

## TRACE EMISSIONS FROM COAL COMBUSTION: MEASUREMENT AND CONTROL

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### INTRODUCTION

Combustion of coal is a potential source of emissions of many trace elements and organic compounds to the atmosphere. It is important that emissions of potentially toxic air pollutants from sources such as coal combustion are measured and, if necessary, controlled in order to limit any environmental effects. Increasing concern about the effects of trace pollutants in the environment may lead to the introduction of emission standards for some of these species. If such emission standards are adopted they must be supported by commercially available equipment which can measure and monitor the emissions with enough accuracy to ensure compliance.

Efficient coal combustion is not a significant source of emissions of organic compounds and therefore these compounds are not discussed further here. However, since there is increasing concern over emissions of mercury from coal combustion, specific attention will be paid to this particular trace element.

Several reviews have been published by IEA Coal Research on emissions from coal combustion. These include the halogens (Sloss, 1992), trace elements (Clarke and Sloss, 1992), organic compounds (Sloss and Smith, 1993), and mercury (Sloss, 1995). A complementary report has also been published on sampling and analysis of emissions of these compounds from coal-fired power station stacks (Sloss and Gardner, 1994). This paper draws together the conclusions from these reports.

### EMISSIONS OF POTENTIAL AIR TOXICS

Various estimates have been published which attempt to evaluate coal combustion as a source of potential air toxic emissions. Data from Nriagu and Pacyna (1988) indicate the importance of coal as a source of some trace elements on a global scale. For example, coal combustion may be responsible up to 21% of Sb emissions, around 18% of Ni and Se emissions and 15% of Cr emissions. Emissions of Cu, Sn, Tl and Zn from coal combustion are also thought to contribute between 5 and 20% of global emissions of these elements.

Estimates from the early 1980s (Pacyna and others, 1993) indicate that coal combustion may be responsible for up to 25% of total global mercury emissions to the atmosphere. There are a few more recent estimates from some countries in the 1990s, for example, coal's contribution to mercury emissions from human activities is 23% in Finland, 27% in the former FRG, about 10% in the Netherlands, 45% in the UK, and 16% in the USA (Sloss, 1995).

Estimation of global and regional budgets is difficult. Emission factors commonly based on a relatively small amount of actual measured data. The wide variation in the composition of coals, in combustion conditions, and in pollution control equipment need to be taken into account when estimating emission factors. Furthermore, many of the techniques used for the measurement of emissions of trace species, and thus for the estimation of emission factors, are still under development and are known to have serious limitations. Estimates for global and even regional emissions of trace species from most sources can therefore be considered as no more than educated guesses.

### LEGISLATION

Concern over the emissions of potential air toxics from all sources and their possible effects in the environment has led to the introduction of legislative controls in several countries. Legislation specific to the emission of individual trace elements has been specified in Austria, Germany and certain states in Australia (AHC, 1992; Maier, 1990; Nilsson, 1991). This legislation is summarised in Table 1.

The 1990 US Clean Air Act requires the evaluation of emissions of several trace elements with a view to the possible introduction of relevant legislation in the future (Chow and others, 1990). Legislation for power stations is also being considered in Canada and the Netherlands. Although no specific emission standards apply in Sweden, electrical utilities are required to fit best available technologies. These include particulate controls and FGD processes and therefore result in a substantial reduction in the emissions of most trace elements (Clarke and Sloss, 1992).

## MEASUREMENT OF EMISSIONS

Sampling and analysis techniques for the measurement of trace species at the concentrations emitted from coal-fired power plants are still under development. Countries such as Germany, Japan and the UK have published guidelines for sampling and analysis of some trace pollutants. In the USA, the methods are specified by law within the Code of Federal Regulations. However, many of these methods are known to have inherent problems and are still subject to review.

The majority of sampling techniques are based, initially, on the separation of gases from particles on filters, in cyclones or in cascade impactors. Each of these techniques are known to have problems such as clogging and irreversible adsorption (Masterson and Barnert-Wiemer, 1987).

Gaseous species may be analysed directly by analytical instruments, but such instruments are rarely portable. Samples are more commonly transported to the laboratory for analysis. Some vapour-phase species may be reduced to liquid form simply by condensation in cooled chambers. Other species are captured in a series of impinger bottles containing solutions which selectively solubilise the species of interest. Activated carbon can be used to capture volatile trace metals such as mercury. Although solid sorbents have the advantage of allowing volatile species to be trapped and transported in a stable form, some have problems with background contamination and decomposition products (Sloss and Gardner, 1994).

The development of sampling and analysis techniques for mercury is proving to be a particularly challenging problem. The speciation of mercury, as oxidised forms such as mercury chloride, or in the elemental form, determines its behaviour in pollution control equipment and in the environment. However, mercury emissions cannot be speciated with the standard methods currently available for sampling emissions of trace metals. New techniques based on sorbents such as activated carbon appear to be the most promising methods (Sloss and Gardner, 1995; Sloss, 1995).

Sampling and analysis techniques are not at the stage where they are accurate enough to produce a single value which would be considered representative. From what is already known of the behaviour of potential air toxics in coal-fired systems, their emissions are never constant, they vary with coal type, combustion conditions, pollution control systems and even depend on the concentration of other pollutants within the flue gas with which they may react.

Continuous emissions monitors produce virtually real-time data, avoiding transport and handling errors, and providing true representation of potential air toxic concentrations over time. However, continuous emissions monitors are not currently available for air toxics. Several systems, such as those based on FTIR, are under development (Sloss and Gardner, 1994).

## EFFECTS OF EMISSION CONTROL TECHNOLOGIES

Currently there are no widely available control technologies designed specifically for the removal of trace elements from coal-fired power stations. However, technologies for the removal of particulates, such as electrostatic precipitators (ESP) and fabric filters, and control technologies for SO<sub>x</sub> and NO<sub>x</sub>, may affect emissions of potential air toxics.

Particulate control systems capture any pollutants which are associated with the particles retained. The capture of individual air toxics thus depends upon their volatility. Most trace elements are not especially volatile and are captured efficiently by particulate controls, for example only 2% of Cd in the flue gas passes ESP uncaptured. However, B and Se are slightly more volatile and between 20 and 30% of these elements may pass uncaptured. Unless lime or a similar sorbent has been used in the boiler, virtually all the halogen gases pass through particulate controls (Clarke and Sloss, 1992; Sloss, 1992).

The capture of mercury by particulate control devices depends upon its speciation. Mercury in the particulate form (<5%) is captured efficiently. Oxidised mercury may also be associated with fly ash or can adsorb onto particles already associated with baghouses. Average mercury capture efficiencies in ESP and baghouses are around 35-40%. Since mercury speciation is temperature dependant, the capture of mercury in particulate control devices can be optimised by keeping temperatures as low as possible (<150°C) to increase the proportion of mercury in the oxidised form (Sloss, 1995).

Wet and dry flue gas desulphurisation (FGD) systems, required in many countries to remove SO<sub>x</sub>, incidentally remove some amounts of potential air toxics. For example, Figure 1 shows the average removal of volatile elements in wet-lime FGD systems in the Netherlands (Clarke and Sloss, 1992). Some FGD systems remove around 50% of the remaining B and Se in the flue gas. Reductions of over 90% for all the halogens have been achieved in such systems (Clarke and Sloss, 1992; Sloss, 1992).

Wet and dry FGD systems have wide ranges of efficiency for mercury capture from 20% up to 90%. Mercury capture in FGD depends upon its speciation. Up to 95% of oxidised mercury can be removed in spray dry scrubbers whereas elemental mercury passes through uncaptured. Capture of mercury in FGD systems can be maximised by increasing the proportion of oxidised mercury in the flue gas (Sloss, 1995).

Combustion modifications for NO<sub>x</sub> control may lead to increased concentrations of unburned carbon in flue gases. It is not clear to what extent this unburnt carbon may affect the distribution and behaviour of potential air toxics. NO<sub>x</sub> control systems do not appear to reduce or increase trace or minor element emissions. However, high dust SCR systems can oxidise up to 95% of the mercury in flue gas, enhancing the capture of mercury in FGD systems downstream (Sloss, 1995).

### SPECIFIC CONTROL OF POTENTIAL AIR TOXICS

There is currently no requirement for the specific removal or abatement of potential air toxics from the flue gas of coal-fired power stations. However, in the future, legislation on air toxics emissions is likely to become more stringent. Some specific technologies for the capture of potential air toxics are already under development and some are commercially available for use on waste incineration units. Concentrations of the more harmful air toxics, such as mercury, may be several orders of magnitude higher in flue gas emissions from waste incinerators than from coal-fired power plants. Work has already been started in several countries to reduce emissions of air toxics from waste incinerators. Some of the technologies used in waste incinerators may be applicable, with modification, to coal-fired units (Clarke and Sloss, 1992).

Sorbents which are available for the removal of heavy metals, such as mercury, from flue gases, include those based on activated carbon, zeolites, siliceous materials, alumina, and calcium compounds. Up to 100% of oxidised mercury and 60% of elemental mercury in flue gas may be captured with activated carbon. Sulphur impregnated activated carbons can capture over 90% of total mercury emissions and iodine impregnated activated carbons are reported to capture up to 100%. Figure 2 shows mercury removal by different types of activated carbon injected upstream of a spray dry scrubber and a baghouse. The use of some sorbents in coal-fired power stations may be limited due to low operating temperatures, harmful secondary effects and the high cost of some sorbents (Mojtahedi and Mroueh, 1989).

### CONCLUSIONS

Coal combustion is an important source of some trace elements to the environment.

Existing legislation for the control of particulate emissions effectively controls emissions of the majority of trace elements. Flue gas desulphurisation technologies may efficiently capture many of the remaining vapour phase pollutants. Over 90% of the halogens and 40-50% of the B and Se may be captured by this means.

The speciation of mercury determines the emissions and effects of mercury from coal combustion. Particulate control devices may capture up to 40% of mercury emissions, and FGD systems commonly up to 70%. These efficiencies may be enhanced by maximising the proportion of mercury present in the flue gas in the oxidised state. More research is required in order to understand mercury speciation and to use this information to determine the most appropriate control strategies.

Emission standards are becoming more stringent and, in the future, it is likely that emission limits for air toxics will be introduced more widely for sources such as coal-fired power plants. However, emission standards are worthless if the emission concentrations they specify cannot be measured accurately and on a regular basis by operators and regulatory authorities.

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**Table 1 National legislation for air toxic emissions from coal-fired power plants**

COUNTRY	AIR TOXIC	LIMIT (mg/m <sup>3</sup> )
Australia	As, Cd, Hg, Ni, Pb, Sb, V	Varies between States and Territories
Austria	Cr, Pb, Zn As, Co, Ni Cd and Hg	2.0 (total of all three) 0.5 (total of all three) 0.05 (total separately)
Germany	<b>Inorganic dust</b>	
Category I	Cd, Hg, Tl	0.2 (total of all three)
Category II	As, Co, Ni, Se, Te	1.0 (total of all three)
Category III	Cr, Cu, Mn, Pb, Pd, Pt, Sb, Sn, V	5.0 (total of all three)
<b>Organic substances</b>		
Category I		20 (total)
Category II		100 (total)
Category III		150 (total)
<b>Carcinogenic substances</b>		
Category I	(including BaP)	0.1 (total)
Category II	As, Co etc	1.0 (total)
Category III	hydrazine etc	5.0 (total)
<b>Planned legislation</b>	<b>Canada, the Netherlands, the USA</b>	

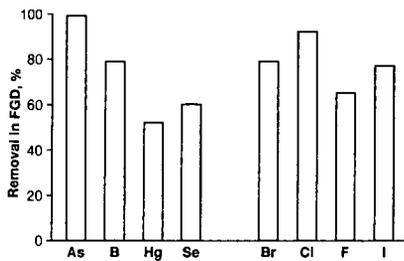


Figure 1 Average removal of volatile elements in wet-lime FGD systems in the Netherlands

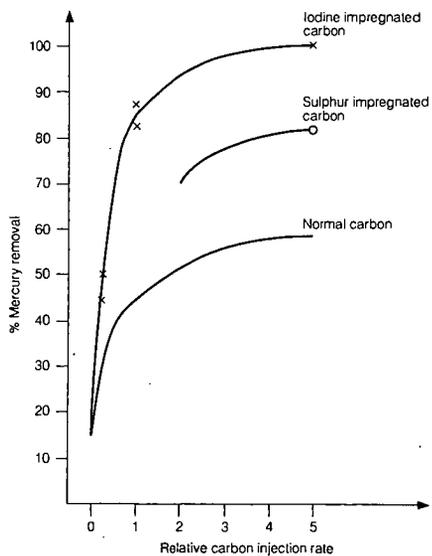


Figure 2 Influence of active carbon type on mercury removal