviour in these systems. In this review the emphasis is on conditions relevant to the Callide Oxy-Fuel Plant. Removal of NO_x and SO_x from CO₂ using compression and water contact with the flue gas has been demonstrated at a range of scales. There is also limited evidence that wet compression may also be effective at mercury removal. It is likely that the success of compression to remove these impurities relies on the significantly higher solubilities of N and S species formed during the compression process, and postulated reactions of mercury with nitric acid to produce soluble Hg(NO₃)₂.

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Table of Contents

1	INTRODUCTION	6
1.1.1	Why is this Research Project needed?	6
1.1.2	Target Species	10
1.1.3	Potential gas quality impacts in oxy-combustion	13
1.1.4	Callide Oxy-Fuel Plant.....	16
2	PREVIOUS RESEARCH – COMBUSTION SYSTEMS	18
2.1	Particulate matter	18
2.2	Trace metals	20
2.3	Mercury	22
2.3.1	Laboratory and pilot scale studies	22
2.3.2	Large scale studies	23
3	PREVIOUS RESEARCH – CO ₂ PLANT	27
4	TRACE ELEMENT MEASUREMENT	29
4.1	Mercury	29
4.1.1	Mercury sampling in combustion systems.....	29
4.1.2	The Ontario Hydro Method.....	30
4.1.3	Dry sorbent-based methods	31
4.1.4	Continuous Emission Monitors (CEMs).....	33
4.1.5	Measurements under oxy-firing conditions.....	35
4.2	Other metals.....	36
5	CONCLUSIONS	38
6	REFERENCES	39

List of Figures

Figure 1: Potential corrosion issues in oxy-fuel combustion systems (Kiga 2010)	8
Figure 2: Mineral transformations and particle formation pathways during coal combustion (from Suriyawong et al (2006))	9
Figure 3: Fly ash particle penetration as a function of particle size for electrostatic precipitators (ESPs) and fabric filters (FFs) for various boilers and fuels (Jokiniemi 2003))	12
Figure 4: Vattenfall 30 MWth Oxy Process Flow Diagram (from (Levasseur et al. 2009)).....	15
Figure 5: Vattenfall’s 30MWth oxy-fuel pilot plant gas treatment and compression process. FGD design by Babcock Noel, flue gas cooler designed by Trema, compression circuit (from Wall et al (2012), based on Ritter et al (2009), Thebault et al (2009), and Stanger and Wall (2011)).....	15
Figure 6: Air Products “Sour Gas Compression” technology (White et al. 2009; Murciano et al. 2011)	15
Figure 7: Callide Oxy-Fuel Project flow sheet for the gas cleaning and compression plant	16
Figure 8: Sub-micrometer particle size distributions of air and 20% O ₂ /80% CO ₂ coal combustion (Suriyawong et al. 2006)	19
Figure 9: Measured elemental compositions in sub-micrometer-sized ash for air and 20% O ₂ /80% CO ₂ combustion (Suriyawong et al. 2006)	19
Figure 10: Particle Number Size Distributions of Utah Skyline, Powder River Basin and Illinois #6 coals combusted in air, and varying O ₂ /CO ₂ mixtures (Jia and Lighty 2012)	21
Figure 11: Proportion of global anthropogenic mercury emissions to air in 2005 from different sectors (UNEP Chemicals Branch 2008).....	23
Figure 12: Mercury speciation from four coals of varying composition studied in a drop tube reactor in air, O ₂ /CO ₂ , and enhanced , O ₂ /CO ₂ (Ma et al. 2011)	24
Figure 13: Behaviour of mercury and SO ₃ in power plants equipped with various air pollutant control devices(Kikkawa et al. 2011).....	25
Figure 14: N, S and Hg chemistry in CO ₂ gas compression and purification; conditions relevant to Callide Oxy-Fuel Plant (Stanger et al. 2012a).....	28
Figure 15: Comparison of solubilities of NO _x and SO _x gaseous species in water using Henry’s Law coefficients (Stanger et al. 2012a; Stanger et al. 2012b).....	28
Figure 16: The Ontario Hydro Method Sampling Train. From Otero-Rey et al (2003)	31
Figure 17: Principles of sorbent trap monitoring (Schmid and DeRosier 2011)	32
Figure 18: Mercury mass balance closures for two scales of pulverized coal furnaces and a circulating fluidized bed while air- and oxy-firing a western bituminous coal (Fry et al. 2011)	36
Figure 19: Schematic of USEPA Method 29 sampling train (see http://www.activeset.org/methods/new/method29/index.htm)	37

List of Tables

Table 1 Illustrative CO ₂ stream compositions, vol% or as stated, for coal-fired CCS technologies (from (Wall et al. 2012)).....	8
Table 2: Gas quality and cleaning issues in oxy-fuel technology. Based on (Li et al. 2012; Wall et al. 2012)	13
Table 3: Global anthropogenic emissions of mercury to air in 2005 from different sectors (UNEP Chemicals Branch 2008).....	22
Table 4: Commercially available mercury CEMs. Based on (CEA 2004).....	34

1 INTRODUCTION

1.1 Description of the Research Project

1.1.1 Why is this Research Project needed?

Carbon dioxide capture and sequestration or 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 underway through the Callide Oxy-fuel Project.

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

A potentially significant component of the risk associated with oxy-combustion will be due to trace species in the CO₂ stream. 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. In this project a combination of laboratory experiments, modelling and computational studies, and field measurements will be used to obtain detailed information on trace components of oxy-fired combustion gases.

It is widely 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 (Toftegaard *et al.* 2010).

Environmental and operational risk will be determined by a range of inter-related considerations including:

- The mass emission rate (mass/time) of trace metals and fine particles 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.

The last issue is particularly important as it is widely recognised that distribution, mobility and bioavailability of any element not only depends on their total concentrations but, critically on their chemical forms and oxidation states (speciation) (Ebdon 2002).

As³⁺ is about 50 times more toxic than As⁵⁺ and several times more toxic than organic forms such as monomethylarsinate (MMA) and dimethylarsinate (DMA) (Hodgson *et al.* 1988). Apart from the environmental and health impacts, it has been also observed that arsenic present in coal, particularly volatilised As₂O₃ generated during combustion, may deactivate selective catalytic reduction (SCR) catalysts used for NO_x control (Staudt *et al.* 2002).

Selenium is one of the essential trace elements which acts as an antioxidant and protects cell membranes. Overexposure to Se, on the other hand, is known to be highly toxic. Selenium toxicity depends on its oxidation form and quantity. There is a small margin between selenium sufficiency and toxicity and hence concentrations of selenium species in the environment need to be carefully evaluated (Greenwood and Earnshaw 1997).

Chromium is a naturally occurring metallic element that has two oxidation states which are stable in the environment: trivalent (Cr^{3+}) and hexavalent chromium (Cr^{6+}). Cr^{3+} is an essential nutrient for humans and animals and has a low level of toxicity. Cr^{6+} originates mostly from anthropogenic sources and is a known carcinogen (U.S. Department of Health and Human Services 2000).

Finally the environmental transport and impacts of mercury depend critically on the relative proportions of elemental and oxidised mercury. Mercury concentrations and speciation in oxy-combustion is of particular importance for both environmental and potential operational reasons. There is a current United Nations Environment Program (UNEP) process aimed at the development of a legally-binding international agreement for the management and ultimate reduction of mercury releases to the environment¹. Coal combustion in power stations is the major anthropogenic source, and the emissions of mercury are strongly influenced by the relative proportions of the insoluble and unreactive elemental form compared to the more soluble and reactive oxidised form (believed to be HgO or HgCl_2). Hence determining how mercury speciation and control may be influenced by firing in oxygen compared to air is a high research priority.

Mercury also has the ability to form an amalgam with aluminium. This property is of potential concern as it may lead to corrosion of heat exchanger elements in the CO_2 processing units of oxy-combustion plants (Bessone 2006; Santos 2008). In fact corrosion is regarded as an important issue relevant to many unit operations in oxy-combustion systems. Figure 1 summarises (Kiga 2010) the potential issues in oxy-fuel combustion systems.

Thus, it is important to analyse these trace element species in coal, combustion residues, wastewater and CO_2 processing plants for the purpose of comprehensive environmental and operational impacts of coal oxy-fired power stations.

According to equilibrium calculations trace metal emissions (such as those for Hg, Cd, As, and Se) are not significantly affected by the combustion medium. However previous work has also demonstrated that the complex multi-phase chemistry in solid fuel combustion systems can result in significant non-equilibrium behaviour. In addition, the less than optimum collection efficiency of these species in air pollution control devices may result in elevated concentrations in the flue gas stream. As a consequence, additional gas treatment may be required to produce gas quality suitable for pipeline transportation and ultimate sequestration.

¹ See <http://www.unep.org/hazardoussubstances/mercury/tabid/434/default.aspx>

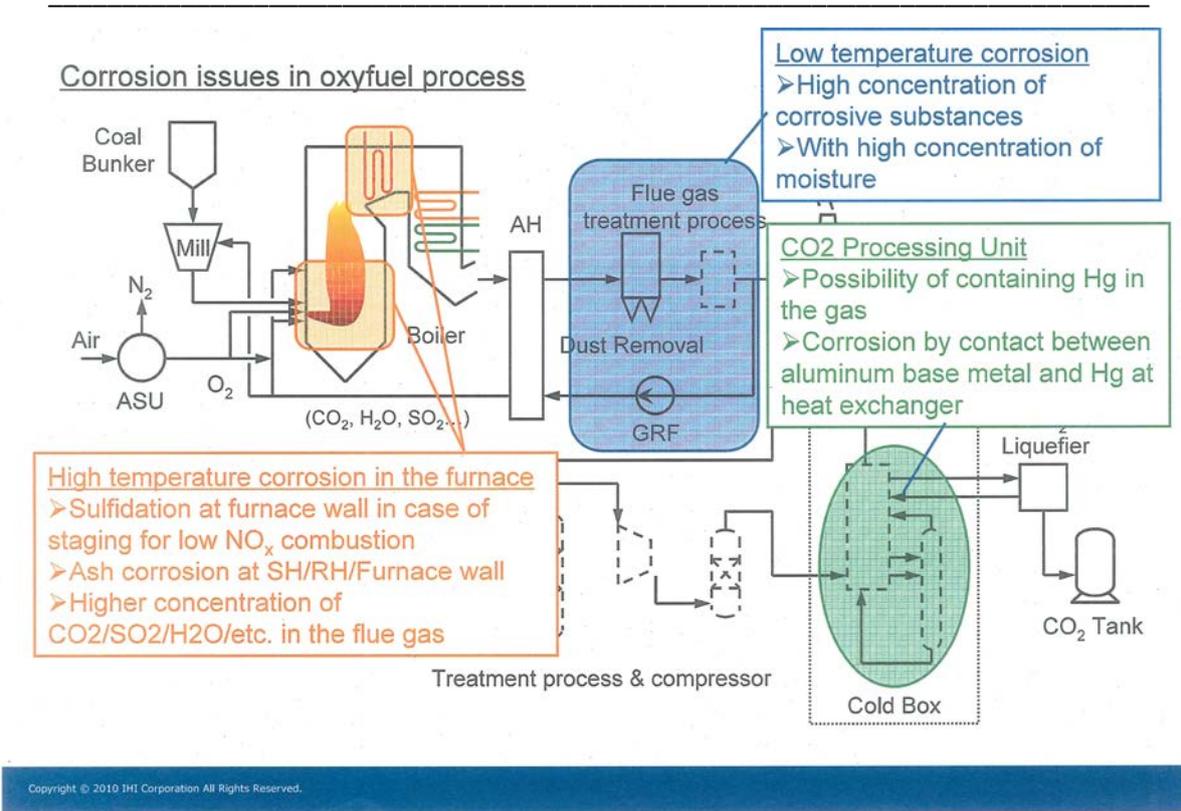


Figure 1: Potential corrosion issues in oxy-fuel combustion systems (Kiga 2010)

Wall *et al* (2012) identify gas quality as an early research and regulation issue as the gas produced from oxy-fuel has higher levels of inert gases, oxygen, sulfur and nitrogen gases, and other trace impurities (see Table 1). Enhanced 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.* 2012).

Table 1 Illustrative CO₂ stream compositions, vol% or as stated, for coal-fired CCS technologies (from (Wall *et al.* 2012))

Gas stream	Oxy-fuel combustion	Post-combustion capture		Pre-combustion capture	
	Raw flue gas prior to the CO ₂ purification plant	CO ₂ product	Raw flue gas prior to gas absorption by solvent (Cottrell <i>et al.</i> 2009)	CO ₂ product	CO ₂ product
CO ₂ (%)	67	>99		>99	95–99
H ₂ O (%)	10			<1	<1000 ppm
Total sulphur (SO ₂ ,H ₂ S, COS)	600–1800 ppm for black coal 300–900 ppm for brown coal	<200 ppm	200–600 ppm for black coal 100–300 ppm for brown coal	2 ppm	3 ppm as SO ₂ ,H ₂ S, COS
Total nitrogen (NO, NO ₂ ,NH ₃ , HCN, etc.)	300–700 ppm for black coal 100–200 ppm for brown coal	<200 ppm	300–700 ppm for black coal 100–200 ppm for brown coal	5 ppm	50–100 ppm as NH ₃ and HCN
Hg (µg/Nm ³)	0.3–1.0	<0.1	1–10	Uncertain	Uncertain, but Hg removal common

Trace element emissions	ppm–ppb level	Uncertain	ppm–ppb level	Uncertain	Uncertain
Combustibles (%) (H ₂ ,CH ₄ , CO, etc.)	0	Trace			0.05–0.02
Inerts (%) (N ₂ , Ar, etc.)	18.4		70–80	Trace	Trace
O ₂ (%)	4.5		5–10	Trace	Trace

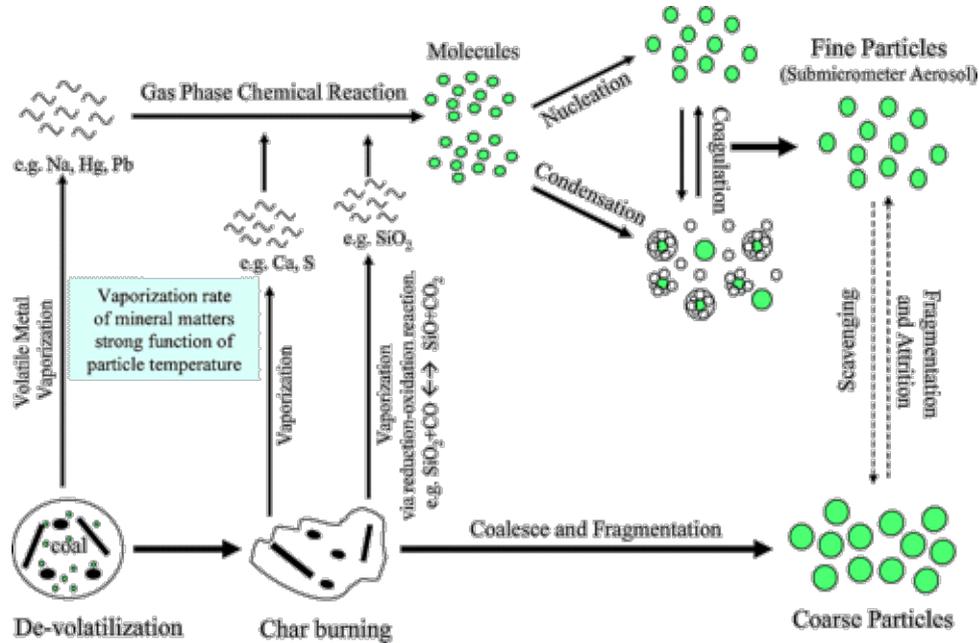


Figure 2: Mineral transformations and particle formation pathways during coal combustion (from Suriyawong et al (2006))

In spite of its potential importance to oxy-fuel combustion the effects of firing in O₂/CO₂ mixtures on trace metal department, speciation, and behaviour in flue gas cleaning systems has not been extensively studied. In one of the few published studies Suriyawong *et al* (2006) determined sub-micrometer particle formation and mercury speciation from the air- and oxy-fuel combustion of a sub-bituminous coal in a laminar reactor. Trace metal behaviour in these systems is complex and illustrated in the figure above (from (Suriyawong *et al*. 2006). There are clear interactions between trace metal release, transformations and speciation and fine particle formation as illustrated.

The sub-micrometer particle formation mechanisms are complex functions of such factors as coal type, combustion temperature, fuel to oxidant ratio, and residence time. This is likewise the case for the resulting particle size distributions, and these variables will impact on the release and speciation of the trace metals. This issue is discussed further below.

Combustion under oxy-fuel conditions is likely to result in a lower adiabatic flame temperature and hence a reduction of the coal burning rate compared to combustion in air. The vaporization of both volatile metals and metal sub-oxides as well as the particle formation rates will thus be significantly smaller, as observed (Suriyawong *et al*. 2006).

Hence based on the considerations outlined above it is clear that a significant component of the risk associated with oxy-combustion may be due to trace species in the CO₂ 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 this project a combination of laboratory experiments, modelling and computational studies, and field measurements are proposed to obtain detailed information on trace components of oxy-fired combustion gases, including:

- Trace metal and fine particulate matter (PM) 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
- 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 CO₂ processing plant;
- Ultimate trace component concentrations in product CO₂, and an assessment of the suitability of the CO₂ for various uses (eg, pipeline quality for transport and storage; comparison with food grade CO₂ and required additional cleaning required to meet food grade standards);
- Modelling and computational studies to assess flue gas composition effects on CO₂ capture, and to support, through predictive capability, the next stage of commercialisation.

1.1.2 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. It is proposed in this project to base the target list of species to be characterised on the list of reportable substances included in the Australian National Pollutant Inventory (see <http://www.npi.gov.au/substances/list-of-subst.html>).

On that basis the target species list for this project is as follows:

- Antimony & compounds
- Arsenic & compounds
- Beryllium & compounds
- Boron & compounds
- Cadmium & compounds
- Chromium (III) compounds
- Chromium (VI) compounds
- Cobalt & compounds
- Copper & compounds
- Lead & compounds
- Manganese & compounds
- Mercury & compounds
- Nickel & compounds
- Selenium & compounds
- Zinc and compounds

Many of these species are almost completely present in the solid phase under coal combustion conditions (Helble 2000). The more volatile may also be enriched in the finer particles due to vaporisation at combustion temperatures and then re-condensation on the available particle surface as the temperature decreases (Helble 2000). For this reason sampling of the particles is crucial for understanding the deportment of the trace metals. In addition it is also important to understand the effects of combustion in CO₂/O₂ mixtures, as compared to firing in air, on particle size distributions.

Particle size distributions of ash produced during coal combustion have long been known to be multi-modal in character. The majority of the mass of the ash is greater than 1 µm in size, and results from pulverized fuel burnout leading to an ash residue, and particle fragmentation processes. A much smaller proportion of fine material is also produced. The nature and composition of this material is of great importance, since:

- Collection efficiency in electrostatic precipitators (ESPs) is lowest for particles in the ultrafine 0.1 - 1 µm size range. This is illustrated in Figure 3 which shows data collected by the VTT Technical Research Centre of Finland (Jokiniemi 2003). The figure also illustrates that particle penetration through fabric filters is generally much lower and less size dependent than through ESPs.
- In the context of toxic trace element deportment, trace elements have been observed to be enriched in the fine fraction (Linak *et al.* 2003).
- The health effects observed recently for PM are associated most strongly with the fine fraction. Increasing toxicity with decreasing PM aerodynamic diameter has been reported (Okeson *et al.* 2003).
- Light scattering is greatest for particulate material in the submicron range; hence visibility impacts are highest for this range.

The nature of the fine particles released from coal-fired power stations has been studied for many years. Early work is excellently summarized and reviewed by Damle *et al.* (1982). More recent work at full scale (Kauppinen and Pakkanen 1990) and at pilot scale (Galbreath *et al.*, 2000) has extended the understanding of the size and composition as a function of size. In results reported for the CRC for Coal in Sustainable Development (CCSD), Nelson and co-workers (Halliburton *et al.* 2006; Nelson *et al.* 2010) reported emissions for a range of New South Wales and Queensland coal-fired power stations as a function of size for both PM and trace components in the PM.

Submicron particulate material produced in combustion processes largely arise from vaporization and condensation processes, although there is some evidence (Linak *et al.* 2003) for a contribution, probably from fragmentation processes, to particles in the 0.7 - 3.0 µm size range.

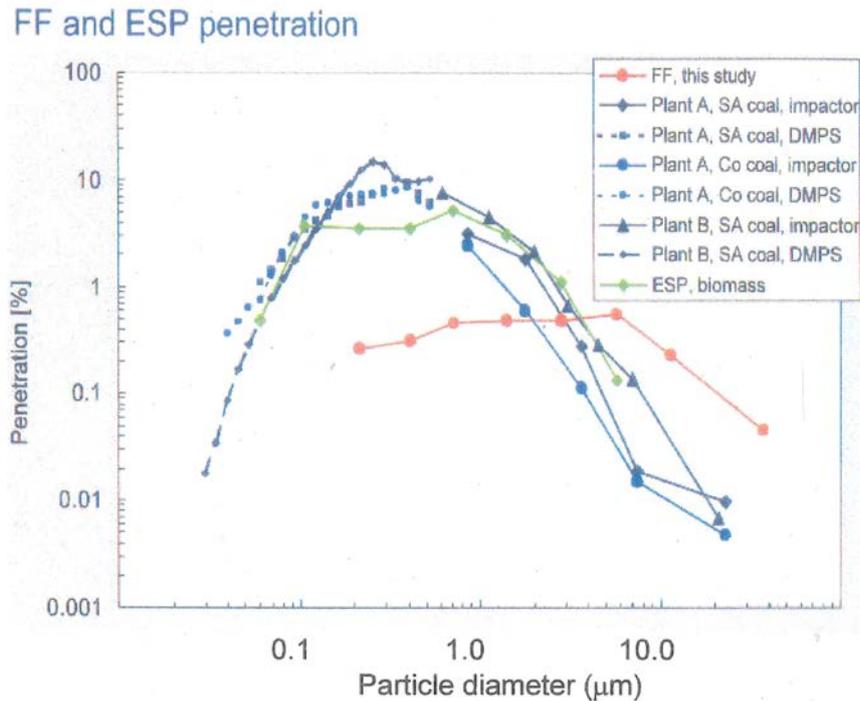
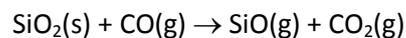


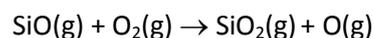
Figure 3: Fly ash particle penetration as a function of particle size for electrostatic precipitators (ESPs) and fabric filters (FFs) for various boilers and fuels (Jokiniemi 2003))

A model for formation of submicron material was developed by Sarofim and co-workers (Haynes *et al.* 1982; Quann *et al.* 1982; Quann and Sarofim 1982) to account for observed distributions of inorganic species in the fine ash products from coal combustion. The main features of the mechanism are as follows:

- During combustion highly reducing conditions can exist inside coal particles
- Under these conditions refractory oxides can be reduced to more volatile suboxides or elements; for example, in the case of Si:



- The volatile species is transported away from the particle into the bulk gas where O_2 concentrations are significantly higher, and the suboxide or element is re-oxidised:



- Provided the vapour pressure of the oxide exceeds the saturated vapour pressure spontaneous condensation will occur, and nuclei of the submicron fume will be formed.

The mechanism was further elaborated by Haynes (1999) who developed a detailed kinetic model for silica vaporization and condensation.

Submicron particle formation is important in trace element department, since although trace toxic species such as arsenic and selenium can also vaporize due to the formation of volatile combustion

products, these species are often not present in sufficient concentrations to homogeneously condense. Condensation of these species on existing particles is, in that case, more likely. The fine particles contribute relatively more to the available surface area, so enrichments in the fine particle fraction are often observed as detailed above.

The deposition mechanism of the vaporised trace elements onto ash particle surfaces can result in a mechanism-specific correlation between trace element concentration and particle size. For example, deposition rate limited by ash particle surface reaction kinetics is governed by the reaction rate at the surface area, and leads to a $1/d_p$ dependence, where d_p is the particle diameter. Such relationships, together with ESP particle penetration information, and similar information for fabric filters, can be useful in developing practical models of trace element emission. Previous work for CCSD (Halliburton *et al.* 2006) examines these relationships for Australian coal-fired power stations.

1.1.3 Potential gas quality impacts in oxy-combustion

Wall and co-workers (Li *et al.* 2012; Wall *et al.* 2012) identify the need for research on gas quality in oxy-combustion due to impacts on materials, transport systems and regulations for CO₂ storage. They note 4 potential technological impacts of gas quality:

- Uncertainties in the oxy-fuel technology flow sheet related to the need for gas cleaning unit operations;
- Higher concentrations of trace components in the furnace and flue gas due to the removal of N₂ from the oxidant;
- Uncertainties in the future regulatory requirements of CO₂ gas quality for transport and storage;
- Uncertainties in the impact on cost and operational issues of impurities on CO₂ recovery and purification, and on the energy required for compression.

Table 2 summarises the issues related to gas quality and resultant gas cleaning issues in oxy-combustion (Li *et al.* 2012; Wall *et al.* 2012).

Table 2: Gas quality and cleaning issues in oxy-fuel technology. Based on (Li et al. 2012; Wall et al. 2012)

Technology block	Gas	Impact	Cleaning
Air Separation Unit (ASU)	Ar	Energy for ASU and CO ₂ compression	
Furnace, and standard gas cleaning	SO _x , NO _x , fly ash and O ₂ and N ₂ from air leakage	Emissions, corrosion, impacts in CO ₂ compression	FGD, low-NO _x burners, catalytic NO _x removal, FF, ESP
Gas scrubbing with NaOH and/ or water	Gases not collected in standard gas cleaning	Impacts in CO ₂ compression	Acid gases removed (SO _x ,NO ₂) but not NO
CO ₂ compression	Gases not collected in standard gas cleaning, and Hg in particular		Options for NO _x , SO _x and Hg removal
CO ₂ transport and storage	SO _x ,O ₂ ,H ₂ O	Pipeline corrosion, and regulations for CO ₂ storage quality	

A previous report by Wall *et al* (2012) discuss the issues related to sulphur. Here we concentrate on the other trace components of the gas, particularly mercury. It is instructive to consider the extant oxy-combustion flow sheets to examine the variable gas cleaning approaches to ensuring acceptable gas quality.

Alstom has been actively evaluating the technical and economic viability of CCS technologies for more than a decade and is focusing on development of post-combustion scrubbing and oxy-combustion, as these are applicable to both new and existing power plants (Levasseur *et al.* 2009). The first complete oxy-fired plant with CO₂ capture, Vattenfall's 30 MWth Schwarze Pumpe oxy-combustion plant has been constructed and successfully operating since September 2008. Alstom supplied the oxy-boiler for this plant and is a partner in the two-year testing program (Levasseur *et al.* 2009; Strömberg *et al.* 2009).

The overall process diagram for the Vattenfall plant is given in Figure 4, and the CO₂ processing plant is illustrated in Figure 5. The gas cleaning in this plant is based on a calcium based flue gas desulphurisation unit (separate capture and sulphite oxidation stages) and a flue gas cooler (separate stages for direct water cooling and NaOH/Na₂CO₃ sprays) prior to compression. Results showed good SO_x removal but no significant NO_x removal (Thebault *et al.* 2009; Stanger and Wall 2011). Mercury removal is achieved in an activated carbon bed, placed prior to the main compression. A recent overview (Anheden *et al.* 2011) of operational experience and results from the Schwarze Pumpe plant reported that “the analysis of the condensate shows no significant accumulation of contaminants such as e.g. heavy metals”.

An alternative approach has been developed by Air Products and is termed “Sour Gas Compression” technology (White *et al.* 2009; Murciano *et al.* 2011; Stanger and Wall 2011), and is illustrated in Figure 6. Two scrubbers and one adsorption bed at pressures of 15 and 30 bar are used to increase surface area and residence time to facilitate gas dissolution. The process has been tested at small scale on a slip-stream to the Doosan Babcock oxy-fuel furnace in Renfrew, Scotland (Sturgeon *et al.* 2009; White *et al.* 2009; Sturgeon *et al.* 2011). Oxidation of NO promotes conversion of SO₂ to H₂SO₄ in the presence of water. Mercury is expected to dissolve in the nitric acid formed. Expertise and IP in this area resides in international gas vendors (Air Products, Air Liquide, Linde and Praxair).

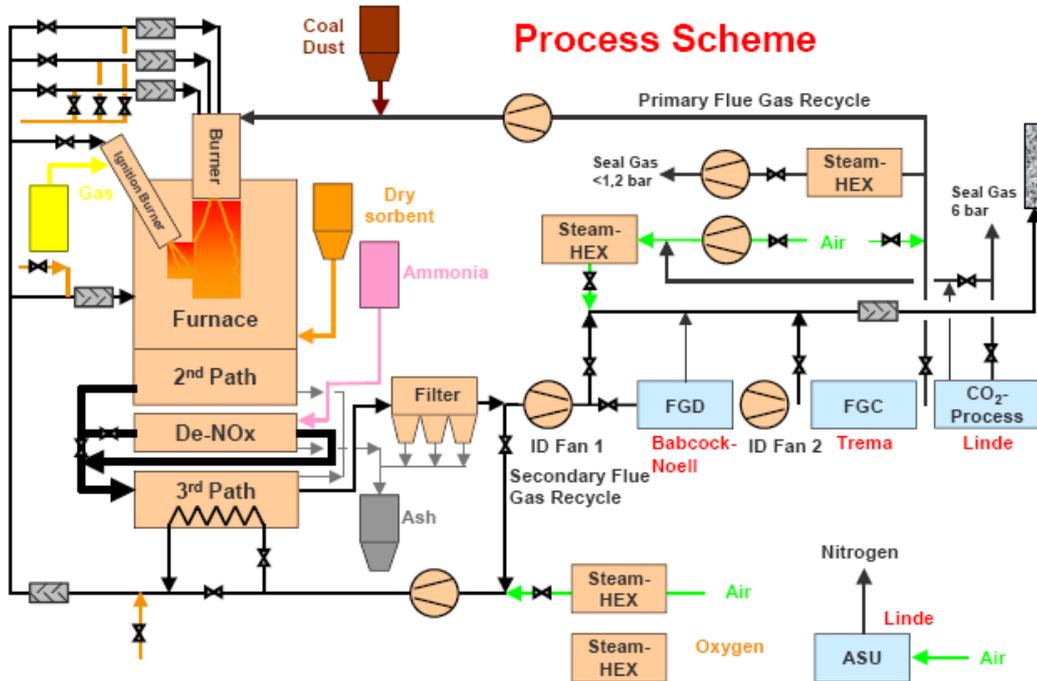


Figure 4: Vattenfall 30 MWth Oxy Process Flow Diagram (from (Levasseur et al. 2009))

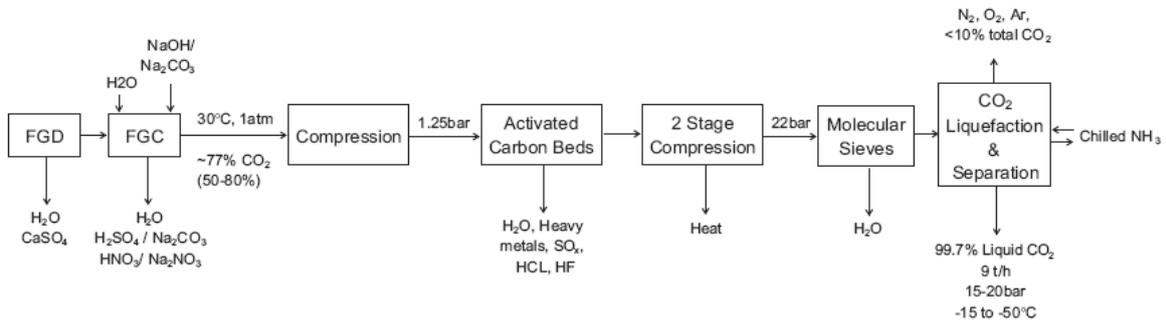


Figure 5: Vattenfall's 30MWt oxy-fuel pilot plant gas treatment and compression process. FGD design by Babcock Noel, flue gas cooler designed by Trema, compression circuit (from Wall et al (2012), based on Ritter et al (2009), Thebault et al (2009), and Stanger and Wall (2011))

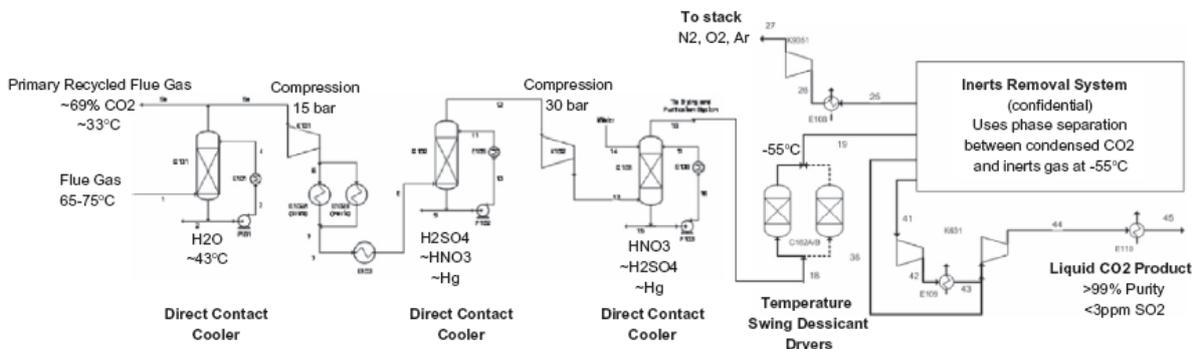


Figure 6: Air Products "Sour Gas Compression" technology (White et al. 2009; Murciano et al. 2011)

1.1.4 Callide Oxy-Fuel Plant

Gas processing at the Callide Oxy-Fuel Plant is based on an Air Liquide process which includes (Wall *et al.* 2012) the following units of operations:

- direct cooling of the flue gas
- compression of wet flue gas
- drying of the flue gas at the outlet of the wet compression step
- flue gas purification
- pressure and temperature adjustment for transport to 30°C and 16 bar
- pumping of the condensed product to storage pressure.

An overall schematic for the Callide system is given in Figure 7. Mercury removal is expected to be achieved as part of the liquid waste from the compression stage, obviating the need for using activated carbon (AC). Mercury removal using AC is widespread in the natural gas industry but the incorporation of these units into a large scale oxy-fuel compression circuit and their effective operation as mercury strippers has yet to be demonstrated (Wall *et al.* 2012). Wall *et al.* (2012) further discuss the differences between the Vattenfall approach to mercury removal and that employed at Callide. The differences in approach to acid gas and mercury removal have implications for the relevance of previous research on trace metal behaviour in the CO₂ processing plants of oxy-combustion systems, as discussed in Section 3 below.

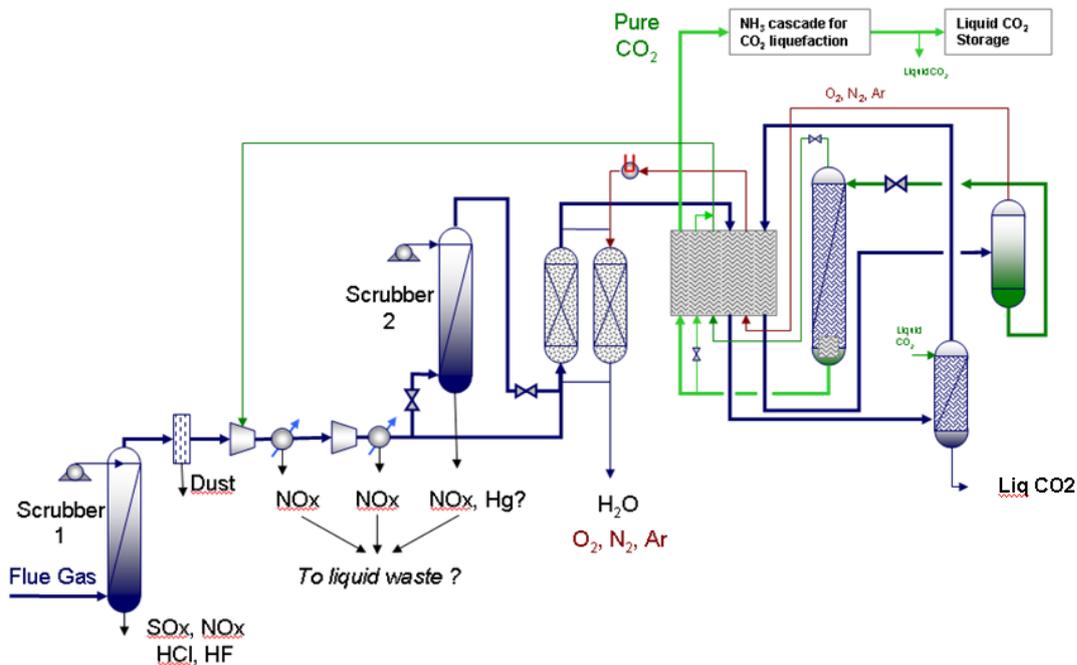


Figure 7: Callide Oxy-Fuel Project flow sheet for the gas cleaning and compression plant

Based on the discussion above it is possible to formulate key questions related to trace inorganic species in oxy-combustion:

1. What is the effect of combustion in CO₂/O₂ mixtures, compared to combustion in air, on the release, speciation and deportment of trace metals?
2. What is the effect of combustion in CO₂/O₂ mixtures, compared to combustion in air, on the absolute amounts of fine particles, and on the particle size distributions?
3. Given the importance of mercury to environmental and operating issues, what is the effect of combustion in CO₂/O₂ mixtures, compared to combustion in air, on the capture and speciation of mercury in the post combustion regime, and in the CO₂ processing plant? The specific design of the CO₂ processing plant will determine the research needs.

These questions provide a focus for the following discussion of previous research.

2 PREVIOUS RESEARCH – COMBUSTION SYSTEMS

There have been previous comprehensive reviews of oxy-combustion (Buhre *et al.* 2005; Wall *et al.* 2009a; Toftegaard *et al.* 2010; Edge *et al.* 2011; Scheffknecht *et al.* 2011) which address the major issues of combustion performance, heat transfer, emissivity, coal reactivity, ignition and ash deposition.

These reviews also address formation and control of the major pollutant gases, NO_x and SO₂. It is not proposed to review this literature but to concentrate here on studies which specifically address PM, trace metals and mercury under oxy-combustion. In general these issues have up till now received less attention but the recent rate of relevant publications is increasing.

2.1 Particulate matter

According to Toftegaard *et al.* (2010) combustion in O₂/CO₂ mixtures when the oxygen concentration is similar to that in air combustion results in lower adiabatic flame temperatures, and hence lower coal combustion rates. As a consequence vaporization of volatile metals and metal sub-oxides and fine particle formation is significantly reduced under oxy-combustion conditions.

Using a drop tube reactor and a Powder River Basin sub-bituminous coal with mean particle size of 50 μm, Suriyawong *et al.* (2006) observed a decrease in the number of sub micron particles for combustion in O₂/CO₂ mixtures compared to combustion in air (see Figure 8).

These workers also measured the distribution of various metals in the sub micron ash and found that a smaller proportion of the metals was present in the ash from combustion in 20% O₂/80% CO₂ (see Figure 9).

It was postulated (Suriyawong *et al.* 2006) that these effects were due in part to the higher bulk gas concentrations of CO₂ which shift the sub-oxides formation equilibria toward the oxide, hence reducing vaporization, and also to the reduced particle temperatures. These workers (Suriyawong *et al.* 2008) have also examined the implications of combustion in O₂/CO₂ mixtures on particle capture in electrostatic precipitators, as have Han *et al.* (2010). The latter found that the electrical mobility of the CO₂ enriched atmosphere was only about 0.6 times that of an air atmosphere, resulting in a lower collection efficiency of the particles.

Sheng and co-workers observed similar trends for PM from Chinese coals (Sheng *et al.* 2007a; Sheng *et al.* 2007b; Sheng and Li 2008). They concluded that the lower particle temperatures with ~20% O₂ in CO₂ might also affect the particle fragmentation and coalescence mechanisms in addition to any effect on vaporization of species such as Si.

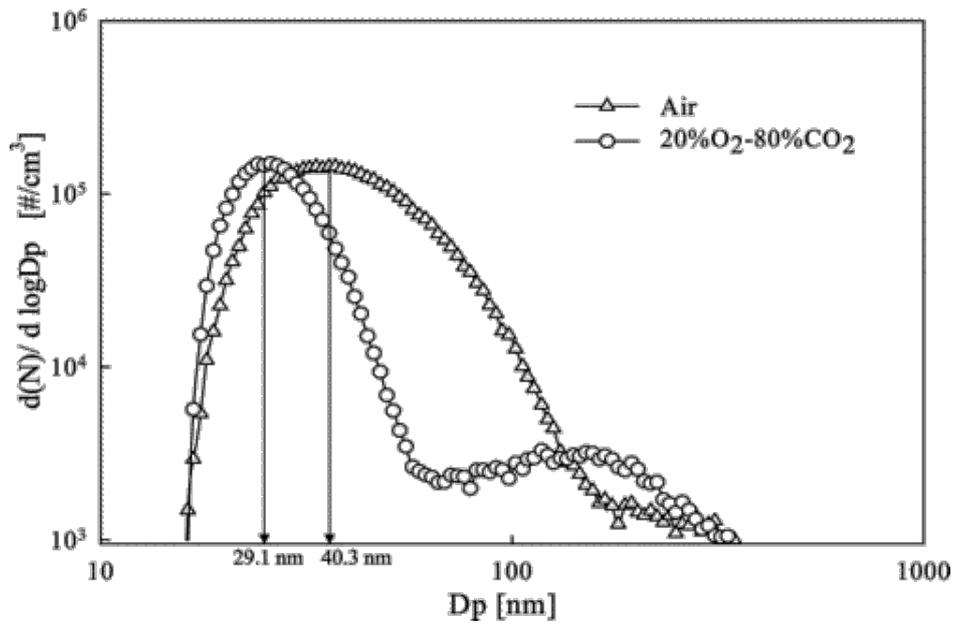


Figure 8: Sub-micrometer particle size distributions of air and 20% O₂/80% CO₂ coal combustion (Suriyawong et al. 2006)

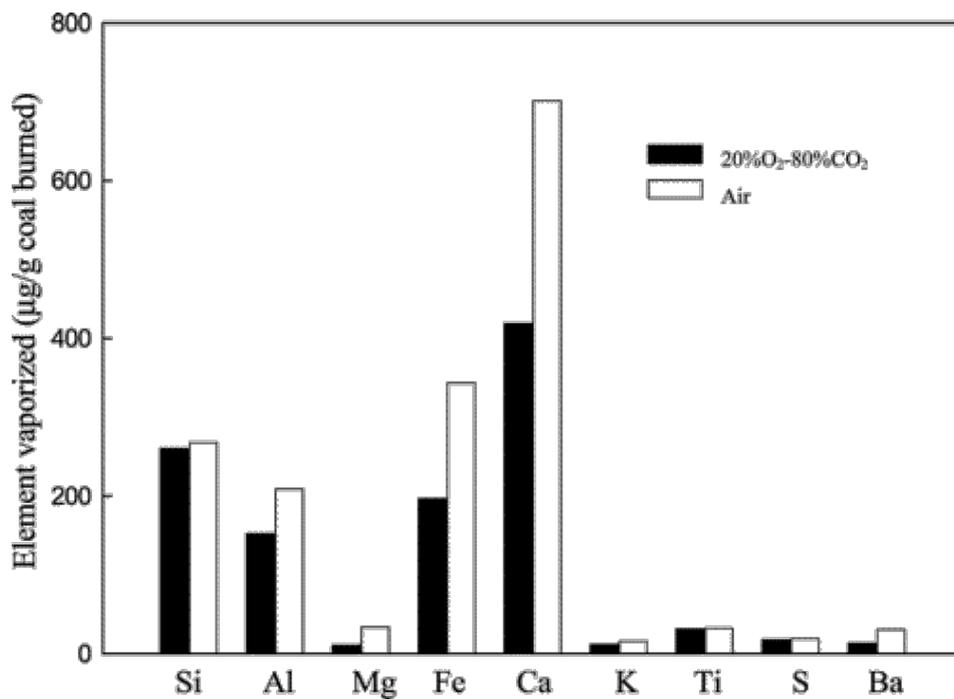


Figure 9: Measured elemental compositions in sub-micrometer-sized ash for air and 20% O₂/80% CO₂ combustion (Suriyawong et al. 2006)

Publications by other researchers also address ultrafine or nano particles formed during oxy-combustion but concentrate on diagnostic measurement techniques using continuous particle measuring instrumentation (Carbone *et al.* 2011), or examine possible control of sub micron particles using kaolin or limestone injection (Chen *et al.* 2011). However these results do not significantly address the key questions posed above.

Very recent work from the University of Utah (Jia and Lighty 2012) also examines particle formation from coal combustion under oxy-fuel combustion conditions. Using a high temperature drop tube furnace, variable O₂ concentrations and CO₂ versus N₂ the impacts of furnace temperature, coal type and gas phase conditions on particle formation were examined (Jia and Lighty 2012).

The results obtained for the sub-micrometer fraction were consistent with those reported by Suriyawong *et al* (2006). Temperature was the determining variable for increasing ultrafine particle formation. Effects of temperature were less pronounced for the fine particle fraction (ie that > 1 µm). Figure 10 shows particle size distributions for three coals combusted in air, and in varying O₂/CO₂ mixtures, and reveals lower submicron particles in 21% O₂/CO₂ compared to air but more as O₂ increases to 31.5%. Based on experiments with the 3 coals (Powder River Basin, Utah Skyline, and Illinois #6), it was found that different metal species (Si for Utah and Ca for Powder River Basin), and S (for Illinois #6) played important roles in sub-micron particle formation. Impacts of S on fine particle formation under oxy-combustion conditions have also been reported in a study using Russian and South African coals (Fryda *et al.* 2010). These workers have also reported (Fryda *et al.* 2012) larger particle sizes for the ash from the Russian coal combusted in O₂/CO₂.

Using a down fired 100 kW combustor, Morris *et al* (2011) emphasize the importance of black carbon (or soot) contributions to ultrafine particle formation, and report lower amounts of black carbon under oxy-combustion conditions.

Additional studies of particle formation have been reported for brown coal (Jiao *et al.* 2011a), and for fluidised bed combustion (Saastamoinen and Tourunen 2012). As the former has a particular emphasis on fouling due to sodium, and the latter deals with char combustion at the lower temperatures applicable to FBC, they have less relevance to potential conditions in the Callide Oxy-fuel plant.

2.2 Trace metals

While there have been relatively few studies of the effects of oxy-combustion on particulate formation, there have been even fewer studies of the effects on the toxic trace metals potentially released in the fine particles. Somewhat more work has investigated the effects of oxy-combustion on mercury but given the importance of mercury from both environmental and operational perspectives the studies relevant to mercury are summarised separately below (see Section 2.3 below).

A comprehensive study of trace species fate and department has been reported for the CIRCE 90kW_{th} bubbling fluidized bed oxy-combustion pilot plant in Spain (Font *et al.* 2012). This shows that most of the potentially toxic trace metals are found in the ash and are very effectively removed by the bag filter unit. No comparative results are presented for firing in air, however, so assessing the impacts of firing in O₂/CO₂ mixtures is not possible.

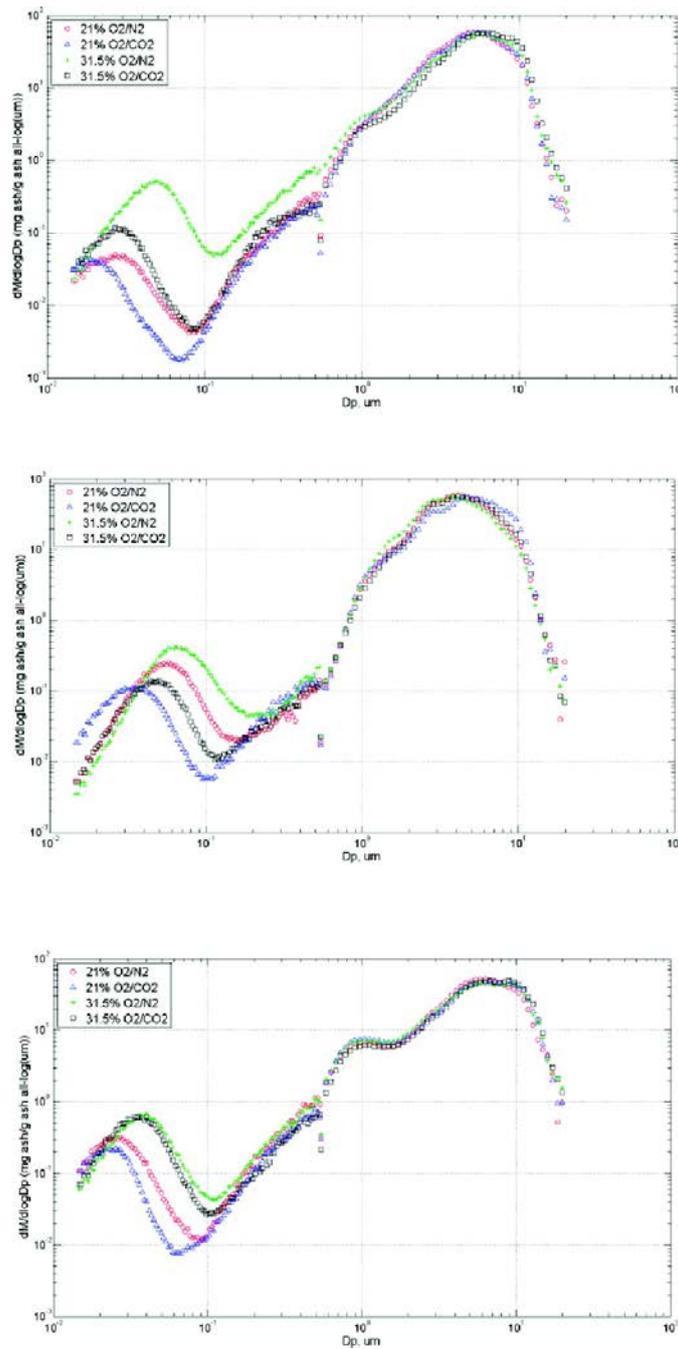


Figure 10: Particle Number Size Distributions of Utah Skyline, Powder River Basin and Illinois #6 coals combusted in air, and varying O₂/CO₂ mixtures (Jia and Lighty 2012)

A more relevant study has been reported for a 173.5 kW_{th} plant with electrostatic precipitator for particle control and a wet scrubber for SO₂ control (Zhuang and Pavlish 2012). Transformation and speciation of hazardous air pollutants (HAPs²), including SO₂/SO₃; NO_x; particulate matter; mercury and other trace elements are reported. The results showed that while the flue gas has higher concentrations of the HAPs, the actual emissions of HAPs per unit of energy produced were much less than those for air combustion. In addition most non-volatile trace elements were less enriched in fly ash from oxy-combustion than from air-firing due to lower temperatures in the oxy-

² HAPs is a USEPA descriptor for particular air pollutants

combustion case. However, both Hg and Se were found to be enriched in the ultrafine fly ash (< 1 µm) in oxy-combustion relative to air-firing (Zhuang and Pavlish 2012).

Of particular interest are two related studies (Jiao *et al.* 2011b; Chen *et al.* 2012) of chromium speciation (ie the relative proportions of Cr(III) and the more toxic Cr(VI)). Performed with brown coals these studies do show that the relative amounts of Cr(VI) remain low (ie less than ~5%) when coal is combusted in O₂/CO₂ mixtures.

2.3 Mercury

Coal combustion is the major anthropogenic source of mercury as illustrated by Figure 11 and Table 3 which are based on revised estimates (UNEP Chemicals Branch 2008; Munthe *et al.* 2010; Pacyna *et al.* 2010; Pirrone *et al.* 2010) of global anthropogenic emissions of mercury in 2005 to the atmosphere.

Table 3: Global anthropogenic emissions of mercury to air in 2005 from different sectors (UNEP Chemicals Branch 2008)

Sector	2005 emission, tonnes	Proportion (%) Of 2005 emission	Range of estimate, tonnes
Fossil Fuel combustion for power and heating	878	45.6	595 – 1160
Metal production (ferrous and non-ferrous, excluding gold)	200	10.4	125 – 275
Large scale gold production	111	5.8	65 – 155
Artisinal and small-scale gold production	350	18.2	225 – 475
Cement production	189	9.8	115 – 265
Chlor-alkali industry	47	2.4	25 – 65
Waste incineration, waste and other	125	6.5	50 – 475
Dental amalgam (cremation)	26	1.3	20 – 30
Total	1930		1220 – 2900

Mercury measurements and speciation in full scale coal fired power stations is difficult and a mass balance is rarely achieved (Edge *et al.* 2011). This needs to be carefully considered when comparing results for Hg from combustion in O₂/CO₂ mixtures compared to those observed in air combustion.

2.3.1 Laboratory and pilot scale studies

Using a laboratory scale reactor Suriyawong *et al.* (2006) compared mercury speciation in oxy- and air-fired systems and concluded that for their particular conditions and coal type the ratios of elemental (Hg⁰) to oxidised mercury (Hg²⁺) were ~4:1 and similar for both types of combustion.

In a collaborative study between Chinese and Canadian researchers mercury release from 4 coals of varying composition was studied in a drop tube reactor (Ma *et al.* 2011). There results (see Figure 12) show that mercury speciation is affected by coal composition (S, Cl and moisture) but that the effects appear relatively minor. For 3 of the coals studied increasing O₂ led to increases in the proportion of oxidised mercury (Hg²⁺). Increasing sulphur may reduce the extent of oxidation.

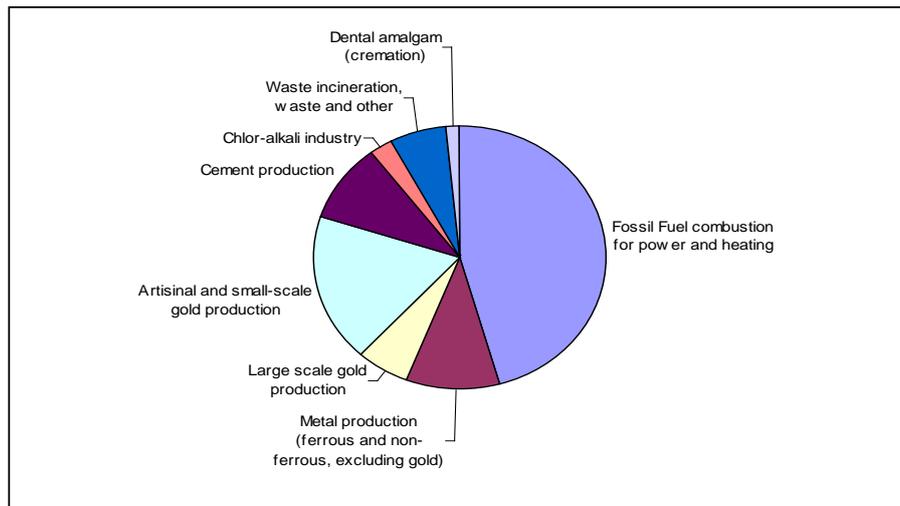


Figure 11: Proportion of global anthropogenic mercury emissions to air in 2005 from different sectors (UNEP Chemicals Branch 2008)

2.3.2 Large scale studies

In contrast to the results above, tests at a 30MW Babcock and Wilcox pilot scale facility (Farzan *et al.* 2009) suggested mercury concentrations in flue gas and its oxidation significantly increased in oxy-firing. Other groups at CANMET and the US DoE are also reported to be making measurements at full scale.

The behaviour of mercury and SO₃ in a Babcock-Hitachi 1.5 MW_{th} test facility equipped with air pollution control devices and CO₂ compression and purification systems has been studied (Mitsui *et al.* 2011). This revealed that installation of a clean energy recuperator and reducing the temperature at the electrostatic precipitator outlet could enhance mercury capture in the plant.

In more recent studies by Babcock-Hitachi (Kikkawa *et al.* 2011) effects of standard air pollution control devices on mercury (and SO₃) behaviour has been studied in more detail. These workers illustrate the complex interactions for mercury and SO₃ in Figure 13. They conclude that:

- mercury removal across the electrostatic precipitator increases with decreasing precipitator temperature, and with sulfur content in coal.
- Adsorption of Hg on ash particles was inhibited under high SO_x conditions.
- Mercury removal at the stack increased from 94% to 97% (ie outlet concentration decreased to 1/3)by decreasing the precipitator temperature from 160 to 90°C.

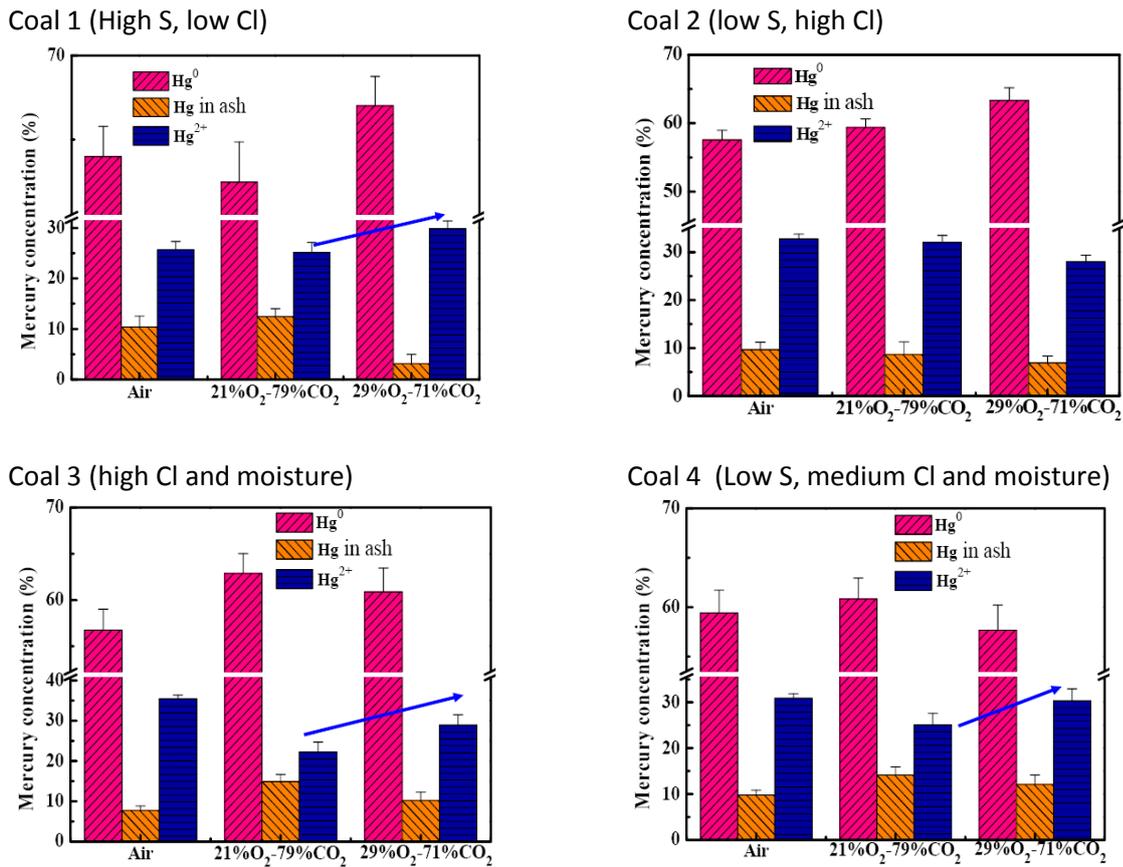


Figure 12: Mercury speciation from four coals of varying composition studied in a drop tube reactor in air, O_2/CO_2 , and enhanced, O_2/CO_2 (Ma et al. 2011)

Higher concentrations (almost double) of mercury when oxy-firing were also observed in a system based on a combustor/ electrostatic precipitator/ wet scrubber (for SO_2 control) configuration (Zhuang and Pavlish 2012). In addition enhanced gas phase to particulate phase mercury conversions, and increased elemental to oxidised mercury oxidation was observed in this system (Zhuang and Pavlish 2012). It is postulated that these enhancements were due to a combination of “continuous interactions of mercury with enriched HCl, unburned carbon³ and other reagents in the flue gas.” (Zhuang and Pavlish 2012).

Pavlish has summarised (Pavlish 2011) the factors which govern mercury emission and control as follows:

- Mercury levels and association (in the fuel or inputs)
- Other constituents in fuels or system inputs
 - Halogens
 - Ash components and quantity
 - Sulfur/acid gases
 - Alkali components
- Mercury variability
- Mercury forms (speciation) in flue gases

³ Higher values for loss on ignition in the ash (LOIs) during oxy-combustion were observed in this study (Zhuang, Y., Pavlish, J. H., 2012. Fate of Hazardous Air Pollutants in Oxygen-Fired Coal Combustion with Different Flue Gas Recycling. Environmental Science & Technology 46, 4657-4665.

- Mercury concentration in flue gases and synthesis gases
- Operational factors such as temperature zones, O₂, recycle loops, flue gas composition, etc.
- Installation and operation of existing control equipment installed for NO_x, SO₂, particulate matter (PM) and possible CO₂ control

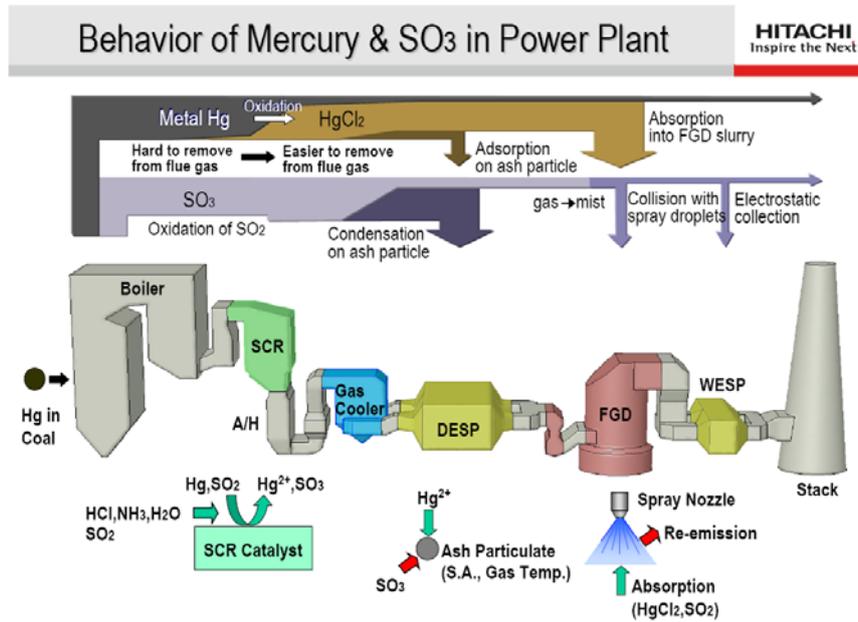


Figure 13: Behaviour of mercury and SO₃ in power plants equipped with various air pollutant control devices(Kikkawa et al. 2011)

Pavlish also concludes that the unique characteristics of oxy-fuel combustion flue gas may:

- Change partitioning and emission of elements including mercury and selenium
- Require validation and/or modification of existing mercury-sampling protocols
- Require mercury control strategies to be re-evaluated for application to oxy-fuel combustion.

The somewhat variable observations for mercury speciation in oxy-combustion probably reflect these factors and the complexity in the homogeneous and heterogeneous reactive pathways for this species in combustion and post combustion environments. For example, interactions and competitive reactions of mercury with unburned carbon, chlorine and bromine species, and SO₃ are all important (Edge et al. 2011) in determining ultimate mercury department. For this reason observations at full scale supported by carefully controlled laboratory experiments are essential for enhancing understanding of this key species during oxy-combustion.

A modelling approach has been developed to predict mercury speciation in air and oxy-fired systems (Gharebaghi et al. 2011), and shown to have comparable trends to power plant data. However modelling advances require significantly more evaluation to account for the effects of coal type and composition, and plant operating conditions.

Emissions of trace elements and mercury from oxy-fuel combustion have also been reviewed by Davidson and Santos at the International Energy Agency Clean Coal Centre (Davidson and Santos 2010). This review concentrates on the combustion stage of the process, and shows that little relevant research has been done on the CO₂ processing stage. Most of the references included have been captured in the present review, and only the additional studies are discussed here.

Tan and Croiset (2005) found that trace elements measured in the flue gas stream upstream of a fabric filter were almost exactly the same whether coal was fired in air or in oxy-fuel.

Stam *et al* (2009) reported concentrations of trace elements as higher in oxy-fuel combustion due to the recycling of the flue gases, although this may be affected for some elements that condense on fly ash. They also report equilibrium calculations which suggest no change in speciation of the more toxic elements (Hg, Se, Cr, and As).

Wall *et al* (2009b) found that the proportion of mercury that reported to the ash for two coals studied increased during oxy-fuel combustion, and that none of this mercury appeared to be leachable.

Santos (2008) has summarised the key issues concerning mercury in oxy-combustion systems:

- What are the acceptable limits to any mercury emissions that could be tolerated the CO₂ processing unit?
- Is the standard limit of less than 0.01 µg/m³ set by the natural gas industry appropriate?
- Is there any change to the speciation of Hg during oxy-fuel combustion compared with conventional coal-fired power plant?
- What could be the impact of higher chlorine species concentration on the level of mercury oxidation?
- What could be the impact of higher NO_x and SO₃ concentrations on any activated carbon based Hg removal system?
- What could be effectiveness of Hg removal during the sour compression process⁴?

Effects of coal type on mercury release have been studied by Guo *et al* (2009) in a small scale quartz reactor and Sethi *et al* (2007) in a combustion test furnace at Western Research Institute. The former found that the rate of release of total mercury under CO₂ conditions was strongly dependent on volatile yield and temperature for all types of coal. The latter found lower emissions of mercury from oxy-combustion of bituminous and sub-bituminous coals but little change for a lignite.

⁴ See Section 3 below

3 PREVIOUS RESEARCH – CO₂ PLANT

As discussed above the specific design of the CO₂ processing plant will have a large influence on the relevant research on this issue. In this review the emphasis is on conditions relevant to the Callide Oxy-Fuel Plant.

Researchers at Imperial College in collaboration with Air Products and Doosan Babcock Energy Limited (White *et al.* 2009; Murciano *et al.* 2011) have studied the effects of pressure, temperature, residence time and water on the removal of NO_x and SO_x from CO₂ using compression and water contact with the flue gas. It was demonstrated (White *et al.* 2009), using both laboratory scale reactors and Doosan Babcock's 160 kW coal-fired oxy-fuel plant, that it was feasible to remove 99% SO₂ and 90% NO_x and H₂SO₄ and HNO₃ respectively. Some measurements of mercury have also been made (White *et al.* 2009), and these suggest that in the Doosan Babcock facility mercury is removed from the gas phase with the first acidic condensate stream.

Wall and co-workers (Stanger *et al.* 2012a) have also studied gas cleaning by compression under conditions relevant to the Callide Oxy-Fuel Plant. The results of these studies so far concentrate on N and S chemistry but experiments to explore mercury fate in this system are in progress (Wall, personal communication). Possible chemical reactions of N, S and Hg species are presented in Figure 14. The success of compression to remove these impurities relies on the significantly higher solubilities (Stanger *et al.* 2012b) of N and S species formed during the compression process (see Figure 15), and postulated reactions of mercury with nitric acid to produce soluble Hg(NO₃)₂.

It is concluded (Stanger *et al.* 2012a; Stanger *et al.* 2012b) that:

- From experiments in the absence of water, the extent of oxidation of insoluble NO to soluble NO_x was found to exceed 90% above a pressure of 15 bar;
- from experiments involving contact with liquid water and water vapour, a significant conversion of NO to higher order oxides may be expected at the saturated conditions and pressures in an oxy-fuel compression circuit;
- during multi-stage CO₂ compression it is likely that SO₂ will be removed during early stages along with most of the water vapour; at pressures below 20 bar, NO oxidation and absorption to form acid may be restricted by the existence of SO_x; and
- the experiments have revealed that the mechanism suggested by the literature is too simplistic, in that additional nitrogen and sulphur species exist as gases and liquids.

Experimental studies of the behaviour of mercury, or of other partially volatile trace metals such as selenium and arsenic, under compression are not currently in the public domain. Hence, the experimental studies of trace metal concentrations in the CO₂ processing plant at Callide will be particularly valuable in providing new information on these contaminants.

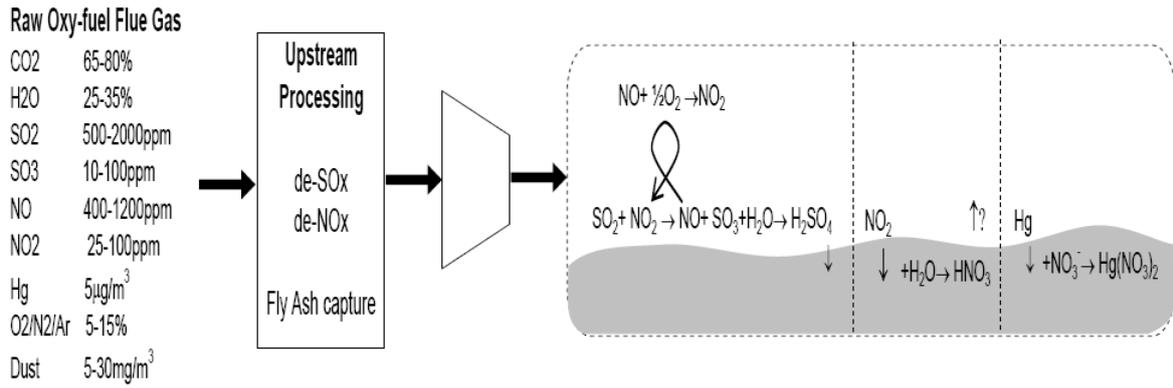


Figure 14: N, S and Hg chemistry in CO₂ gas compression and purification; conditions relevant to Callide Oxy-Fuel Plant (Stanger et al. 2012a)

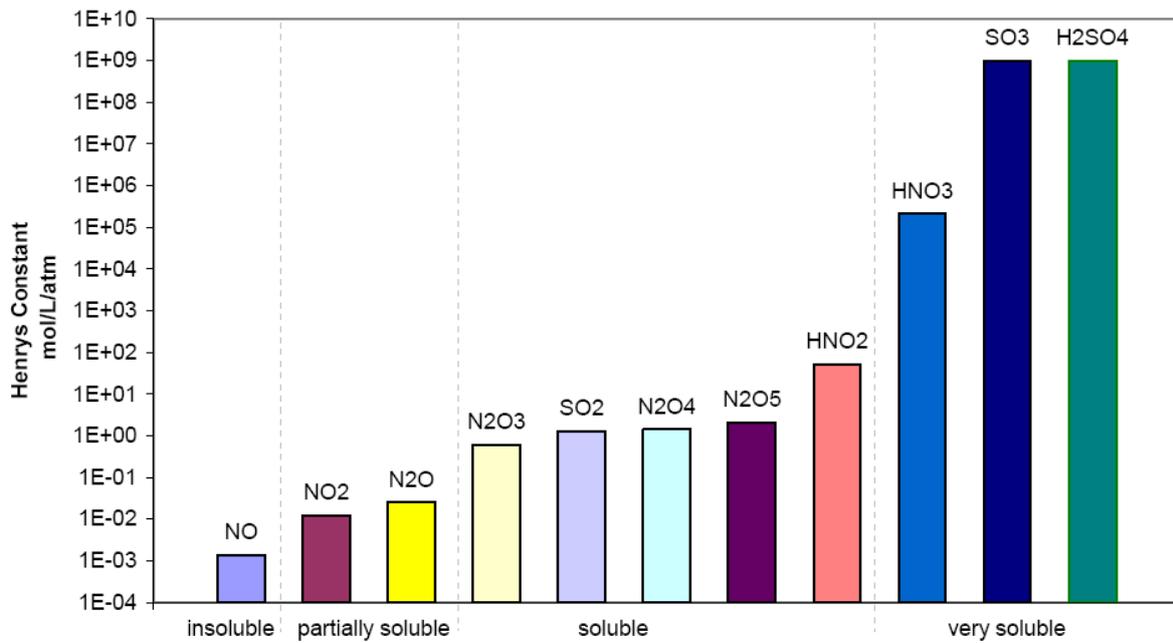


Figure 15: Comparison of solubilities of NO_x and SO_x gaseous species in water using Henry's Law coefficients (Stanger et al. 2012a; Stanger et al. 2012b)

4 TRACE ELEMENT MEASUREMENT

4.1 Mercury

4.1.1 Mercury sampling in combustion systems

Accurate mercury measurement in power station combustion systems is an essential need to enable the estimation of emissions, to assess potential environmental impacts, to demonstrate compliance with emissions regulations and to enable evaluation of control technologies. As noted above it is particularly important in oxy-combustion systems because of the corrosive effects of mercury on heat exchanger systems.

Mercury sampling and subsequent analysis from combustion systems is challenging. In part this arises from the generally low concentrations of mercury in the feed coal (usually less than 1 ppm), and in the combustion gases (of the order of $1 \mu\text{g}/\text{m}^3$). However modern analytical systems have largely solved these problems and detection limits are now low enough for all potential situations. Cold-vapour atomic absorption spectroscopy (CVAAS), cold-vapour atomic fluorescence (CVAFS) and energy-dispersive x-ray fluorescence (EDXRF) are used to quantify the collected mercury species (CEA 2004). These analytical techniques are much more standardized than the sampling procedures (CEA 2004).

Additional issues arise because of the need to obtain measurements of the speciated forms of mercury, ie. elemental mercury (Hg_0), oxidized mercury (Hg^{2+}) and particulate phase mercury, Hg_p , in addition to total mercury, Hg_{total} . An understanding of the speciated forms of mercury is important for the following reasons:

- The form of the mercury is of crucial importance in determining atmospheric dispersion, and potential environmental impacts
- Mercury speciation is important for control of mercury emissions, since oxidized and particulate phase mercury are more efficiently captured by APCDs

In the particular case of large coal-fired power stations the collection of a flue gas sample representative of typical operations is difficult (CEA 2004) due to:

- Complex flue gas chemistry
- High temperatures
- Mercury reactivity, and inter-conversion between elemental and oxidized mercury, and
- particle loading

Considerable research and development of sampling and analysis methods for mercury in combustion systems has been conducted in the last 10-15 years. In general the methods for mercury sampling and analysis fall within three broad categories:

- Sampling train methods

- Dry sorbent-based methods
- Mercury Continuous Emission Monitors (CEMs)

A comprehensive review of these methods has been prepared for the Canadian Electricity Association (CEA 2004). This review draws on work done largely in the US and Canada.

The sampling train methods include (CEA 2004):

- EPA Method 29
- Tris Buffer Method, developed by Radian International (now URS)
- The Ontario Hydro Method, originally developed by Dr Keith Curtis and co-workers at Ontario Hydro Technologies, Toronto

As the last of these methods is to some extent a modification of the original EPA method 29, designed to address some shortcomings in that method, and has become a standard method for mercury sampling in coal combustion systems (it is now ASTM Method D6784-02), it will be described in some detail, below.

4.1.2 The Ontario Hydro Method

The Ontario Hydro method consists of a sampling train with 8 impingers. A schematic of the sampling train is given in Figure 16. The large number of impingers is necessary to address identified issues in the sampling of combustion streams, including:

- The aqueous potassium chloride (KCl) solutions are used to more selectively capture Hg^{2+}
- The acidified peroxide impingers are used to absorb SO_2 , thus allowing the permanganate (KMnO_4) solution to be largely used for reaction with the elemental Hg; it is assumed that any mercury captured by the acidified peroxide will be elemental (CEA 2004)

In addition, early tests showed that a substantial proportion of the mercury was lost from the solutions (EPRI 1999). In order to overcome this, acidified permanganate, dichromate or acidified peroxide solution is added to the KCl solution immediately following sampling.

The Ontario Hydro method has been evaluated using EPA Method 301, and shown to satisfy the statistical criteria included in that method (CEA 2004), although the standard deviations and variability remain quite high.

There a number of limitations and difficulties with the Ontario Hydro Method which should be emphasized:

- The method is difficult to apply in practice, and requires very careful attention to ensuring: leak-free sample collection; cleanliness of glassware; careful choice of sampling locations; prescribed method carefully followed in sample recovery and analysis (Curtis 2003; CEA 2004; Curtis 2005);

- The method (like all the sampling train methods) is designed to be used after the particle collection device on the plant (ie fabric filter or electrostatic precipitator); reactive particles can bias the result to produce either high Hg^{2+} or high Hg_p
- It is only possible to collect information on discrete samples representative of average plant conditions over a period of time

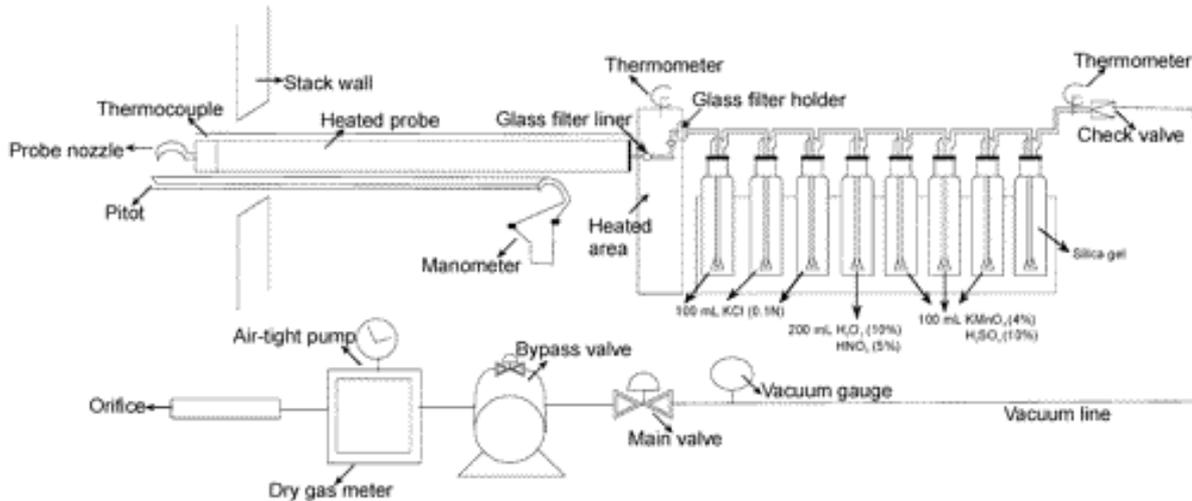


Figure 16: The Ontario Hydro Method Sampling Train. From Otero-Rey et al (2003)

Nevertheless, the Ontario Hydro Method has now been broadly accepted (Pavlish *et al.* 2003) as the standard method for sampling train methods, and was selected by the USEPA as its recommended method for making flue gas measurements under the EPA’s Information Collection Request (ICR). The ICR includes data on the mercury and chlorine contents of coals used in US coal-fired power plants, and on mercury emissions at selected plants using different coal types and APCDs.

4.1.3 Dry sorbent-based methods

Gaseous mercury species (Hg^{2+} and Hg^0) can also be selectively sampled on solid sorbents. The capture of these species may be due to:

- Adsorption
- Amalgamation
- Diffusion, and/or
- Ion-exchange processes.

Sorbent-based sampling techniques have some advantages over solution-based techniques, including greater stability and ease of handling (CEA 2004). Two methods based on solid sorbents have been developed:

- The flue gas mercury sorbent speciation (FMSS) method, developed by Frontier Geosciences; this enables speciation using a mini quartz filter, and KCl/quartz and Iodated Carbon sorbents; analysis is performed by CVAFS (CEA 2004). The FMSS method is reported to exhibit good agreement with the Ontario Hydro Method.

- The Quick SEM™ (QSEM) method, developed by EPRI, ADA Environmental Solutions and Frontier Geosciences; this will only measure total gas-phase mercury (CEA 2004), and is designed for low dust situations. The sorbent is an iodine-impregnated carbon trap, and analysis is by CVAFS.

The development of sorbent trap techniques was originally conceived as an alternative to the Ontario Hydro method in order to reduce the complexity of that method (Schmid and DeRosier 2011). However after successful validation (US DoE 2001), it has now been adopted by the USEPA as a reference method (US Environmental Protection Agency 2007) and is now widely used by the industry due to its high sensitivity and ease of use (Schmid and DeRosier 2011).

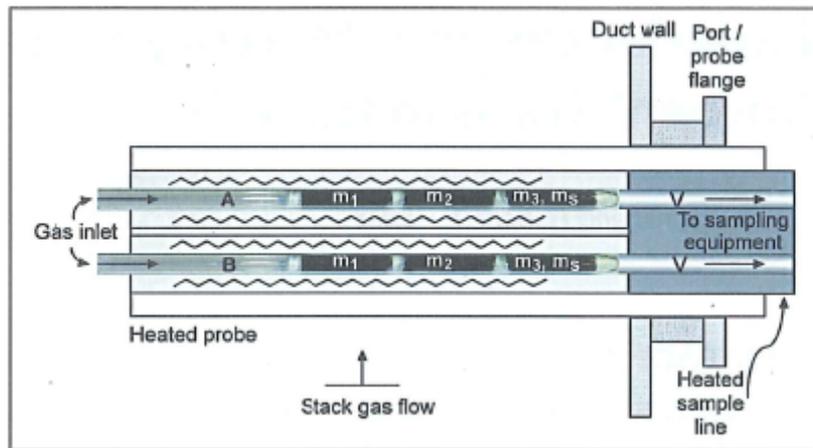


Figure 17: Principles of sorbent trap monitoring (Schmid and DeRosier 2011)

Figure 17 shows the basic principles of operation of the sorbent trap method. Measured volumes of gas are drawn through a pair of in-stack sorbent traps. At the completion of the sampling period (which can be matched to the required sensitivity and flue gas concentration), the traps are analysed using the desired method and analyzer for the total mass of mercury captured during the sampling period.

As described by Schmid and DeRosier (2011) each section of the trap serves a specific purpose:

The first section that the sample-gas contacts is for primary capture of the total gaseous Hg. The second section is designated as a back-up section indicating whether any significant breakthrough (B) of total gaseous Hg has occurred during the sampling period. The performance specification requires that the mass of mercury collected on the second section (m_2) does not exceed 5 % of the mass of mercury collected on the first section (m_1) of the sorbent trap...

The third section is spiked with a known amount of Hg prior to sampling (m_3), which must be within + 50 % of the Hg mass expected to be collected on the first section during the monitoring period. After retrieval from the stack, the third section is analyzed separately for its Hg content (m_5) and compared to m_3 to determine the sample recovery efficiency and to assess any sample matrix interference. Spike recoveries (R) must range between 75 and 125 % for the sorbent trap results to be considered valid.

The USEPA has now issued performance standards for determining Hg emissions using the sorbent trap method (US Environmental Protection Agency 2010), and the method is now the method of choice for measuring mercury in power plants. For that reason it was chosen for mercury measurements at the Callide Oxy-fuel Plant.

4.1.4 Continuous Emission Monitors (CEMs)

The sampling train and sorbent-based methods have been shown to provide accurate data when used in accordance with strict protocols by experienced operators. However the desirability of real time monitors, or CEMs has led to extensive development work in recent years. These monitors can be expensive to install, operate and maintain, but they offer significant advantages, including (CEA 2004):

- Real time (or near real time) data
- Evaluation of control techniques
- Data which can be used to control operating parameters to reduce emissions
- Greater understanding of process variability and operation
- Greater public reassurance

Development of these devices has required the solution of a range of problems, including (Pavlish *et al.* 2003):

- Low concentrations of mercury to be measured, typically below 10 $\mu\text{g}/\text{m}^3$
- Presence of potentially interfering substances (fine particles and acid gases such as HCl, SO₂ and NO_x)
- Lack of direct measurements of particle-bound Hg
- Adsorption or oxidation of gas-phase mercury by fly ash particles

As recently as 2003, Pavlish and co-workers (Pavlish *et al.* 2003) reported that:

Additional development and applications testing are needed before CMMs (Continuous Mercury Monitors) can provide reliable field measurements without regular verification by wet-chemical methods.

However this is a rapidly developing field, and recent experience with CEMs reported at the IEA Workshops on Mercury in Coal, held every year, reports performance comparable to the Ontario Hydro Method for several commercial devices.

Mercury CEMs still present challenges, particularly in terms of on-going maintenance, collection of a representative sample from particle-laden flue gases, and flue gas conditioning (CEA 2004). Performance of mercury CEMs therefore depends very significantly on the APCDs used in the power plant, and the impact that configuration has on the trace composition of the gas. For example, a plant equipped with ESPs, wet scrubbers and an SCR will have very low concentrations of trace potentially interfering particles and gases such as CO, SO_x, NO_x, HCl, NH₃ and Cl₂. Mercury will also be almost completely present in the elemental form, and measurement by CEMs is, in that case, relatively straightforward (CEA 2004).

In order to be useful for compliance purposes, mercury CEMs must satisfy the USEPA Performance Specification 12A⁵ (PS-12A). PS-12A effectively requires mercury CEMs to exhibit the following features (CEA 2004):

- Capable of measuring total concentrations of Hg (regardless of speciation) in $\mu\text{g}/\text{m}^3$ and recording that concentration on a dry basis, corrected to 20°C and 7% CO₂
- Must include a diluent (CO₂) monitor and an automatic sampling system
- Particle bound mercury need not be included
- Procedures are specified for measuring accuracy, measurement error and drift

All mercury CEMs must (CEA 2004):

- Filter particles from the sample gas, without allowing significant contact of the gas with fly ash
- Reduce the moisture content of the gas so that the sample can pass to the instrument
- Condition the sample to reduce all forms of mercury to Hg⁰
- Measure the mercury in the gas sample

Mercury CEMs may be distinguished by their measurement detection principles (CEA 2004). CEMs based on the following methods have been developed:

- Pre-concentration by gold amalgamation with CVAAS detection
- Zeeman-modulated CVAAS
- Pre-concentration and gold amalgamation with CVAFS detection

AES and laser technologies have also been used.

Full details of the most common commercially available systems are given in Table 4, derived from (CEA 2004). That reference also describes these systems in some detail, including their strengths and weaknesses.

Table 4: Commercially available mercury CEMs. Based on (CEA 2004)

Manufacturer	Description	Method of Analysis	Pretreatment/ Conversion	Speciation
Durag	HM-1400 TR	Atomic absorption	Thermal Catalytic	Hg ^{total} (g)
EcoChem Analytics	Hg-MK II	Atomic absorption	Thermal Catalytic	Hg ^{total} (g)
Envimetrics	Argus-Hg 1000	Atomic Emission	Thermal Catalytic	Hg ^{total} (g)
Nippon	DM-6	Atomic absorption	Thermal Catalytic	No
Nippon	DM-6A/ MS-1A	Atomic absorption	Wet chemistry and thermal catalytic	Yes
Nippon	DM-6B	Atomic absorption	Thermal Catalytic	Yes
Nippon	AM-2/ AM-3	Atomic absorption	Wet chemistry	Hg ^{total} (g)
Ohio Lumex	RA-915+	Atomic absorption	None available	No
Opsis AB	HG200	Atomic absorption	Dilution System	Yes

⁵ See <http://www.epa.gov/mercury/pdfs/OAR-2002-0056-2922.pdf> , accessed 8th August 2005

PS Analytical	Sir Galahad	Atomic fluorescence	Wet/dry chemistry	Yes
Semtech	Hg 2010	Atomic absorption	Wet chemistry	Hg ^{total} (g)
Metallurgy AB				
Sick UPA GmbH	MERCHEM	Atomic absorption	Wet chemistry	Hg ^{total} (g)
ST2 Technologies	Sm-3	Atomic absorption	Thermal Catalytic	Yes
Tekran, Inc	3300	Atomic fluorescence	Dilution System	Yes

Laudal (2005) reports a study of the advantages and disadvantages of a range of CEMs, based on personal experience in using these systems at a range of power plants over a range of conditions. He concludes that it is possible to achieve good performance, but notes the need for trained personnel to operate them, and the significant demands on time (for set-up), space, power and temperature control.

The breakout session at the IEA Mercury Workshop held in May 2005 in Ottawa concluded that mercury CEMs are:

- Now reliable
- Have passed USEPA trials on power plant measurements
- A requirement for any successful cap and trade scheme

4.1.5 Measurements under oxy-firing conditions

The discussion in Sections 4.1.1 to 4.1.5 above demonstrate that accurate mercury measurement and speciation in air-fired combustion systems can be achieved using mercury specific sampling discreet systems (Ontario Hydro, USEPA Method 30B) and continuous analysers. Considerably less work has been reported on the precision and accuracy of the measurement of mercury under oxy-firing conditions.

Zhuang *et al* (2011) used bench-scale tests to evaluate the accuracy of measurements using continuous mercury monitors (CMMs), with and without a flue gas preconditioning unit, in a simulated oxy-combustion flue gas with varied CO₂ concentrations. They identified potential problems with mass flow rate determinations and precipitation of solids in the wet chemical conversion units, but conclude that accurate measurements of total mercury are possible with flue gas dilution. Speciation of mercury is more problematic and may require additional development.

Based on mass balance determinations in two scales of pulverized coal furnaces and a circulating fluidized bed while air- and oxy-firing a western bituminous coal, Fry *et al* (2011) conclude that a modified USEPA 30b method provides acceptable precision and accuracy. These results are summarised in Figure 18.

4.2 Other metals

Measurement of mercury presents particular issues in combustion systems as, due to its volatility, most of the mercury is present in the gas phase. In addition the effects of mercury speciation on the extent of capture in air pollution control devices, and on its environmental and operational effects, make sampling and analysis of the different forms of mercury a high priority.

Sampling and analysis of the other target trace metals is less challenging. The proportion of metals apart from mercury and selenium present in the particulate phase in the flue gases from power stations exceeds 95% (Helble 2000), and hence successful sampling and analysis of these target species is largely based on iso-kinetic sampling of the flue gases and subsequent chemical analysis using standard high sensitive techniques including Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

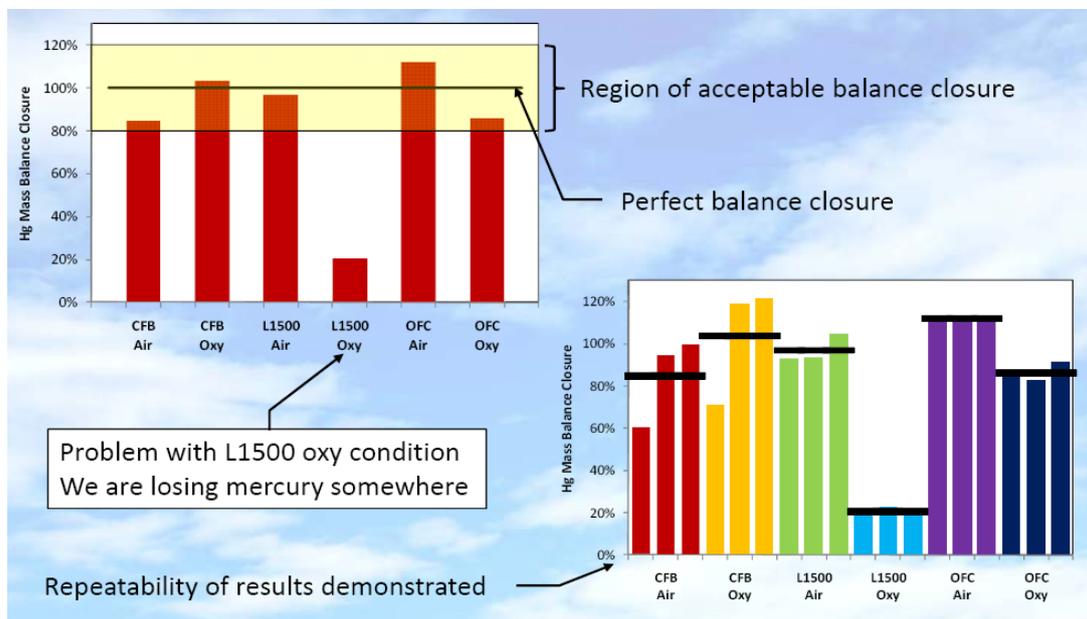


Figure 18: Mercury mass balance closures for two scales of pulverized coal furnaces and a circulating fluidized bed while air- and oxy-firing a western bituminous coal (Fry et al. 2011)

Mercury sampling and analysis is described above. Other trace metals are commonly determined using standard techniques such as the USEPA Method 29 (USEPA 2000) for which the sampling train is as illustrated in Figure 19. In Australia, methods developed by state agencies such as the New South Wales EPA for the analysis of trace metals in source emissions are largely based on Method 29 (DEC 2006).

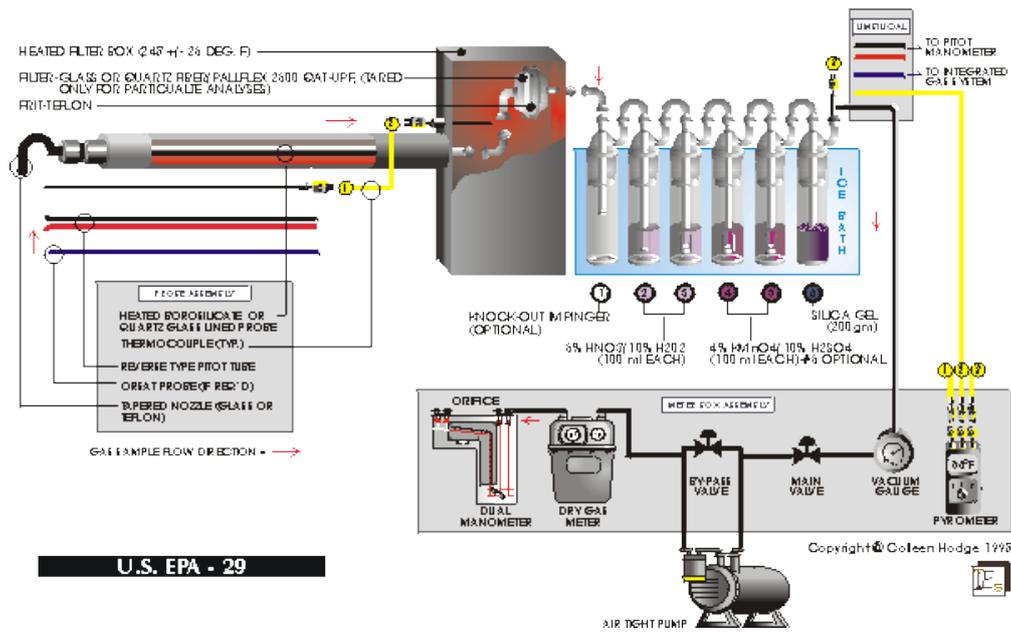


Figure 19: Schematic of USEPA Method 29 sampling train (see <http://www.activeset.org/methods/new/method29/index.htm>)

5 CONCLUSIONS

A review of the published research on the impacts of firing in CO₂/O₂ mixtures, compared to combustion in air, results in the following conclusions:

1. A small number of studies have shown that there is a decrease in the number of sub-micron (or ultrafine) particles for combustion in O₂/CO₂ mixtures compared to combustion in air. It is believed that this effect is due in part to the higher bulk gas concentrations of CO₂ in oxy-combustion which shifts the more volatile suboxides formation equilibria toward the oxide, hence reducing vaporization, and also to the reduced particle temperatures.
2. Reduced enrichment of key species such as Fe, Ca and Si in the sub-micron fraction has also been observed and is consistent with the postulated mechanism described in 1.
3. Researchers from the Energy & Environmental Research Center at the University of North Dakota reported results for the transformation and speciation of hazardous air pollutants (HAPs), including SO₂/SO₃; NO_x; particulate matter; mercury and other trace elements. These showed that while the flue gas has higher concentrations of the HAPs, the actual emissions of HAPs per unit of energy produced were much less than those for air combustion.
4. In the same study it was found that most non-volatile trace elements were less enriched in fly ash from oxy-combustion than from air-firing due to lower temperatures in the oxy-combustion case.
5. Extant research reports variable observations for the impact of oxy-combustion on mercury concentrations and speciation. Results obtained using a laboratory scale reactor concluded that the ratios of elemental to oxidised mercury were ~4:1 and similar for both types of combustion. By contrast tests at a pilot scale facility suggested mercury concentrations in flue gas and its oxidation significantly increased in oxy-firing.
6. The somewhat variable observations for mercury speciation in oxy-combustion probably reflect the complexity in the homogeneous and heterogeneous reactive pathways for this species in combustion and post combustion environments. Interactions and competitive reactions of mercury with other flue gas species determine ultimate mercury department.
7. The specific design of the CO₂ processing plant used in an oxy-fuel combustion system will have a large influence on trace species removal, capture and behaviour in these systems. Removal of NO_x and SO_x from CO₂ using compression and water contact with the flue gas has been demonstrated at a range of scales. There is also limited evidence that wet compression may also be effective at mercury removal. It is likely that the success of compression to remove these impurities relies on the significantly higher solubilities of N and S species formed during the compression process, and postulated reactions of mercury with nitric acid to produce soluble Hg(NO₃)₂.

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