

Monitoring and Control of Trace Elements

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TECHNOLOGY STATUS REPORT

CLEANER FOSSIL FUELS PROGRAMME

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TECHNOLOGY STATUS REPORT:

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Figure 1. Coal-fired power station with flue gas desulphurisation (courtesy of Powergen)

SUMMARY

Until recently, emissions of trace elements from coal combustion and gasification facilities have not been the subject of regulatory attention. A number of national and international agreements have been reached to reduce anthropogenic emissions of trace elements but few have translated into stack emission limits.

Some countries (eg Germany) do have stack emission limits, but generally these limits can be met without installing specific flue gas cleaning equipment. The vast majority of trace elements is retained within the ash and effectively removed by existing equipment such as the electrostatic precipitators (ESPs) or flue gas desulphurisation plant (FGD). However, certain more volatile elements such as selenium and mercury may still occur in the vapour phase at flue gas exit temperatures and may escape to atmosphere. Of all the elements, mercury is of most concern, owing to its toxicity and bio-accumulation. In communities that consume predatory fish, exposure to high levels of mercury is possible. In the USA, mercury is a key environmental issue, with 41 states having issued guidelines to limit fish consumption. The US Environmental Protection Agency (US EPA) was set to rule on a proposal to limit mercury emissions from coal-fired power plant in December 2003, with compliance by December 2007. It is not yet clear what form the legislation will take, but significant reductions in mercury emissions have been suggested.

In order to develop adequate abatement strategies for control of trace elements, particularly mercury, it is important to understand their speciation in the flue gas. Vapour-phase mercury can exist in two different forms that have differing properties in terms of reactivity and solubility. Mercury can also be associated with particulate material, and shows a particular affinity for carbon. Measurement of these species is extremely difficult owing to their low concentration and the risk of altering the speciation during sampling.

Work is under way to examine methods of maximising the production of the oxidised and particulate forms of mercury, which are the easiest to remove in existing pollution control devices. Methods include coal blending and addition of chlorine salts which appear to be crucial components in the oxidation mechanism for elemental mercury. Mercury-specific oxidation catalysts have also been studied, as well as the effect of existing selective catalytic reduction (SCR) catalysts on NO_x control. Depending on coal type, use of SCR catalysts has been shown to result in significant oxidation of elemental mercury and, as such catalysts are normally installed upstream of any ESP or FGD plant, then the combination of SCR/ESP/FGD is capable of removing up to 90% of the total mercury. In the absence of such technologies, or if more stringent reductions in mercury are required, then sorbent injection may be required using activated carbons or inorganic sorbent materials. Although sorbents are less sensitive to the different species of mercury than other control technologies, the costs can be high and the presence of carbon can affect the saleability of the fly ash as a cement substitute. Multipollutant control technologies are being developed and these have the potential for very effective control of emissions of a number of pollutants, including mercury.

Currently, the majority of the R&D in this area is undertaken in the USA, but the UK does have centres of expertise which should be encouraged. Depending on progress with legislation, there is scope for UK involvement at a much higher level than at present.

BACKGROUND

Trace elements in the atmosphere occur naturally as part of the biogeochemical cycling process. Most natural and manmade (anthropogenic) releases are in the form of particulate material, but a proportion of the more volatile species such as mercury (Hg) may exist in the vapour phase, even under ambient conditions. Natural sources include the weathering of rocks, volcanism, sea spray, thermal springs, vegetation and forest fires. Anthropogenic inputs include mining, smelting, combustion, industrial processes, agriculture, tyre wear and cremation. Both anthropogenic and natural emissions can cause local enrichment around a source, but trace elements that are less reactive can show enrichment on both regional and global scales [1].

In recent years worldwide emission inventories for trace elements, based on annual estimates of emissions, have been compiled. These are often a requirement for industries in the developed world. However, the accuracy of emissions estimates, particularly in the developing world is questionable and it is therefore difficult to compare the contributions from anthropogenic and natural sources.

Currently, the trace elements considered to be of most importance are arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg). Mercury is of primary concern because of its toxic effects on the environment and human health. There is no known beneficial effect of mercury in the

Table 1. Comparison of estimated global anthropogenic emissions of trace elements in the mid-1990s with estimates from natural sources (103te/yr) [2]

Trace element	Anthropogenic emissions	Natural emissions median values	Anthropogenic/natural emission ratios
Arsenic	5.0	12.0	0.42
Cadmium	3.0	1.3	2.3
Chromium	14.7	44.0	0.33
Copper	25.9	28.0	0.93
Mercury	2.2	2.5	0.88
Manganese	11.0	317.0	0.03
Molybdenum	2.6	3.0	0.87
Nickel	95.3	30.0	3.2
Lead	119.3	12.0	9.9
Antimony	1.6	2.4	0.67
Selenium	4.6	9.3	0.49
Vanadium	240.0	28.0	8.6
Zinc	57.0	45.0	1.3

environment. Once it is deposited on land or in water, bacteria produce methyl mercury (CH_3Hg^+) that bioaccumulates in the food chain. As a consequence, predatory fish and other species can contain mercury levels many times higher than those in the surrounding environment. Mercury is currently the subject of much debate, particularly in the USA. Where the primary source of human exposure to mercury is through consumption of contaminated fish. The consequences are most serious for women who are, or who are likely to become, pregnant, nursing mothers and young children. The US Food and Drug Administration (FDA) has issued guidelines to these groups of people to avoid the consumption of predatory fish, and to limit their consumption of other seafood. A total of 41 US States has issued guidelines to limit consumption of predatory fish species [3].

The atmospheric chemistry of mercury is complex and it can be present as gaseous elemental mercury, Hg^0 (unreactive and insoluble), reactive gaseous mercury (RGM), Hg^{2+} (reactive, soluble) and particulate bound, Hg_p . Elemental

mercury has an atmospheric lifetime of between 12 and 18 months, resulting in it being transported around the globe before deposition. Oxidised mercury has an atmospheric lifetime of between 5 and 14 days and tends to be deposited locally to the source, along with particulate-bound mercury. Once deposited, mercury can be re-emitted into the atmosphere because of its high volatility. Natural emissions and re-emissions consist primarily of Hg^0 , whilst anthropogenic emissions can consist of all three mercury species described, with the proportion of each varying widely among sources.

Anthropogenic emissions of mercury are estimated at about 2000te/year, but large uncertainties exist for individual sources. Mercury emissions from coal-fired power plant in the USA are probably better known than any other source type due to the Information Collection Request (ICR) of the US EPA in 1999. Based on the emission measurements, approximately 48 tonnes of mercury was emitted from US coal-fired power plant that year, equivalent to about 40% capture in existing pollution control devices [4]. Estimates of total atmospheric

mercury from anthropogenic sources in the UK in 2000 are shown in Figure 2.

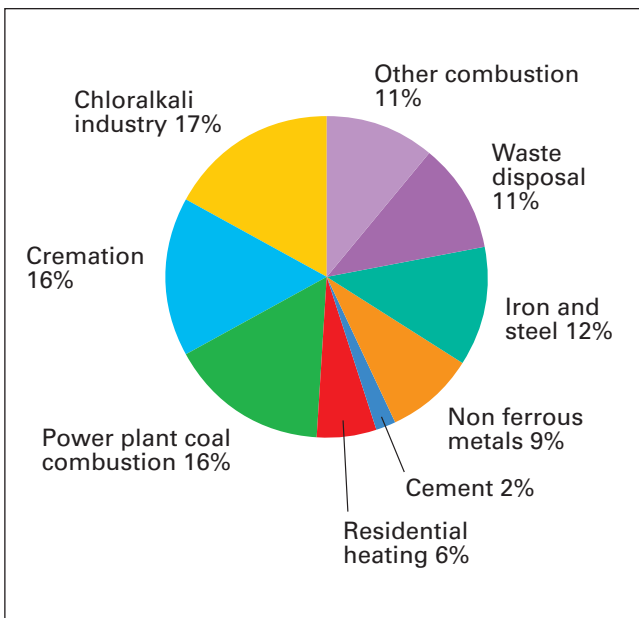


Figure 2. Anthropogenic emissions of total mercury in the UK in 2000 (total 8.35te) [5]

According to emission estimates, anthropogenic emissions of mercury in the Western World have shown a decrease since the 1980s, primarily due to improved flue gas cleaning equipment and fuel switching at large stationary combustion sources. However, although major progress has been made in recent years, knowledge of mercury emissions on a global scale is still incomplete. For the developing world, emission estimates are less accurate, but emissions in these regions are thought to be increasing. It is estimated that Europe and the USA contribute approximately 25% of the global anthropogenic emissions of mercury to the atmosphere. The majority of emissions originates from Asian countries, such as China, India and South and North Korea where combustion of coal is and will remain the main source of energy. It is clear that, despite the activities of the US EPA to regulate emissions of mercury from coal-fired power plant, a global effort will be required to reduce these emissions [6].

In the light of the above, the objectives of this Technology Status Review are to report on the current situation regarding legislation for emissions of trace elements to the atmosphere from coal combustion facilities. In addition, the behaviour of trace elements in combustion and gasification systems has been investigated, together with methods for measuring trace elements in flue gas. Control options for trace elements have been reviewed, including state-of-the-art multipollutant control technologies. Finally, the current activities and capabilities of UK organisations working in this field have been investigated and recommendations for priority areas for funding have been made. This Technology Status Review is supported by a full, detailed report that is available from the Department of Trade and Industry (DTI) Cleaner Fossil Fuels Programme [7].

TRACE ELEMENTS IN COAL

Because coal is a natural substance comprising not just the organic coal matter, but also inorganic material from the earth's surface, practically every element from the Periodic Table is present to varying levels. In the context of this Review, trace elements are those present at relatively low concentrations, normally taken as <1000ppm, but mostly <100ppm. The trace elements of environmental concern can be taken from relevant national and international regulations. One complication in doing this is the lack of agreement between, for example, Europe and the USA in this area. The European Pollutant Emissions Register (EPER) requires the reporting of the emissions to air of eight metal elements – arsenic, cadmium, copper, chromium, mercury, nickel, lead, and zinc – see Table 2. In the UK, the reporting of trace element emissions began in 1997 as the Chemical Release Inventory (CRI). This has subsequently become the Pollution Inventory (PI). Table 2 illustrates the range of trace elements under consideration by various regulatory bodies.

Table 2. Trace elements of regulatory interest

Element	Symbol	European Pollutant Emissions Register	UK Pollution Inventory	US Clean Air Act Amendments (1990)	US Toxic Release Inventory
No. on list		8	15	11	17
Arsenic	As	X	X	X	X
Cadmium	Cd	X	X	X	X
Chromium	Cr	X	X	X	X
Copper	Cu	X	X		X
Mercury	Hg	X	X	X	X
Nickel	Ni	X	X	X	X
Lead	Pb	X	X	X	X
Zinc	Zn	X	X		X
Antimony	Sb		X	X	X
Beryllium	Be		X	X	X
Boron	B		X		
Fluorine	F		X		
Manganese	Mn		X	X	X
Selenium	Se		X	X	X
Vanadium	V		X		X
Cobalt	Co			X	X
Barium	Ba				X
Silver	Ag				X
Thallium	Tl				X

As far as the mode of occurrence and levels of trace elements in coal is concerned, it is widely recognised that Swaine's book "Trace Elements in Coal" provides the most comprehensive general review [8]. To summarise the literature, it is clear that the current understanding of the mode of occurrence of individual trace elements varies considerably.

The greatest confidence in the mode of occurrence is for those that occur predominantly as sulphides. Of the 15 elements in the PI list, seven metals (As, Cd, Cu, Pb, Hg, Sb, and Zn) fall within this group which also includes selenium (Se). The modes of occurrence are believed to be as follows:

- As - arsenopyrite
- Cd - in association with zinc in sphalerite, ZnS

- Cu - chalcopyrite
- Pb - galena, PbS
- Hg - in association with pyrite or sphalerite
- Sb - uncertain, but may be fine sulphide grains within organic matter
- Se - in pyrite and galena, and may also be organically bound
- Zn - sphalerite, ZnS.

Nickel (Ni) may also occur as a sulphide, but most of the published work concludes that "there is a great deal of uncertainty about the mode of occurrence" [9]. Of the remaining six elements in the PI list, a further four are thought to be predominantly inorganically bound (Cr, F, Mn, V) and two organically bound (B, Be).

In the UK, the coal fired in combustion systems is predominantly bituminous in

nature and the trace element concentrations fall within fairly well-defined ranges. In this context, the concentrations of the PI elements generally fall into three concentration groups:

- < 1ppm – cadmium and mercury
- 1-10ppm – antimony, arsenic (can be up to 50ppm), beryllium, and selenium
- 10-100ppm – boron, chromium, copper, fluorine, lead, manganese (often >100ppm), nickel, vanadium, and zinc.

LEGISLATION

To date, emissions of trace elements from coal combustion devices have not been an issue of major concern in worldwide legislation. There are exceptions, the obvious one being the USA, which is currently working toward implementing mercury emission limits at coal-fired power plant. There are a number of international and national agreements designed to reduce trace element emissions, but very few of these have translated into limits on stack emissions from point sources utilising coal. Certain countries do have their own emission stack limits for certain trace elements from stationary combustion sources, but these can generally be met with existing pollution control devices.

Within Europe, the Integrated Pollution Prevention and Control (IPPC) Directive is applicable to certain industrial activities, including combustion installations with a thermal input exceeding 50MW_{th}. The directive covers “metals and their compounds” and requires the use of Best Available Technology (BAT) to reduce emissions to air. The Directive also provided for the setting up of the European Pollutant and Emissions Register (EPER), which reports annually on emissions of many species to air, land and aqueous systems [10]. The Large Combustion Plant Directive (LCPD) recognises that many trace elements

are associated with dust emissions and sets limits for total dust emissions of <50mg.m⁻³ for plant ≥500MW_{th}. Of particular interest is the review due by 31 December 2004, whereby the Commission must submit a report to the European Parliament assessing the amounts of heavy metals emitted by large combustion plant, the cost-effectiveness of further emission reductions for combustion plant and the need for further measures [11].

On an international level, the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP), was implemented on 29 December 2003. This protocol targets three metals; cadmium, lead and mercury and commits parties to reduce emissions below 1990 levels through the application of BAT to stationary industrial sources, combustion processes and waste incineration. The UK is already compliant in all respects.

In terms of mercury-specific activities, the United Nations Environment Programme (UNEP) Global Mercury Assessment Report was published in December 2002 and summarises information on the chemistry, toxicology and impacts of mercury on human health, the environment and on the global sources of mercury. The report concludes that there is “sufficient evidence of significant global adverse impacts to warrant international action to reduce the risks to human health and/or the environment arising from the release of mercury” [12]. In addition, the European Commission has begun preparation of a mercury strategy which is likely to be published in 2004. As part of this development, a Mercury Workshop, sponsored by the EU, will be held in Brussels in March 2004.

The most progress with developing legislation for mercury control has been in the USA. The 1990 Clean Air Act (CAA)

Amendments required the US EPA to conduct an assessment of health and environmental effects posed by the emission of a range of trace chemicals from coal-fired power plant. Two reports to congress were issued, Mercury Study to Congress and Utility Air Toxics Report to Congress. Prior to 1990 there were few data available on mercury concentrations and behaviour in the combustion system, and the US EPA authorised an Information Collection Request (ICR) in 1999 [13]. This generated a large database that contains information on all US coal-fired utility boilers, coal analyses for mercury, chlorine, sulphur, moisture, ash and calorific value for 1143 US generating units, and air pollution control device inlet and outlet flue gas analysis for total and speciated mercury for 84 of the above units.

Regulation of mercury in the USA is proceeding on two tracks, mercury-specific legislation and so-called “multi-pollutant” legislation. The CAA obliges the US EPA to develop a so-called Maximum Achievable Control Technology (MACT) standard for mercury. The EPA was obliged to publish a proposal for a MACT standard by 15 December 2003, issue a final rule by December 2004 and implement the final rule by December 2007. The MACT legislation is likely to be stringent and will not allow mercury trading. In parallel with the development of the MACT standard, progress is being made with multi-pollutant legislation. Integrating a mercury emissions reduction programme with other emission reduction programmes has the potential to save money whilst resulting in similar environmental benefits. In February 2002 the US President announced the “Clear Skies” initiative. This is a multi-pollutant approach to reducing NO_x, SO₂ and mercury emissions from power plant by approximately 70% over the next decade by using a market-based cap and trade approach. Clear Skies would cap mercury emissions at 29te in 2010 and at 17te in

2018 and would replace the MACT approach described above. In addition to Federal regulation, individual states may also set their own control requirements and standards, and many have expressed an intention to limit mercury emissions.

It is clear that the mercury issue is a global problem and modelling studies have indicated that more than 70% of mercury deposited in the USA is from external sources. The impact of the UNEP Global Mercury Assessment and the EU Mercury Strategy remains to be seen, but these initiatives combined with pressure from the USA have the potential for introducing more widespread emission limits. A key issue not yet resolved is the lack of an effective mercury control technology that is applicable to all sources. With regard to other trace elements, it is likely that these will take second place to mercury in any legislative programme. It should be emphasised that trace element emissions are falling, even without specific legislation, through continuous reduction in emission limits for species such as dust and SO₂ and the co-benefit obtained from any improvement in existing pollution control equipment.

EMISSIONS OF TRACE ELEMENTS FROM COAL COMBUSTION & GASIFICATION

Coal Combustion

Coal combustion in utility boilers takes place at operating temperatures of over 1400°C. The coal is injected as a fine powder and ignited in suspension. As the particles are heated, volatile matter is released, char is formed and mineral matter is exposed to rapid heating and high temperatures. This exposure may result in thermal decomposition, fusion, disintegration and agglomeration. Any trace elements in the mineral matter may be released and dispersed among the fly ash, bottom ash and combustion flue gases,

depending on the degree of volatilisation of their particular geochemical modes of occurrence. Those elements that are volatilised during combustion of the coal are carried through the high temperature regions of the furnace with the flue gases. Those elements that are not volatilised during combustion form a melt of fairly uniform composition that comprises the matrix of both fly ash and furnace bottom ash. A portion (~20%) of this non-combustible mineral matter is retained within the furnace. Furnace bottom ash tends to be fairly coarse and can include massive fragments. This ash experiences extremely high temperatures initially, but once it has fallen to the floor of the furnace it undergoes rapid cooling, remains in a fairly inert stagnant atmosphere, and is not in intimate contact with flue gas. This is important in explaining the generally low trace element content of this material. Only those elements that are completely involatile are retained in the bottom ash, the remainder are depleted to some extent. The remainder of the ash (~80%) is carried through the furnace along with the flue gases. This suspended ash is commonly known as fly ash or pulverised fuel ash (pfa). The partially and fully vaporised trace element species in the flue gas undergo further transformations and partitioning as the flue gas starts to cool in the post-combustion zone of the upper furnace and heat recovery sections of the combustion system.



Figure 3. Pulverised fuel flame (courtesy of Powergen)

As the flue gases containing vaporised trace elements and entrained ash leave the furnace and pass through to the convective section of the boiler, the temperature starts to fall. A number of physicochemical processes occur including coalescence, condensation, nucleation and agglomeration. Just prior to reaching the air heater the flue gas temperature is approximately 400°C. After exchanging heat with the clean combustion air in the air heater, the flue gas temperature falls rapidly to approximately 130°C, resulting in further reaction and partitioning of the vapour phase species onto particulate material.

Many researchers have grouped trace elements according to their volatility and hence partitioning behaviour during combustion. Elements are often categorised into three broad groups according to their behaviour [14].

Group I These elements are generally involatile or have very low volatility. They tend to be retained in all ash streams at broadly the same concentration, (typically the lithophile elements Ba, Ce, Cs, Mg, Mn, Th).

Group II These elements have limited volatility and tend to show slight enrichment in particulate that has been exposed to flue gas compared with the coarse slag and bottom ash, (typically the chalcophile elements As, Cd, Cu, Pb, Sb, Se, Zn).

Group III These elements volatilise most readily. They are found in the vapour phase even at flue gas exit temperatures of just over 100°C and are depleted in all solid phases, (typically Hg, Br, I).

In reality, the situation is not that simple, with many elements showing partitioning behaviour intermediate between the groups

shown above. If elements remained completely involatile, the ash remaining after combustion would contain the same elements as were contained in the coal, but enriched in the ash by a factor equal to $100/(\text{ash content in } \%),$ ie

$$[\text{Ash}] = [\text{coal}] \times 100/ (\% \text{ ash in coal})$$

Clarke and Sloss have categorised trace elements into three groups, but include overlap between groups to represent those elements that show intermediate behaviour as shown below in Figure 4 [14]. Because specific surface area increases with decreasing particle size, elements that are vaporised at high temperatures and subsequently condense back onto the flyash particles will tend to be more enriched on the smaller particles. Hence, as the emitted dust, ie that portion that is not collected in an ESP, is finer than the inlet dust, individual elements will be enriched to varying degrees, depending on their volatility. Only for B, Se and Hg is this phenomenon relatively unimportant.

In the UK, this behaviour is recognised in the methodology for estimating annual trace element emissions from coal-fired power stations to the atmosphere. This methodology has been developed by UK electricity generators in agreement with the UK Environment Agency in order to report

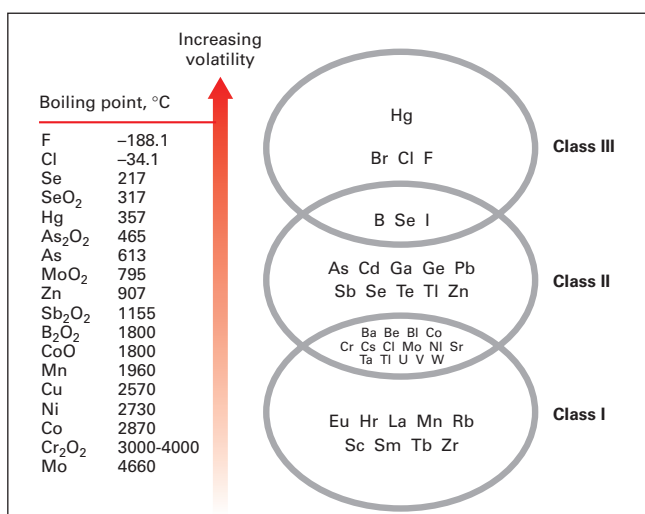


Figure 4. Trace element groupings [14]

consistent and accurate emissions data. The methodology takes account of the retention of trace elements in bulk pfa by using retention factors that are based on measurement campaigns in the UK. A retention factor of one would indicate that 100% of the trace element is retained in the pfa and none is emitted in the vapour phase, whilst an emission factor of 0.5 indicates that 50% of the material is emitted in the vapour phase [15]. In addition to the retention factor, account is taken of the enrichment seen in the fine particulate material which can be emitted from the particulate removal device. The enrichment factor is simply a ratio of the concentration of trace element in the emitted dust compared with that in the bulk ash. The current PI values for retention and enrichment factors are shown in Table 3:

Table 3. Retention and enrichment factors for trace elements in the UK Electricity Supply Industry Pollution Inventory Methodology [15]

Element	Retention factor	Enrichment factor
Arsenic	1	0.9
Selenium	0.8	10.3
Lead	0.98	1.3
Antimony	1	1
Boron	0.74	1
Nickel	1	1.7
Chromium	1	3
Copper	1	2.5
Manganese	1	0.9
Vanadium	1	1.3
Zinc	1	1.7
Beryllium	1	1
Cadmium	0.9	5.3
Mercury	0.48	1.8

These data have been compared with data available from the UNECE Emissions Inventory Guidebook and other utilities in Europe and are generally in agreement. The retention factor of 0.48 for mercury is worth noting. Although retention of mercury can show significant variation, this figure is

known to be robust. Mercury shows extremely complex behaviour on combustion and of all the trace elements, its behaviour has been studied in the most detail. The boiling point of mercury is 360°C and therefore, at typical combustion temperatures of around 1500°C it is completely volatilised. Typical concentrations of mercury in flue gases from coal combustion range from 1 to 20 µg.m⁻³. However, the amount of mercury remaining in the vapour phase at the stack can vary widely, depending on flue gas temperatures, cooling rates, coal type and combustion conditions, particularly carbon-in-ash levels [4].

Whatever the form of mercury in the coal, elemental mercury (Hg⁰) is assumed to be formed immediately on combustion, and until fairly recently, all was assumed to be released to the atmosphere in the vapour phase. Further investigation has shown this not to be the case and subsequent reactions with various flue gas species can result in some of the elemental mercury being oxidised to Hg²⁺. Both forms of mercury may also be adsorbed onto particulate matter and there is considerable evidence for affinity with carbonaceous material. The behaviour of Hg⁰ and Hg²⁺ in downstream flue gas cleaning equipment is quite different, and in order to develop effective control strategies it is necessary to try to predict relative proportions of each. Results obtained from the US EPA's ICR in 1999 indicated that coal containing low levels of chlorine results in flue gas where elemental mercury (Hg⁰) predominates. However, flue gases from coals containing high chlorine (>500 µg/g Cl) have a much higher proportion of oxidised mercury (Hg²⁺). Generally, combustion of bituminous coals gives an approximately 50:50 split of Hg⁰ and Hg²⁺ in the emitted flue gas.

Although the major reaction pathways for mercury during coal combustion are known with some degree of confidence, it is not

yet possible to make quantitative predictions of the emission of specific mercury species from coal-fired power plant. The ultimate aim is to develop a predictive model so that emissions of total and specific mercury species can be formulated. During recent years, progress in this area has been rapid with mechanisms being developed for homogeneous oxidation reactions involving primarily chlorine species, followed by combination with heterogeneous oxidation reactions involving carbon-in-ash and transition metals.

Trace Element Monitoring



Figure 5. Flue gas sampling in-stack (courtesy of Powergen)

Accurate and reliable measurement data of trace elements in the vapour and particulate phase are critical to the understanding of their behaviour during combustion and gasification processes. Accurate data are also important to aid the formulation of control strategies and for reporting mass emissions to national inventories. Virtually all of the trace element sampling undertaken uses manual sampling methods, most of which rely on wet chemical methods to capture and retain species from the flue gas. The solutions are then analysed in a laboratory. Concentrations of trace elements in flue gas are extremely low, and most manual sampling requires the collection of at least one cubic metre of

sample gas. The sampling system must be capable of removing any dust remaining in the flue gas as well as retaining vapour phase trace elements. Although manual sampling is widespread and can provide reasonably accurate data, it is time-consuming and requires highly trained staff operating complex equipment.

Most of the methods for the analysis of trace elements in flue gas streams are taken from standards introduced by the US EPA and are based on their Method 5 sampling train shown in Figure 6.

The sampling train consists of a heated glass probe to allow for isokinetic withdrawal (the extraction of a sample of flowing gas and any entrained particles in such a manner that the probe inlet velocity matches the local duct velocity) of a sample from the flue. The sample is then passed through a heated

filter to remove particulate matter, which can be analysed separately. The sample is then drawn through a series of impingers containing chemical solutions, which capture and retain trace elements. Finally the flue gas is dried and passes through a gas meter to determine the volume sampled.

A variation on this sampling train is US EPA Method 29 which is used to measure concentrations of up to 17 trace elements in both the gaseous and particulate phase. It is virtually identical to Method 5 except for the addition of further impingers. Method 29 employs two impingers containing a solution of 5% nitric acid in 10% hydrogen peroxide which is used to capture the majority of the vapour phase trace elements. The final impingers contain an acidified solution of 4% potassium permanganate, and are used specifically to capture elemental mercury.

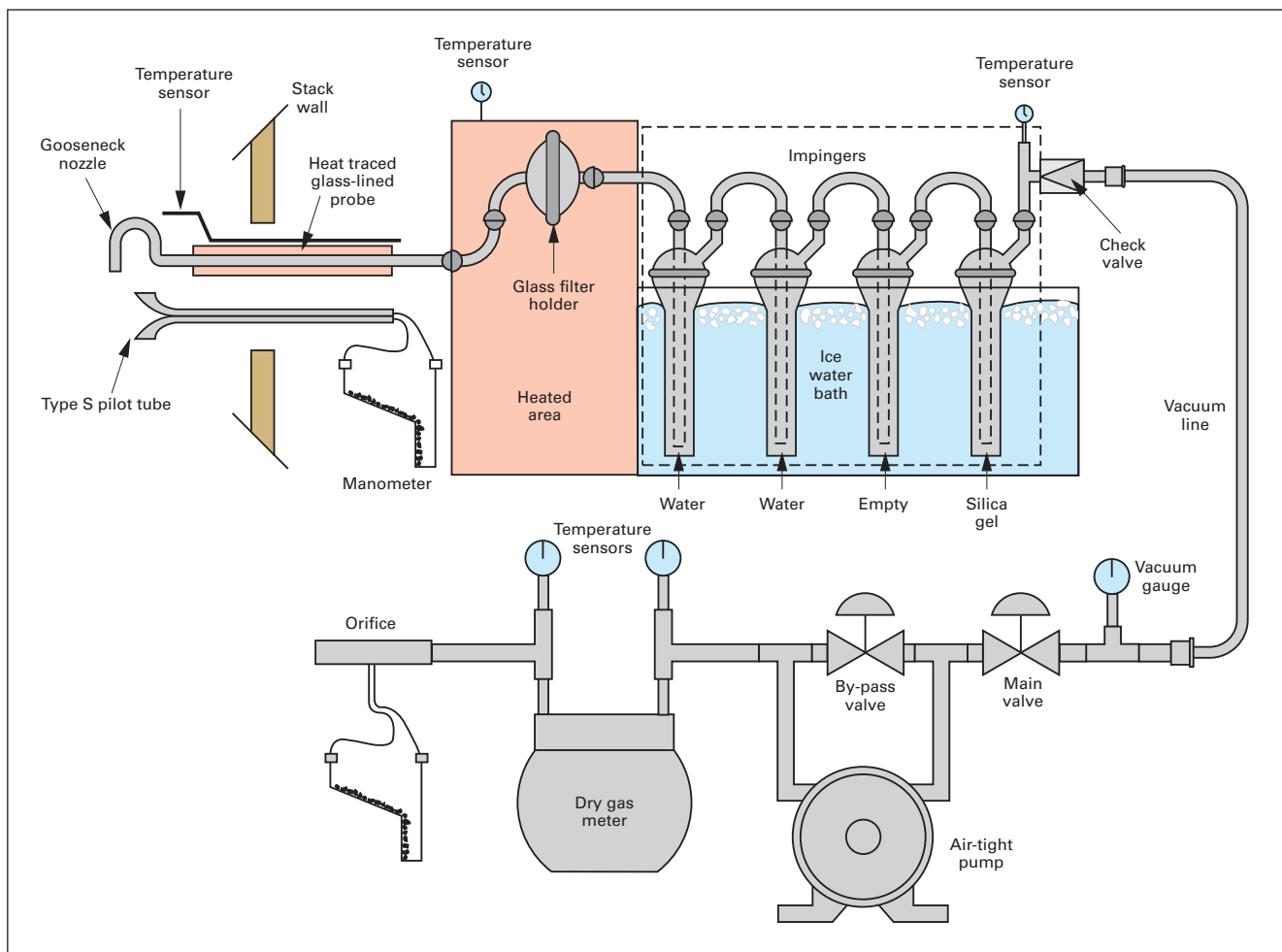


Figure 6. US EPA Method 5 sampling train (adapted from ref [22])



Figure 7. Flue gas sampling using EPA Method 29 for multimetals on the Powergen Combustion Test Facility (courtesy of Powergen)

While Method 29 is used to determine multimetals, various sampling trains have been developed specifically for mercury. US EPA Method 101A is again almost identical to Method 5, but utilises three impingers, each containing acidified 4% potassium permanganate solution. Determination of each of the separate forms of mercury (Hg^0 , Hg^{2+} and Hg_p) is more difficult and the Ontario Hydro Method has been adopted as an ASTM standard. This uses a similar arrangement to Method 29, but replaces the nitric acid with potassium chloride which is claimed to retain only oxidised mercury. The acidified potassium permanganate captures any remaining elemental mercury.

The European Standard EN 13211:2001, has been validated for the determination of total mercury in waste incinerator flue gas, but cannot speciate between the three forms of mercury. EN 14385, for the determination of the several trace elements in waste incinerator flue gas, is currently in draft.

Other methods have been used for the sampling of mercury and other trace metal species in power plant flue gas although, as

these have not been validated by the relevant agencies, they are not in widespread use. These include modified wet chemistry techniques and the use of specific solid sorbents or resins designed to capture certain species. E.ON Engineering of Germany has developed a method for the solid state determination of mercury in power plant flue gas using a commercially available DOWEX™ resin to capture oxidised mercury, and an iodinated activated charcoal to capture elemental mercury. This may prove to be more reliable than the Ontario Hydro method, but this has yet to be confirmed.

Trace element CEMs are preferable to manual sampling technique, but there are none currently available commercially. Several have been evaluated by the US Department of Energy (DOE), but have not progressed further owing to the lack of legislation controlling the emission of trace elements both in the USA and abroad. The majority of trace element CEMs proposed have utilised UV or X-Ray spectroscopy to determine the instantaneous concentrations of many components. The University of Sheffield currently has a mobile Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) laboratory which is operational for the analysis of multiple components in waste incinerator flue gas.

Through the impending legislation on mercury control from coal-fired power plant in the USA, development of mercury CEMs is much more advanced than the corresponding trace element CEMs. The majority of mercury analysers relies on atomic absorption spectroscopy (AAS), but this may be subject to interference from SO_2 . Some instruments utilise atomic fluorescence (AF), which uses a similar principle to AAS, but is not as sensitive to interfering components. AF is inherently linear, operates over wider ranges and is more selective than AAS.

There are over twenty known suppliers of commercially available mercury CEMs

around the world. Some of these systems have been evaluated by the US DOE producing some promising results. However, more research is required to develop trace element CEMs that give reliable, unattended operation.

Control Options and Technologies

Coal Cleaning

Coal cleaning is a mature technology and in the Northern Hemisphere most run-of-mine bituminous coal for power station use is routinely cleaned in order to meet specifications for sulphur and mineral matter content. Coals from the Southern Hemisphere can be more difficult to clean, because of more finely disseminated mineral matter. However, most export coal from Australia and South Africa is washed to some degree. Many elements of environmental concern such as Zn, As, Cd, Hg and Pb are associated with pyrite or accessory sulphide minerals, making coal cleaning a useful method of trace element control. However, the economics of the subject are complex and are still primarily dependent on ash reduction and associated increase in heat value. While there is a general relationship between trace element and overall ash removal, the results available suggest that the percentage removal is specific to the coal and also to the cleaning process used. It has been estimated that current coal cleaning practices reduce the potential emission of mercury in the USA by approximately 37%. Unfortunately, the advanced coal cleaning processes necessary to remove additional mercury are not thought to be competitive with other post-combustion mercury control options. Consequently, the US DOE and National Energy Technology Laboratory (NETL) no longer support coal-cleaning research for mercury control in the USA and post-combustion capture of trace elements appears to be the favoured approach.

Combustion NO_x Control

Combustion NO_x control systems such as low-NO_x burners, overfire air and coal reburn reduce NO_x emissions but often have an adverse impact on carbon-in-ash levels. While this is a disadvantage in terms of thermal efficiency and ash saleability, high levels of carbon have been demonstrated to adsorb vapour phase mercury which can then be removed from the flue gas in an ESP or baghouse. This process is similar to activated carbon injection for mercury capture, but uses the carbon in fly ash generated *in situ* by combustion [16]. There is also increasing evidence that carbon-in-ash is a requirement for heterogeneous oxidation of elemental mercury in flue gas to produce oxidised mercury, which can be subsequently removed by a wet scrubber [16].



Figure 8. Low-NO_x burner (courtesy of Powergen)

Despite the obvious attraction of using fly ash as a mercury sorbent, intuition and available data suggest that it is a much less effective sorbent than commercial activated carbon. A comparison of the properties of activated carbon and carbon-in-ash are shown in Table 4.

The typical surface area and therefore sorption capacity of carbon in fly ash is significantly lower than that of activated carbon. In addition, the high levels of carbon-in-ash required for mercury capture are not attractive in terms of subsequent

Table 4. Comparison of physical properties of unburnt carbon and activated carbon [17]

Property	Unburnt carbon (char)	Activated carbon
Particle Size	Variable	15-18 μ m
Large Fraction	180-350 μ m	120 μ m
Smallest Fraction	Submicron soot	2-5 μ m
Particle Shape	Amorphous char (irregular/porous) Graphitic char (crystalline/structured) Soot	Irregular and porous
Surface Area	1-60m ² .g ⁻¹	500-1100m ² .g ⁻¹
Bulk Density	0.26g.cm ⁻³	0.5g.cm ⁻³

ash saleability and disposal. However, pilot-scale testing and economic estimates have suggested that up to 90% mercury reduction at 50% of the cost of activated carbon injection can be achieved through combustion optimisation and combustion modification for bituminous coals. These techniques offer simple and low-cost methods of giving some degree of mercury control for older, short-life and lower merit sites.

Post-combustion NO_x Control

Post-combustion NO_x control using selective catalytic reduction (SCR) is widely applied to meet NO_x emission limits. Measurements have indicated that elemental mercury can be oxidised across an SCR catalyst. Since SCR is normally installed upstream of other pollution control equipment, its influence on mercury speciation in terms of promoting Hg²⁺ and Hg_p formation may greatly impact mercury retention across ESPs and FGD plant.

Behaviour of mercury in SCR catalysts has been studied over a number of years, particularly in Germany and more recently in the USA. It has been suggested that the presence of high concentrations of ammonia may inhibit mercury oxidation. There is also evidence for the requirement

of HCl in flue gas to promote the oxidation of mercury on the catalyst. A number of full-scale experiments are under way in the USA to determine the impact of SCR catalysts on mercury speciation with a wide variety of coals and catalyst types/ages. The evidence to date suggests that SCR catalysts have a significant impact on mercury oxidation, particularly for bituminous coals where >90% oxidised mercury is possible at the SCR exit. The oxidation rate at sites firing low-rank coals is significantly lower and may be due to reduced HCl concentrations in flue gas. More data from representative sites are needed, but the combination of SCR and FGD appears to offer excellent removal efficiencies for mercury, illustrating the benefits of co-control of pollutants [18].

Particulate Controls

The majority of trace elements, while volatilised in the furnace, condense onto particulate material as the flue gas temperature falls. Therefore, particulate control devices are crucial in determining emissions of most trace elements.

Electrostatic Precipitators (ESPs)

ESPs are normally situated downstream of the air heater and operate at flue gas temperatures of <150°C. Accordingly, any condensable trace element species are likely to be associated with the fly ash. Because of stringent dust emissions limits, ESPs are extremely efficient (>99.5%) at capturing fly ash and, therefore, the majority of trace elements.

Fabric Filters

Fabric filters (baghouses) are less common, but have an even better capture efficiency than ESPs. They are also superior at controlling fine particulate matter and less sensitive to particulate loading and fly ash



Figure 9. Electrostatic precipitator refurbishment (courtesy of Powergen)

characteristics. However, baghouses can cause a large pressure drop, require regular cleaning and replacement, and can become blocked. Flue gas temperatures in fabric filters are often limited to avoid damage to the bags, this can assist in trace element capture, allowing further condensation of volatile species. It is also possible that a proportion of trace elements remaining in the vapour phase will also be removed due to intimate contact with and subsequent adsorption by the collected dust cake.

Particulate Control Devices and Mercury Emissions

The effectiveness of particulate control devices in removing mercury from flue gas is entirely dependent on the proportion which is present in the solid phase. This in turn is dependent on the device itself, carbon-in-ash levels, flue gas temperatures, and mercury speciation. Mercury removal in a cold side ESP has been shown to be directly related to the level of chlorine in the coal, suggesting that oxidised mercury is more easily captured than elemental mercury. As noted previously, there is also

significant evidence that unburnt carbon-in-ash acts as a catalyst to oxidise elemental mercury as well as adsorbing mercury [19]. Fabric filters have shown the highest mercury removal efficiency of all particulate removal systems studied.

Flue Gas Desulphurisation (FGD) Systems

The most common FGD systems in use worldwide are wet scrubbers or spray dry systems. While FGD is primarily designed to control SO₂ emissions, most FGD systems also result in the capture of the small amount of particulate matter remaining in the flue gas after the particulate collection device. Most systems operate at a reduced flue gas temperature, between 50 and 100°C, resulting in additional condensation of species that may be still volatilised upstream of the FGD.



Figure 10. Ratcliffe-on-Soar FGD plant (courtesy of Powergen)

Wet Limestone FGD Systems

Virtually all trace elements have been shown to be almost totally removed by wet FGD plant. In the UK, based on plant measurements, within the PI methodology an additional retention factor for both the solid and vapour phase to account for trace element removal in the FGD plant is applied: The solid retention factor simply accounts for the dust removal across the FGD plant and the change in characteristics of emitted dust. The vapour phase retention factor can be seen to vary between elements, with mercury showing a relatively high removal figure. However, as this work was undertaken with a UK high chlorine coal it is likely that a high proportion of mercury was in soluble oxidised form [15].

Table 5. FGD retention of trace elements [15]

Element	FGD retention factor (solid)	FGD retention factor (vapour)
As	0.91	–
Se	0.58	0.82
Pb	0.9	0.37
Sb	0.9	–
B	1.0	0.8
Ni	0.86	–
Cr	0.88	–
Cu	0.69	–
Mn	0.93	–
V	0.92	–
Zn	0.84	–
Be	0.95	–
Cd	0.8	0.52
Hg	1.0	0.76

Mercury Behaviour in Wet FGD Systems

The removal efficiency of mercury in a wet FGD plant is entirely dependent upon its speciation. Because oxidised Hg^{2+} is water soluble, wet scrubbers can effectively remove this form whilst insoluble elemental mercury Hg^0 is not removed to any great degree. FGD plant on boilers

burning bituminous coals are reasonably effective at mercury removal. However, for boilers burning low-rank coals and lignites, the flue gas mercury can be predominantly elemental and removal efficiencies across the FGD plant can be lower. It has been found that oxidised Hg^{2+} can be (re)converted into elemental Hg^0 , resulting in higher emissions of elemental mercury leaving the system than entering. The re-emission of elemental mercury from FGD systems is a key concern and several mechanisms involving sulphur species have been proposed.

Mercury in Dry FGD Systems

For the US EPA ICR, data were collected for a number of FGD Spray Drier Absorbers (SDAs). The majority of the plant tested was installed with SDA/fabric filter, and the results suggest a strong correlation with chlorine content. The data appears to show that SDAs show a similar removal efficiency for oxidised mercury as wet FGDs, but often remove elemental mercury as well, particularly for those boilers that burn bituminous coal. The total mercury removal in dry FGD systems increases as the proportion of particulate mercury increases. Because the testing of the dry FGD systems in the ICR also included the downstream particulate collection device, very high overall removal efficiencies were seen. There will be close to 100% collection of any particulate mercury in the particulate collector downstream of the SDA.

In summary, coal rank appears to be the dominant factor in determining the ability of FGD systems to remove mercury. For mercury removal, the best combination of fuel type and FGD system is bituminous coal and dry FGD systems. The worst performance was from lignite coal and dry FGD systems [16].

Improving the Mercury Removal Efficiency Across FGD Systems

Although FGD is a cost-effective, near-term, mercury emission control option, there are concerns over elemental mercury re-emission from wet FGD and the ability to maximise the proportion of oxidised mercury in flue gas to enable efficient capture. There are a number of studies under way to oxidise elemental mercury artificially, including catalytic, chemical and corona discharge which are under investigation, as well as studies to investigate additives that minimise elemental mercury re-emission.

Sorbents for Mercury Control

A promising approach for control of trace species remaining in the vapour phase at flue gas exit temperatures is the injection of an effective sorbent upstream of the particulate control device [20]. Almost all coal-fired combustion systems are equipped with electrostatic precipitators or a fabric filter and sorbent injection upstream of such a collection device is attractive as it has the potential to control both Hg^0 and Hg^{2+} .

The effectiveness of sorbent injection depends on flue gas composition, and the nature of the particulate control device used. With a fabric filter, mercury removal efficiencies of 90% are possible with relatively low sorbent injection rates. This is due to a combination of in-flight and dust cake capture. Sorbent capacity, rather than mass transfer limitations, is more likely to be the limiting factor in fabric filter applications. With ESPs the majority of mercury capture is thought to be in flight and mass transfer limitations rather than sorbent capacity are important.

A standard powdered activated carbon has been adopted as the "baseline" sorbent for many studies. This is a lignite-derived

carbon sorbent produced by Norit Americas. It has a surface area of $600\text{m}^2.\text{g}^{-1}$ and has been proved at full scale to be effective in the removal of mercury, dioxins and other trace contaminants present in combustion flue gases. Its open pore structure and fine particle size permit rapid adsorption, which is critical where flue gas/solid phase contact times are short.

With stringent opacity limits in place at many coal-fired facilities, the addition of further particulate material to the flue gas stream may be a significant worry to plant managers. Full-scale testing in the USA using carbon injection at ESPs has indicated that there was no effect on dust emissions. However, all the plant tested had large ESPs and it remains to be seen what effect carbon injection would have on sites installed with older, smaller ESP equipment [21]. This is also likely to be a high cost option, with the US DOE estimating the cost of Hg removal at \$60,000-140,000 per kg.

Novel Sorbents

Despite the success of activated carbon, there is a great deal of work being undertaken to develop novel sorbents, both carbon and non-carbon. These materials are being developed in response to potential demand and the high cost of existing sorbents. Novel sorbents have the potential for improved performance and can utilise waste materials such as tyres. Inorganic materials such as silicates and zeolites are also being developed that are cost-competitive with activated carbon and do not compromise ash quality in terms of use in concrete manufacture. Fly ash from coal combustion is also under evaluation as an alternative low-cost sorbent.

Multipollutant Control Technologies

Multipollutant control technologies for fossil-fuelled generating plant are being developed

predominantly in the USA, where impending legislation is forcing electrical power generators to control levels of NO_x , SO_x and mercury simultaneously. The majority of these technologies is designed for retrofit applications, although these systems could be fitted to new-build coal-fired plant.

The majority of multipollutant control technologies consists of a method of oxidising SO_x and NO_x in the flue gas stream allowing their efficient capture as sulphurous and nitrous acids downstream in a wet scrubber or condensing electrostatic precipitator. These oxidation technologies also promote the capture of trace elements, particularly mercury. There are other multipollutant control technologies available, for example involving wet or dry scrubbing, or combustion modifications.

Many of the technologies are at a theoretical or laboratory-scale phase, although two are at the commercial demonstration phase - Powerspan's Electro Catalytic Oxidation (ECO™) Process, and LG&E Energy's Airborne Process. The Powerspan design utilises the oxidation of SO_x and NO_x by electron bombardment in a barrier discharge reactor to produce sulphurous and nitrous acid mists. These mists are then removed downstream in a wet ammonia scrubber, producing saleable fertiliser. Powerspan claims effective SO_x and NO_x removal along with a >80% removal efficiency for mercury and other trace elements. LG&E Energy's Airborne Process involves the injection of sodium bicarbonate sorbent into the flue gas stream downstream of the existing ESPs. The sorbent reacts with the SO_x and NO_x in the flue gas to produce sodium sulphate and sodium nitrate, which are then absorbed into solution in a wet scrubber where any unreacted SO_x and NO_x also combine to produce sodium nitrate and sodium sulphate. The solution is passed through a filter where trace elements and particulate matter are removed. Following the filter, commercially available ammonia together with CO_2 captured from the power plant is

added to produce ammonium bicarbonate. The solutions pass to a reactor, where sodium bicarbonate is precipitated, then recycled back into the scrubbing process. In a full-scale facility, the ammonium bicarbonate could be combined with a binder and granulated to produce a high value fertiliser. A commercial demonstration facility is under construction at LG&E Energy's Ghent generating station.

Summary of Control Options

Because of the high degree of emission control provided by existing pollution control devices, it is likely that no further action will need to be taken to control trace element emissions. A possible exception is mercury. With the rapid expansion of SCR and FGD installations for NO_x and SO_2 control and the high degree of co-control offered by such technologies for mercury abatement, it is likely that longer-life, high merit plant will be able to achieve significant mercury reductions simply by the installation of these technologies. However, their effectiveness with certain coal types is unclear, and depending on how the mercury reduction targets are set, additional mercury removal may be required above that achieved by a combination of ESP/SCR/FGD. Combustion modifications to increase carbon-in-ash and activated carbon injection will probably find most application at shorter-life, lower merit plant in order to meet required mercury emission limits. However, these



Figure 11. LG&E Energy's Ghent generating station (courtesy of LG&E Energy)

technologies may also find application at longer-life plant burning sub-bituminous and lignite coals that do not require sulphur abatement. Activated carbon injection has the advantage of being less sensitive to mercury speciation between its oxidised and elemental forms than any other removal technology.

As yet, there is no proven technology that has been successfully demonstrated to achieve very high levels of mercury control under all conditions, and given the complications of the systems involved, it is unlikely that such a technology will appear in the short term. In the longer term, research indicates that the most cost-effective approach to high levels of mercury control may be an integrated multipollutant (SO₂, NO_x, particulate and mercury) control technology. A number of these technologies are in the pilot-scale development stage in the USA, but have not generally been demonstrated at full scale.

Activities and Capabilities of UK Organisations

Basic Research

Work on trace element emissions from coal utilisation is mainly limited to fundamental research undertaken at UK universities. Coal research is widely spread across UK universities, but there is a clear focus on four institutions, namely, Nottingham, Sheffield, Leeds and Imperial College, London.

In terms of industrial research, very few externally published studies have been produced. Powergen has utilised its 1MW combustion test facility (CTF) with DTI and EPRI providing funding to investigate the behaviour of trace elements. The UK electricity supply industry Pollution Inventory methodology is also available in the public domain, although the research that underpins this work remains confidential. Individual electricity generators have also undertaken a

number of internally funded projects which remain unpublished on trace element behaviour in full-scale utility boilers.

Trace Element Monitoring Systems

Manual Sampling

There are many independent UK consultants who have expertise in measuring trace element emissions in stack by manual methods, mainly using US EPA Method 29. The Source Testing Association (STA) acts as a co-ordination group and disseminates and consults on forthcoming standards. There is little experience in the use of speciated mercury techniques, primarily because there is no requirement to undertake such measurements in the UK.

CEMs – Multimetals and Mercury

Sheffield University is unique in the UK in developing a continuous emission monitor (CEM) for multimetals in incinerator/power plant flue gases. The only UK manufacturer of



Figure 12. The ICP-OES spectrometer at Sheffield University (courtesy of Powergen)

a mercury CEM is PS Analytical, who is actively researching into the area of mercury CEMs and funds a full time PhD position. The majority of its instruments is in use in the USA where they have a strong market presence.

Enhancing UK Market Opportunities

In the short to medium term the largest market opportunity for R&D in this particular field is for mercury control in the USA. Once the regulations for mercury are clear, there will have to be significant investment over the next five years by US utilities for improving existing pollutant controls, together with mercury-specific controls. With one or two exceptions, the UK is poorly placed to meet this demand. It is difficult to envisage how the UK could benefit significantly from this work.

However, it is likely that in the future more opportunities will be forthcoming. In terms of coal utilisation, and in reducing emissions of trace elements, these opportunities are likely to include:

- Improving emission inventories, primarily in the developing world, but also in developed areas.
- Improving modelling capabilities for trace element behaviour, partitioning, dispersion and long range transport.
- Advice and support to policy makers.
- Advice and support for re-powering and upgrading existing coal facilities in the western and developing world.
- Development and construction of new conventional coal facilities.
- Development and construction of new generation coal technologies.

CONCLUSIONS

(1) Coal-fired power stations and, to a lesser extent, other coal combustion and gasification plant are a significant source of

trace elements in the global environment. This is especially true of mercury, which is the trace element of greatest concern.

(2) Emissions from coal combustion are decreasing in Europe and the USA because of the retrofitting of SO₂ and NO_x control technologies and increasing use of gas for electricity generation. Furthermore, trace element emissions from other sources such as incinerators are decreasing much more rapidly through the introduction of regulatory controls. However, there will be a marked increase in emissions in the developing world, in particular in China and much of Asia.

(3) For most trace elements of interest the mode of occurrence in coal is fairly well understood. Many occur as sulphide minerals, and this includes mercury and some of the other elements of particular concern such as cadmium and lead. Others such as chromium and vanadium are believed to be associated with the clay minerals in coal. Finally, some elements are organically bound and this probably includes beryllium and boron.

(4) In the UK, much of Europe and the US there are established protocols for the reporting of trace element emissions on an annual basis. The UK's Pollution Inventory lists 15 trace elements and the emissions are estimated from the concentrations in the coal burned and an understanding of their behaviour in a power station boiler.

(5) Certain European countries, eg Germany, have existing trace element emission limits, but these can comfortably be met by existing standard control technologies. However, in the USA, legislation to control mercury emissions from coal-fired power stations is planned. The impact of this legislation will depend on whether it is based on an emissions limit or percentage removal efficiency. No such legislation is

currently planned in Europe, but there is increasing awareness of this whole issue.

(6) The fate of trace elements in a power station boiler is generally well understood. The majority are relatively involatile and are retained in the ash. The emission of these elements is, therefore, primarily a function of the efficiency of the particulate collection equipment, normally an ESP. However, for elements that are potentially volatile at high temperatures because of their finer particle size and, therefore, the higher specific surface area of the emitted dust, an enrichment factor is applied in determining the concentration in emitted dust. A small number of elements are volatile and are emitted in the vapour phase. These include boron, fluorine, and selenium.

(7) The behaviour of mercury is complex and less well understood. Mercury is present in three forms – as elemental mercury, Hg^0 , as oxidised mercury in the volatile phase, Hg^{2+} , and in the solid phase, ie within the fly ash, adsorbed as either elemental or oxidised mercury. Historically, it was believed that the majority of mercury was in the vapour phase and would, therefore, be emitted to atmosphere. Recent work has demonstrated that this is incorrect and, on average, around 50% is retained in the fly ash. However, the relative proportions of the different forms of mercury are variable and will depend on factors such as coal rank and composition, boiler design and operating conditions, and the installation of emissions control equipment such as SCR and FGD. It has been demonstrated that SCR plant promotes mercury oxidation and that wet FGD systems effectively remove oxidised mercury.

(8) In a coal gasifier, because of the higher outlet temperature, $>250^{\circ}C$, the trace elements will tend to partition more to the volatile phase. However, hot gas clean up systems for the necessary removal of fine

particulate, alkalis and other species can also be designed to remove trace elements.

(9) For the monitoring of trace element emissions there are well established, standardised protocols for both solid and vapour phase measurements. These are time-consuming, expensive and require a high level of expertise to obtain reliable results. These include total mercury, but the development of a reliable method for mercury speciation measurements, ie separate determinations of elemental and oxidised mercury, has proved more difficult. In the USA, the so-called "Ontario Hydro" method has been adopted as an ASTM standard, but there remain concerns about its accuracy. In Europe, alternative methods are being developed. It should be noted that the low levels of mercury in coal, normally $<0.2ppm$, make this an analytically challenging area of study.

(10) Impending mercury control legislation in the USA has prompted a considerable R&D effort to produce a reliable mercury CEM. There are a number of approaches to sampling and conditioning, but analysis is based on either Atomic Absorption or Atomic Fluorescence. At present, the best available instruments are semi-continuous and require a considerable maintenance effort. Calibration is currently also a problem, though a certified standard calibration gas should soon be available.

(11) The development of a multimetals CEM is less well advanced because there is no imminent legislation.

(12) Control systems for major pollutants (SO_2 , NO_x , and dust) offer significant co-control benefits for trace elements, including mercury. For example, for bituminous coals the combination of SCR/ESP/FGD will give $>80\%$ mercury removal. In the absence of these technologies, sorbent injection techniques



Figure 13. Coal-fired power station (courtesy of Powergen)

developed for incinerators can be successfully used for mercury emissions control in coal-fired power stations.

(13) As many of the most sensitive elements, including mercury, occur as sulphide minerals in coal, conventional coal cleaning techniques could potentially be used to control trace element emissions. However, because the sulphide minerals tend to be finely disseminated through the coal matter, this approach is not economic.

(14) A number of technically innovative multipollutant control technologies are under development, mainly in the USA. Most of these are oxidation-based and will potentially remove trace elements, in addition to the major pollutants. However, they are not yet commercially proven and are more likely to be applicable to new-build plant than as a retrofit option.

(15) Because of impending mercury control legislation and the size of the market, the vast majority of the trace element R&D effort is in the USA. In the UK there is a modest R&D effort, primarily involving a number of universities as listed on page 19. The key areas where future R&D efforts should be focused are:

- Development of reliable CEMs, initially for mercury.
- Development of reliable methods for mercury speciation measurements and, thereby, an improved understanding of the controlling mechanisms.
- Investigation of possible oxidation technologies to promote mercury capture in wet FGD systems.
- Development of sorbents for trace element and other pollutant capture.
- Development of hot gas clean up systems for the capture of trace elements.

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