

# Chapter 8 Trace elements, alkali metals

## 8.1 Introduction

The term “trace elements” refers to chemical elements present in a natural material at concentrations  $< 0.1$  %wt, besides the minor elements (0.1 - 1 %wt) and the major elements ( $> 1$ %wt). For fossil mineral fuels such as coal or peat the ash-forming elements, *i.e.* Si, Al, Fe, Ca, Mg and sometimes also the alkali elements Na and K form the most important minor elements. The trace elements may then cover roughly the whole Periodic Table of the Elements after calcium (atomic number 20), although the elements beryllium (Be, atomic number 4) and boron (B, atomic number 5) should be included as well. The most important trace elements considered here are marked with \* in the periodic chart given in Figure 8.1. Also the halogen compounds F, Cl and Br (7 chapter 7) are often present as trace elements. A sub-class of the trace elements are the “heavy metals”, with a density of approx.  $5000 \text{ kg/m}^3$  or higher, such as Cd, Pb, Hg, Zn and Cu. Trace elements occur naturally in the ecosystem, with large variations in concentration, in part stemming from anthropogenic sources, *i.e.* pollution. In wastes and waste-derived fuels the “trace elements” can be present in such large amounts that they are actually minor or major elements. Electronic circuit boards in electric and electronic equipment (E&EE) waste contain  $\sim 1\%$   $\text{Sb}_2\text{O}_3$  as a flame retardant, used in combination with brominated flame retardants.

Motivations for controlling trace element concentrations in gas streams are diverse. Trace elements may form a threat to the environment or to human health (*e.g.* Hg, Cd, Pb, As, Cr, Tl), they may give corrosion problems (*e.g.* Na, K, V, Zn, Pb), lead to fouling of turbine blades (mainly Ca) or pollute or poison catalysts (mainly As) or sorbents downstream. Also fuel cell electrodes and electrolytes (7 chapter 2) may be deactivated by small amounts of trace elements. Within the European Community the 13 elements of highest concern are As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Sn, Tl and V: emissions of these elements are regulated for waste incinerators and cement plants (L section 8.4). In the USA of the 189 elements and compounds that are defined as HAPs (hazardous air pollutants), “known or suspected of causing cancer or other serious health effects” (see also Table 6.2), 11 are metals: As, Be, Cd, Co, Cr,

Hg, Mn, Ni, Pb, Sb, Se (CCT, 1997). Some of these elements are in very small amounts necessary for humans (Cu, Se, Cr, Ni) whilst others are carcinogenic or toxic at small or very small amounts, affecting for example the central nerve system (Hg, Pb, Se, As), the kidneys or liver (Hg, Pb, Se, Cd, Cu) or the skin, bones or teeth (Ni, Sb, Cd, Se, Cu, Cr). Vanadium (V) is relatively harmless. Zinc (Zn) is the second metal present in the human body (~ 2 g), after iron (~ 4 g) but before copper (~ 0.2 g).

PERIODIC CHART OF THE ELEMENTS																				
IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES					
1 H 1.00797															1 H 1.00797	2 He 4.0026				
3 Li 6.939	4 Be 9.0122														5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11# Na 22.9898	12 Mg 24.312														13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19# K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24* Cr 51.996	25* Mn 54.9380	26* Fe 55.847	27* Co 58.9332	28* Ni 58.71	29* Cu 63.54	30* Zn 65.37	31 Ga 69.72	32 Ge 72.59	33* As 74.9216	34* Se 78.96	35 Br 79.909	36 Kr 83.80			
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42* Mo 95.94	43* Tc [99]	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48* Cd 112.40	49 In 114.82	50 Sn 118.69	51* Sb 121.75	52* Te 127.60	53 I 126.904	54 Xe 131.30			
55 Cs 132.905	56* Ba 137.34	57* La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80* Hg 200.59	81 Tl 204.37	82* Pb 207.19	83* Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)			
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (268)	110 ? (271)	111 ? (272)	112 ? (277)									
Numbers in parenthesis are mass numbers of most stable or most common isotope.		* Lanthanide Series																		
Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.		58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97					
The group designations used here are the former Chemical Abstract Service numbers.		† Actinide Series																		
		90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)					

Figure 8.1 Periodic chart of the elements, indicating the most important trace elements with \*, alkali elements with #

In biomass-type fuels such as straw the alkali metals sodium (Na) and potassium (K), indicated with # in Figure 8.1, may lead to corrosion and deposit formation on heat-exchanger surfaces. Alkali metals are also a problem for new, advanced technologies based on gas turbines or expansion turbine turbines, such as coal-fired PFBC and IGCC and especially biomass-fired IGCC.

Below, the control of trace elements in gases, being mainly flue gases and gasifier product gases, is discussed. After a discussion on concentrations of trace elements in fuels, wastes and waste-derived fuels, and in what form these will eventually be present in flue gases or fuel gases, a few emission control standards are given. This is followed by three sections addressing trace elements, mercury taken separately and alkali metals, respectively.

## 8.2 Trace elements in fuels

Many different elements referred to as trace elements are found in mineral fossil fuels like coal and peat. In these fuels the trace elements are present as organic salts or carboxyl groups (-COOH) and inorganic minerals such as pyrites and other sulphides, (alumino-)silicates and carbonates (Benson *et al.*, 1996, Vassilev *et al.*, 1999). Typical for coal are rather high levels of lead (Pb), boron (B), chromium (Cr), nickel (Ni) and vanadium (V). The last two are also found in fuel oils, and also Orimulsion™ contains ~ 120 ppmw Ni, ~ 400 ppmw V. In wastes and waste-derived fuels the range of elements is less wide but some elements may be present at concentrations up to and over 1 %-wt, such as zinc (Zn), manganese (Mn), copper (Cu) and lead (Pb). Some typical data are given in Table 8.1. Mercury, Hg, is by far the most problematic trace element. Hg is found mainly in coal, municipal solid wastes (MSW), refuse-derived fuel (RDF) and sewage sludge. Processing MSW into an RDF may reduce trace elements concentrations by 1-2 orders of magnitude.

**Table 8.1 Trace element concentrations in some fossil fuels and waste-derived fuels (in mg/kg, i.e. ppmw, dry)**

	Coal	Peat	Heavy fuel oil	Pet coke	MSW	RDF	Wood	Waste wood	Waste paper	Scrap tyres	Sew. sludge
Hg	0.02-3	~ 0.07	< 0.01		< 15	1 - 10	0.01-0.2		~0.08		0.5 - 10
As	0.5 - 10	1 - 3	1 - 2		0.5-500	~ 3	~0.2				0.1-100
B	5-100				< 0.5				~ 0.5		
Be	0.1 - 10	~ 0.1	~ 0.01		1 - 40	~ 1			~ 0.8		
Cd	0.05-10			0.1-0.3	< 100	1 - 10		~ 0.5	~ 0.7	5 - 10	1 - 10
Co	0.5 - 20	1 - 2	~ 0.5		< 20		~ 0.1				~5
Cr	0.5 - 60	0.5 - 2	~ 0.5	5 - 104	< 1500	50-250	~ 1	1 - 4	~ 6	~ 100	~ 100
Cu	5 - 60	~ 10	< 0.1		< 2500	< 1000	0.5 - 3	~ 15	~ 18		200-700
Mn	5 - 300	30-100	0.5 - 1		< 1000	~ 250	10-1000		~ 27		~ 200
Ni	0.5-100	5 - 10	20 - 50	200-300	< 5000	10-100	~0.5	< 20	~ 7	~ 75	~ 50
Pb	1-300	1 - 5	1 - 5	6-100	< 2500	100-500	1 - 20	< 50	~ 8	60-760	100-300
Sb	< 1				< 80	< 5			~ 5		100-500
Se	0.2 - 3	~ 1	~ 0.1		< 10	3 - 6	~ 0.2		~ 0.08		
Sn	< 10				3 - 100	~ 500			~ 8		
Tl	~ 1			0.04-3						~ 0.25	
V	1-100	5 - 50	100-200	400-900			~ 2				
Zn	1-1000	~ 20	~ 10		~ 2 %	300-800	5 - 150	< 30	~ 150	1-2 %	~ 1000

Wood is a relatively clean fuel when it comes to trace elements, but chromated copper arsenate-treated wood (CCA wood) contains ~ 15 ppmw Cr, ~ 5 ppmw Cu and ~ 10 ppmw As (Helsen and van de Bulck, 2000). Car tyre scrap contains large amounts of various metals, mainly Zn, Pb, Cr and Cd. Sewage sludge is a rather “dirty” fuel, with trace element concentrations higher than coal or RDF.

### 8.3 Trace elements in flue gases and fuel gases

The behaviour of trace elements and other pollutants during combustion, gasification, incineration *etc.* is illustrated by Figure 8.2 for a coal combustion process with particulate- and SO<sub>2</sub> control. Many factors influence whether and in what form a trace element eventually ends up in the gaseous or particulate phase. This is decisive

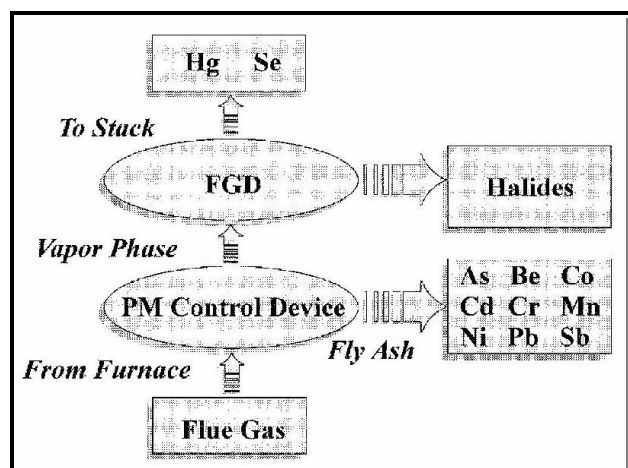


Figure 8.2 Behaviour of trace elements in coal combustion flue gases (FGD = flue gas desulphurisation, PM = particulate matter) (picture from CCT, 1997)

for the choice and efficiency of a certain gas clean-up method. The most important factors are

- 1) how the trace element resides in the incoming material (“fuel”),
- 2) temperature and pressure,
- 3) oxidizing or reducing conditions,
- 4) the presence of halogens, most importantly chlorine and
- 5) the presence of compounds that can act as sorbents, such as calcium.

Following Meij and others (*e.g.* Meij, 1989), many studies showed that the trace elements may be classified into

three classes as shown in Figure 8.3. Class I elements do not volatilise during combustion or gasification and distribute more or less equally over bottom ashes and fly ashes. Class II elements are vaporised but are found mainly in the fly ashes after condensation on particulates and nucleation mechanisms as a result of decreasing temperature in *e.g.* the flue gas duct. A significant part of these fine particles are in the sub-micron size class where dust control systems are less effective. Class III elements are vaporised and condensate only partly within the installation (Kema, 1997, Couch, 1995). Figure 8.3 gives also the boiling points for several compounds. Combined with information on toxicity and harmful effects on process equipment this classification gives first indication on which trace elements will need special attention.

This classification of trace elements is connected to the concept of enrichment: the relative enrichment factor (RE) of an element in an ash is defined as

$$RE = \frac{\text{element concentration in ash}}{\text{element concentration in fuel}} \times \frac{\% \text{ ash in fuel}}{100} \quad (8-1)$$

For class I elements, RE ~ 1 for bottom ashes and fly ashes, for class II elements RE < 0.7 for bottom ashes and ~ 1.3-4 for fly ashes, for class III elements RE << 1 for bottom ashes and RE >> 10 for fly ashes. These numbers are based on pulverised coal combustion (dry bottom), with ESP (Kema, 1997).

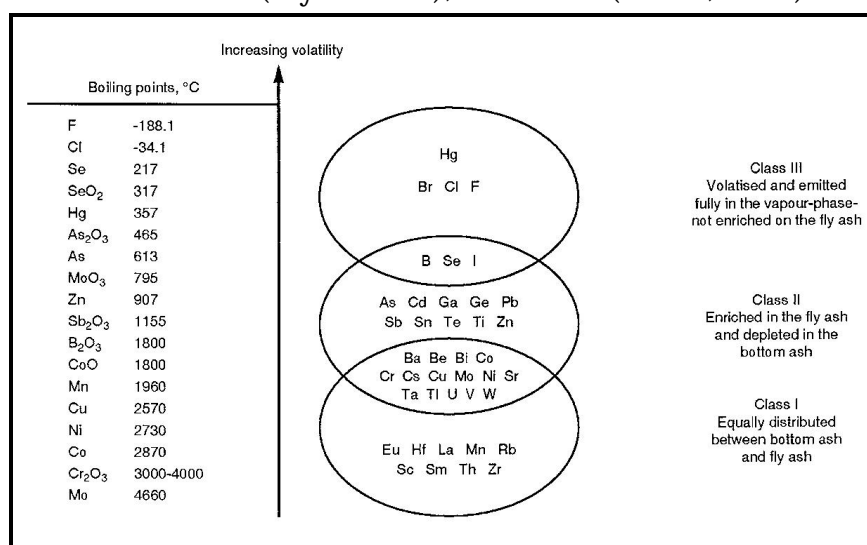


Figure 8.3 Classification of trace elements according to their behaviour during combustion or gasification (picture from Couch, 1995)

Measurements and thermodynamic calculations have given much information on in what form the trace elements will be present in a flue gas or fuel gas. For typical coal combustion the most important gaseous species are As as AsO, As<sub>4</sub>O<sub>6</sub> and As<sub>2</sub>O<sub>5</sub>, Cd as CdE

(i.e. elemental Cd) and CdO, Cr as CrOOH, CrO<sub>2</sub>OH, CrO<sub>2</sub>OH and CrO<sub>2</sub>(OH)<sub>2</sub>, Hg as HgE (elemental mercury), Pb as PbE and PbO, Sb as SbO, Se as SeO<sub>2</sub>, V as VO<sub>2</sub> and Zn as ZnE. Co, Cu, Ni and part of the Cr are not volatilised and were found in PM<sub>2.5</sub> fly ash particles as ferrite spinels AB<sub>2</sub>O<sub>4</sub>, with A<sup>2+</sup> = Fe, Mg, Ni, Co, Cu, B<sup>3+</sup> = Al, Fe, Cr. For gasification the situation is less clear, the most volatile elements Hg, Sb and Se will be present mainly as HgE, SbS and H<sub>2</sub>Se (Frandsen *et al.* 1994, Benson *et al.*, 1996, Helble, 1996, Senior *et al.*, 1998, Galbreath *et al.*, 2000).

Particle size was found to have no effect on the vaporisation of trace elements (Senior *et al.*, 1998). It is mainly the temperature that dictates whether a certain trace element or trace element compound will be volatile. It was found that the newer “clean” coal technologies PFBC and IGCC show lower trace element (excluding mercury) releases into the gas cleanup system than a pulverised coal combustor. This is due to lower temperatures and an effective cyclone system for the PFBC, and the fuel gas cooling

and sulphur removal stages with IGCC (Erickson *et al.*, 1996). Not surprisingly, it was recently reported that “the higher the dedusting temperature the lower the concentrations of heavy metals in the fly ash” (Klensch and Reimert, 1999). A second important factor is stoichiometry, or air factor. Many species are more volatile in a reducing atmosphere than under oxidising conditions, resulting eventually in more fly ash after cooling downstream of the gasifier. A third but very important factor is the presence of halogens, most importantly chlorine. For example in waste incineration the amount of chlorine is often sufficient to react with a significant fraction of the trace elements to form chlorides that are more volatile than the elemental or oxide form. This is illustrated by Table 8.2 for incineration of wastes with 0% and 10% chlorine, respectively. Clearly, Pb, Ag (silver) and Ni are much more volatile as chlorides. This may influence the formation of dioxins and furans (7 chapter 7).

**Table 8.2 The effect of chlorine on trace element volatility**  
(data from Seeker, 1990, Huotari and Vesterinen, 1995)

	Incineration 0 % chlorine	Volatilisation temperature EC	Incineration 10 % chlorine	Volatilisation temperature EC
Chromium	CrO <sub>2</sub> / CrO <sub>3</sub>	1613	CrO <sub>2</sub> / CrO <sub>3</sub>	1611
Nickel	Ni(OH) <sub>2</sub>	1210	NiCl <sub>4</sub>	693
Beryllium	Be(OH) <sub>2</sub>	1054	Be(OH) <sub>2</sub>	1054
Silver	Ag	904	AgCl	627
Barium	Ba(OH) <sub>2</sub>	849	BaCl <sub>2</sub>	904
Thallium	Tl <sub>2</sub> O <sub>3</sub>	721	TlOH	138
Antimony	Sb <sub>2</sub> O <sub>3</sub>	660	Sb <sub>2</sub> O <sub>3</sub>	660
Lead	Pb	627	PbCl <sub>4</sub>	- 15
Selenium	SeO <sub>2</sub>	318	SeO <sub>2</sub>	318
Cadmium	Cd	214	Cd	214
Osmium	OsO <sub>4</sub>	41	OsO <sub>4</sub>	41
Arsenic	As <sub>2</sub> O <sub>3</sub>	32	As <sub>2</sub> O <sub>3</sub>	32
Mercury	Hg	14	Hg	14

A fourth factor of importance is total system pressure. From a comparison between conventional pulverised coal combustion and pressurised systems such as PFBC and IGCC it was concluded that a higher pressure allows for a higher temperature for effective trace element removal by the dust control system: at 1 bar, ~ 500EC gives sufficient removal, whilst at 20 bar, ~ 600EC is allowed (Erickson *et al.*, 1996).

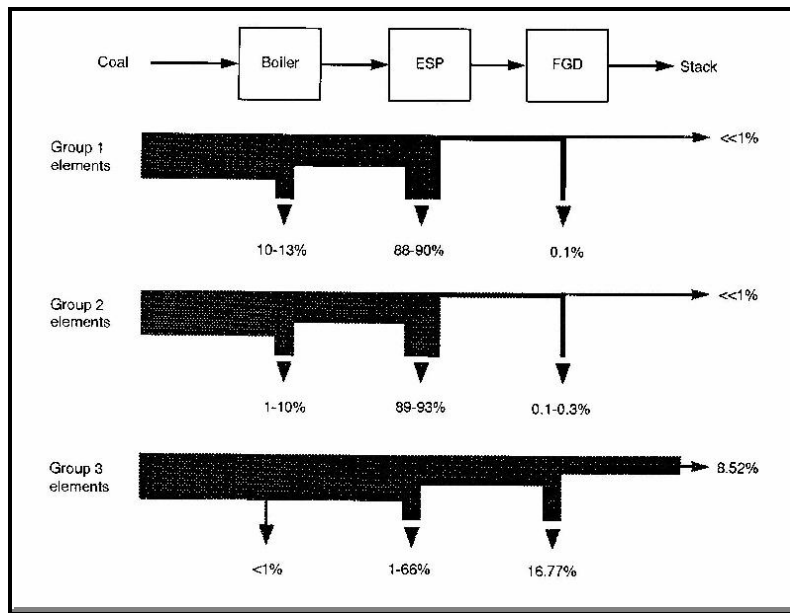


Figure 8.4 Partitioning of trace elements in a pulverised coal combustion plant (Gelderland, the Netherlands) (picture from Couch, 1995)

As an illustration the trace element partitioning in a pulverised coal combustion plant with ESP and (dry) FGD is shown in Figure 8.4. It shows that ~ 90 % of the class (group) I and class II trace elements are collected in the fly ash, and that a significant part of the class III elements, (~ 17%) is removed by the FGD unit.

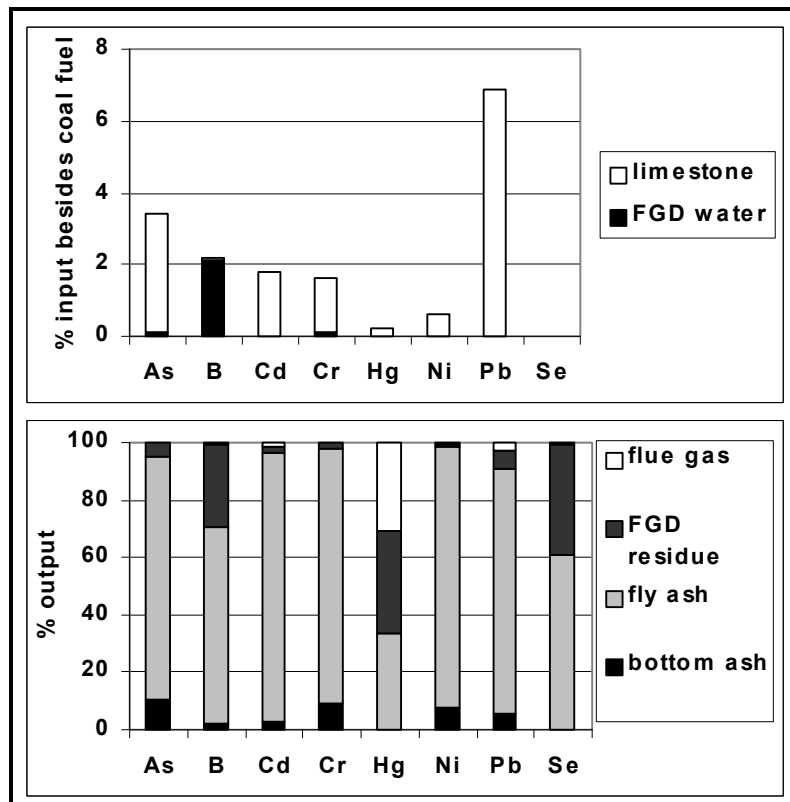


Figure 8.5 Trace element partitioning at a Danish pulverised coal combustion plant (Studstrup 3) (data from Couch, 1995)

A more detailed analysis for eight elements is given in Figure 8.5. Gaseous emissions are significant for Hg, Pb and Cd. Removal by the (wet) FGD unit is significant for Hg, B and Se. As, Cr and Ni behave similarly and are mainly collected in the fly ash. It is also demonstrated that not all trace elements enter the system with the fuel. Some B (boron) enters with the water to slurry the FGD lime. The FGD limestone introduces significant amounts of Pb and other trace elements such as As, Cd, Mn but also Fe, Mg, Si, and Ti (titanium) (Kema, 1997).

Based on the discussion above, the combustion temperature of a waste incinerator, (where power efficiency is not a first objective) can be optimised to give sufficient burnout of the organic waste fraction without excessive vaporisation of trace elements. For conventional pulverised coal combustion with dust control and wet FGD the only species of concern are HgE, HgCl<sub>2</sub>, SeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>, the remainder (mainly Class II elements) is removed by 90-99% (Kema, 1997). Advanced coal technologies show inherently better trace element retention (excluding Hg) as a result of lower temperatures or a different flue/fuel gas treatment. With increasingly powerful hot gas clean-up methods (*e.g.* candle filters, 7 chapter 5.11.2) there is a risk of increased trace element volatiles emissions from IGCC units (Helble, 1996). A US study classified the 11 trace metal HAPs for emission control technology development (for coal) as highest priority for Hg, Se, As, moderate priority for Cd, Sb, Ni and low priority for Cr, Co, Pb, Be, Mn (Senior *et al.*, 1998).

#### 8.4 Emission standards and gas turbine specifications for trace elements

Current emission regulations for trace elements typically do not apply to power plants. Only waste incinerators and cement plants are regulated. Recent developments, however, point to a near-future regulation for mercury for power plants as well (CCT, 2001). Some standards, including the directive suggested recently by the EU are given in Table 8.3 (Finland, 1994, Foster Wheeler, 1997, Werther, 1999). Regulations other than these apply to ferrous and non-ferrous metal industries.

**Table 8.3 Emission standards for trace elements for various processes and locations (MSW = municipal solid waste)**

<b><i>mg/m<sup>3</sup><sub>STP</sub></i> <b>@ 11 % O<sub>2</sub> dry</b></b>	<b>Power plant Finland (1990+)</b>	<b>MSW incinerator Finland (1994)</b>	<b>MSW incinerator EU * (2000)</b>	<b>Power plant Germany (1999)</b>	<b>MSW incinerator Germany (1999)</b>	<b>Waste incinerator USA (1995)**</b>
<b>Hg</b>	no standard	0.05	0.05	no standard	0.03	0.06/0.061 or 85% red.
<b>Cd only</b>						0.03/0.015
<b>Cd + Tl</b>	no standard	0.05	0.05	no standard	0.05	
<b>As+Co+Cr+Cu+Mn +Ni+Pb+Sb+Sn+V</b>	no standard	0.5	0.5	no standard	0.5	
<b>Pb only</b>						0.37/0.15

\* Includes waste co-firing in cement kilns

\*\* Two values: existing / new



Gas turbine manufacturers give regulations for trace elements considering high temperature corrosion, fouling *etc.* Some data from the 1990s are given in Table 8.4.

**Table 8.4 Gas turbine specifications for trace elements in gasifier product gas (data from Alderliesten et al., 1990; Mitchell, 1997)**

Element	Regulation 1 (1990) (ppmw)	Regulation 2 (1997) (ppmw)	Motivation
Na + K	0.06	0.03	hot corrosion
Pb	0.12	1	hot corrosion
V	0.06	0.05	hot corrosion
Ca	1.3	1	fouling
Zn	0.24		affects additives against Vanadium corrosion

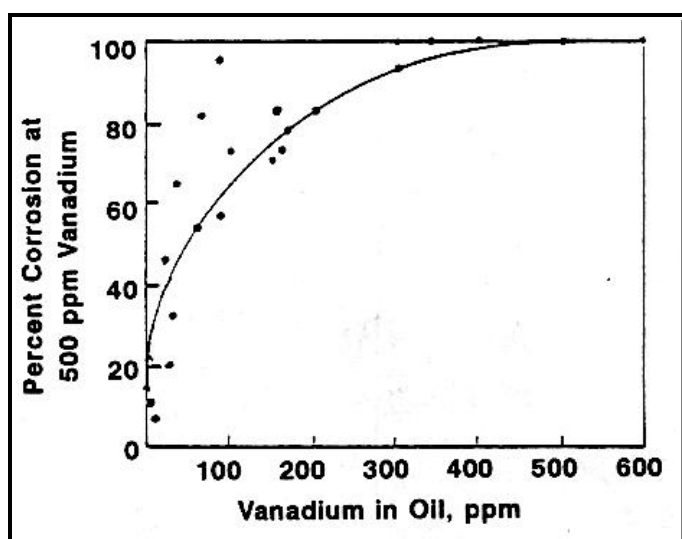
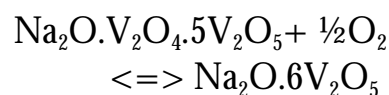
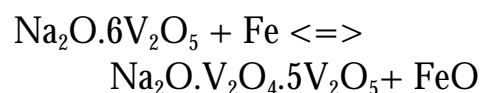


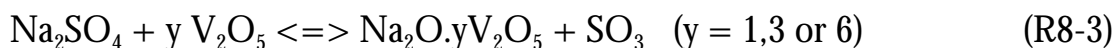
Figure 8.6 Vanadium corrosion by oil ash (picture from Bryers, 1996)

Vanadium, found in coal, pet coke and oil-derived fuels may corrode metals after oxidation to  $V_2O_5$  via a complex chemistry that also involves sodium and the oxidation of  $SO_2$  to  $SO_3$ :



(R8-1,2)

and



Magnesium is used as an additive to inhibit this corrosion, by:

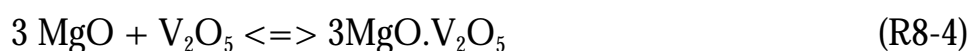


Figure 8.6 shows experimental data on vanadium corrosion by oil ash. More detail on vanadium corrosion and corrosion inhibiting additives is given by Bryers (1996).

### 8.5 Trace elements emissions control (**excl.** mercury)

From the discussion above it can be concluded that the trace elements that are found in fossil fuels and wastes can be grouped into three classes: class III (Hg, Se, As) will pass the gas cleanup devices for dust and sulphur dioxide in significant amounts, class II elements will be retained at 90 - 99% (*e.g.* Pb, Cd, Sb, Ni), whilst class I elements are removed by the dust control system at more than 99% with the particulates. Based on this the systems used for trace element control can be divided in two groups: 1) systems based on trace element removal in the equipment for particulate or SOx control, and 2) systems specifically designed for the removal of trace elements. In general NOx control systems have little influence on trace element behaviour or removal (CIEMAT, 1998). As, however, is a poison for SCR catalysts (Kema, 1997).

Most fossil fuel-fired facilities belong to the first group, relying on their dust and SOx control system for trace element control, and on the use of additives such as MgO against vanadium corrosion, *e.g.* when firing heavy fuel oil or Orimulsion™.

**Table 8.5 Trace elements emissions from several coal, peat or oil-fired power plants (data from Huotari and Vesterinen, 1995).**

Process	Heavy fuel oil spray combustion	Pulverised peat combustion	Grate peat combustion	Pulverised coal combustion	Circulating FBC peat
Particulate control system efficiency, %	-	98.7 - 99.5	59 - 81	95.6 - 99.5	99.5 - 99.8
Emissions, µg/MJ					
Hg	0.0011	0.11	0.10	0.12	0.03
As	1.5	< 1.5 - 2.3	2 - 10	2 - 39	< 0.1 - 1.6
Be	< 0.004	0.05	0.1 - 1.5	5	0.01 - 0.3
Cd	0.008	< 0.002 - 0.13	0.8 - 4	0.5 - 1.8	0.1 - 0.4
Co	3	0.3 - 1.2	0.06 - 0.2	1 - 22	0.3 - 4
Cr	3	3 - 79	0.6 - 3	8 - 230	0.7 - 1.3
Mn	< 14	10 - 26	17 - 31	2 - 230	0.6 - 6
Mo	3	< 1 - 11	< 0.07 - 0.9	< 1 - 41	< 1.5 - 2.3
Ni	310 - 540	< 33 - 54	< 1 - 5	< 15 - 170	9 - 13
Pb	5	3 - 4	40 - 200	20 - 120	1 - 11
V	1300	4 - 6	0.7 - 7	10 - 88	9
Zn	15	< 6 - 12	7 - 37	20 - 220	1 - 11

Trace element emissions from some large scale (35 - 600 MW<sub>thermal</sub>) coal, peat and heavy fuel oil-fired power units are listed in Table 8.5.

A widely used method to control trace elements is by pre-cleaning (“washing”) the fuel. Removal of pyrite (FeS<sub>x</sub>) during the milling of coal will also remove As, Se and significant amounts of Hg from the fuel. Miller *et al.* (1998) showed that especially the elements related to sulphide minerals (pyrite, sphalerite) can be largely removed by coal pre-cleaning: As, Cd, Co, Cu, Hg, Mo, Ni, Pb, Se, and Zn.

ESP and baghouse filter removal efficiencies are of the order of 99-99.9 % for most trace elements (Takeshita, 1994, Ruth, 1998) being of the order 95-99 % for some Class II elements, such as Pb, Cd, Ni, Mn, and less for the Class III elements. Trace elements that are not removed by an ESP or bag house filter may be removed downstream by a wet or dry scrubber for SO<sub>2</sub> control. One benefit is the lower temperature (60-70EC for a typical wet FGD); also some sub-micron particles that passed the ESP or baghouse filter may be removed. Typical data for the removal of some trace elements (from pulverised coal firing) by wet FGD are given in Table 8.6.

**Table 8.6** Typical removal efficiency for volatile trace elements by FGD downstream of particulate control. (data from Kema, 1997)

	Removal efficiency %	Outlet concentration µg/m <sup>3</sup> <sub>STP</sub>
Hg	~ 50	~ 1.5
Se	~ 60	~ 10
Be	~ 80	~ 250
Fly ash	90 ~ 99	1000 ~ 10000

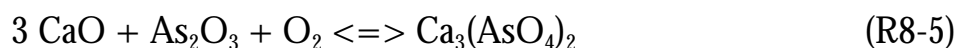
For waste incineration flue gases it is often needed to install extra equipment to control the emissions of Pb, As, Se and Cd, and of course Hg. (Mercury will be discussed separately in the next section). For this purpose sorbents such as activated carbon, aluminum silicates or clay can be used, injected into the gas phase, to be removed in the dust control system, or in a separate reactor such as the STEAG a/c/t<sup>TM</sup> process (Brüggendick and Gilgen, 1996) in Figure 6.4. Large amounts of sorbent are needed to compensate for often low removal efficiencies.

A list of sorbents by Mojtahedi and Mroueh (VTT, Finland) for trace elements is summarised in Table 8.7. For large scale applications their application suffers from excessive costs, the low operating temperature or other side-effects (CIEMAT, 1998).

**Table 8.7 Sorbents for the removal of trace element from gas streams (after data in CIEMAT, 1998)**

Sorbent	Element	Temperature range
<b>Based on zeolites</b> - impregnated with sulphur - impregnated with iodides - Ag and Hg ion exchanged	Hg	low temperatures, up to 400EC
<b>Based on activated carbon</b> - activated carbon - activated carbon impregnated with sulphur, chlorine, iodides - oxidised activated carbon	Hg  at higher temperatures also Cd, Pb	low temperatures, up to 300EC
<b>Siliceous materials</b> - Mg, Ca, Al silicates - Mixed silicates, silicate -fly ash mixtures, impregnated siliceous materials	V, Pb, Ni, Zn  at low temperatures also Hg, Cd	high temperatures 600-1000EC  low temperatures <i>e.g.</i> < 100EC
<b>Based on alumina</b> - activated alumina gel, - alumina coated steel wool, - alumina impregnated with alkali carbonate or phosphate	Pb	at up to 700EC
<b>Calcium compounds</b> - hydrated lime/fly ash - limestone/fly ash, limestone/silica - hydrated lime + Sn, limestone, calcium chloride	Hg, Zn, V, Ni at low temperature  As at high temperature	Hg at up to 300-400EC,  V, Ni, As at high temperatures
<b>Other materials</b> - MgO, Mg(OH) <sub>2</sub> , - Cr, Ni compounds - Fe compounds, <i>e.g.</i> blast furnace dust	Hg, V, Ni, Pb, As	V, Ni at up to 550EC  As at high temperatures

Arsenic (As) and selenium (Se) may be removed by calcium. For fuels or waste mixtures with more than 0.1 % Ca (and with oxygen in the gas phase !), As is almost completely scavenged as calcium arsenate (Kema, 1997):



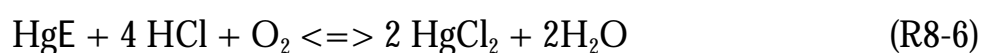
Se and As can be removed from flue gases at 350-600EC by calcium based sorbents, forming  $\text{CaSeO}_3$  and  $\text{Ca}_3(\text{AsO}_4)_2$  provided that  $\text{SO}_2$  has been removed to low concentrations upstream, to prevent competitive sulphation of the sorbent (Ghosh-

Dastidar *et al.*, 1996). Thermodynamic calculations and experimental work showed that at low temperature the major Se species in typical flue gases are H<sub>2</sub>Se and SeCl<sub>2</sub>, at higher temperatures S, Se and SeO<sub>2</sub> (Yan *et al.*, 2001). Se can be removed from gases by activated carbon at 125-250EC. Removal efficiency increases with gas moisture content (Se reacting with the sorbent as H<sub>2</sub>SeO<sub>3</sub>) and internal surface of the sorbent but decreases with temperature, indicating a physisorption mechanism (Agnihotri *et al.*, 1998).

Sorbents such as silica, alumina, kaolinite, limestone, emathlite, bauxite, titania have been widely tested for trace elements control at 400-1000EC, by direct injection into the gas or in packed or fluidised beds. Based on thermodynamic calculations (covering 400-1400EC), alumina may be a good sorbent for As, Be and fairly active for Cd and Ni, silica may be a good sorbent for Cd, Pb and Hg, whilst titania may be a good sorbent for Cd and Pb. Experiments with kaolinite injection showed a high removal efficiency for Pb, which was much less active when excess chlorine was present. Other tests showed that kaolinite effectively removes Ni, Cd and Pb, again limited by presence of chlorine. Also limestone can be used to capture Pb and Cd species, and Sb, Hg, Se and As as well (Biswas & Wu, 1997).

## 8.6 Mercury emissions control

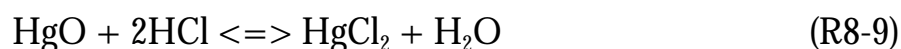
Mercury (Hg), a metallic liquid at ambient conditions, is very problematic owing to its toxicity and its volatility (boiling point 357EC). In combustion or gasification plants typically less than 10% of the incoming Hg is found in fly ashes and other gas cleanup residues, whilst more than 90% may be released as vapour via the stack. Hg release from fuels may start at ~ 150EC, mainly as HgE, HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub> and HgS, being almost complete at 500 - 600EC (Galbreath and Zygarlicke, 1996, Merdes *et al.*, 1998). At high temperatures HgE is the thermodynamically stable form in flue gases and gasifier product gases. Under oxidising conditions, in the presence of HCl and Cl<sub>2</sub>, HgE is oxidised to HgCl<sub>2</sub> at 300-400EC, *e.g.* by :



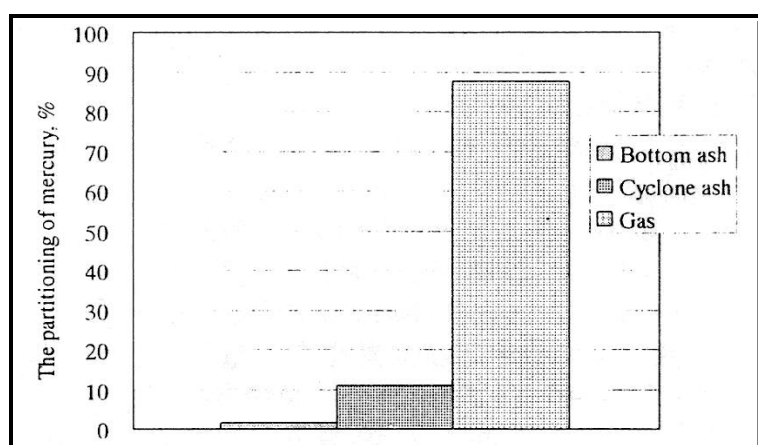
Elemental mercury may also be oxidised by NO<sub>2</sub> (Brown *et al.*, 1999, Schager, 1990):



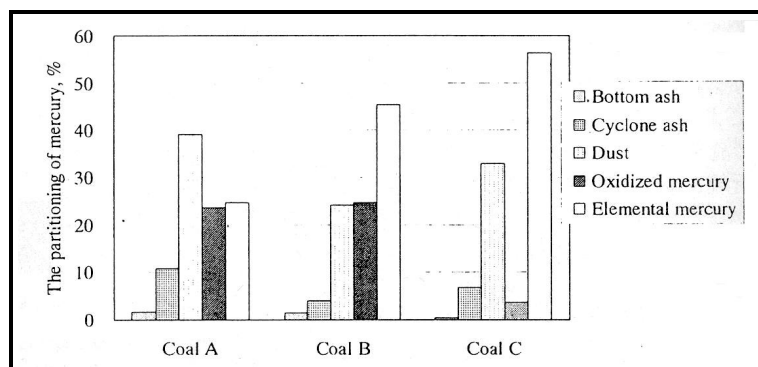
which will, again, form  $\text{HgCl}_2$  at temperatures below 450EC:



Elemental mercury is also oxidised to  $\text{Hg}^{2+}$  by SCR catalysts: measurements showed that 51% and 28% of the total mercury was present in the gas as HgE before and after an SCR unit, respectively (Kema, 1997).



**Figure 8.7** Partitioning of coal mercury into bottom ash, fly ash and flue gas in lab.scale pulverised coal combustion (picture from Tsuji *et al.*, 2000)



**Figure 8.8** Partitioning of coal mercury into ashes, flue gas dust and oxidised and elemental flue gas mercury during lab.scale pulverised coal combustion (picture from Tsuji *et al.*, 2000)

An example of fuel Hg partitioning over fly ash, bottom ash and exhaust gas is shown in Figure 8.7 for pulverised coal combustion. Further analysis of the exhaust gas shows that three different mercury species must be considered: gaseous, elemental mercury (HgE), gaseous, oxidised mercury ( $\text{HgCl}_2$ , HgS, HgO,  $\text{HgSO}_4$  *etc.*) and particle-bound mercury (Hg-p). For three coals, this speciation of the flue gas mercury is shown in Figure 8.8. It is observed that 40-60% of the fuel mercury is released as HgE vapour.

In the atmosphere the emitted particulate mercury (Hg-p) is deposited slowly within a few kilometers from the emission source. The oxidised, gaseous mercury,

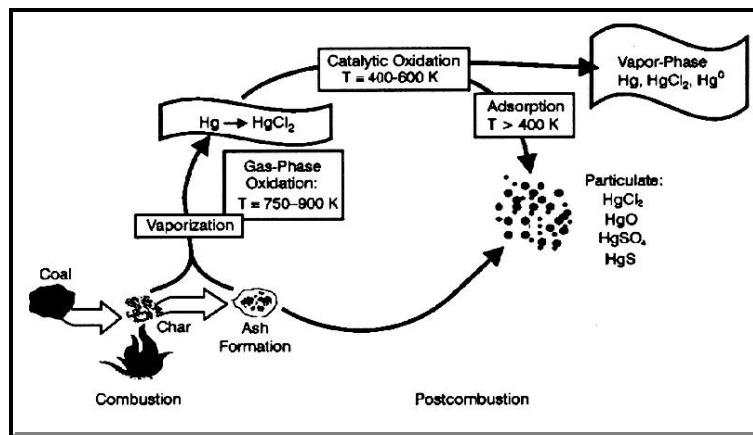
mainly  $\text{HgCl}_2$ , is very well soluble in water and rapidly forms the highly toxic methyl mercury in aquatic environments. It enters the food chain through fish rather close to where it was emitted into the atmosphere. Elemental mercury vapour is very stable and can travel long distances, forming a global problem (Sheu and Mason, 2001).

**Table 8.8 Mercury emissions from several US coal-fired boilers in mg/GJ. 1 GJ ~300 m<sup>3</sup><sub>STP</sub> flue gas. (table from Podolski et al., 1995)**

Boiler type	Coal		
	Bituminous	Sub-bituminous	Lignite
<i>Utility</i>			
Pulverized-coal dry-bottom			
Uncontrolled	1.7-133	—	—
With multiclone	—	—	1.9-2.8
With ESP	0.17-9.5	1.8	<0.1
Pulverized-coal wet-bottom			
Uncontrolled	—	—	—
With ESP	1.1-2.7	—	—
Cyclone furnace			
Uncontrolled	4.3	35	—
With scrubber	—	2.1	—
With ESP	1.7-7.7	—	0.63
With cyclone	—	—	9.5
Spreader-stoker			
Uncontrolled	—	—	—
With multiclone	—	—	2.4
With ESP	—	—	0.23
<i>Industrial</i>			
Pulverized-coal dry-bottom			
Uncontrolled	1.81-1.89	—	—
With ESP	—	—	—
Spreader-stoker			
Uncontrolled	0.3-5.2	0.26-7.3	—
With multiclone	2.5-10.8	—	—
With ESP	0.43-1.8	—	—
With cyclone/ESP	—	0.2-0.3	—
Overfeed stoker			
Uncontrolled	0.0043-0.91	—	—
Dust collector	0.17-0.52	—	—

Table 8.8 lists mercury emissions from US coal fired boilers, for bituminous coals, sub-bituminous coals and lignites containing < 0.01-3.3, 0.01-8 and 0.03-1 mg Hg/kg fuel, respectively. This explains at least partly the deviations in Table 8.8. Another explanation may be the difficulties in producing reliable measurement data.

Hence, one conclusion may be that the uncontrolled emissions from coal-fired power plants for electricity generation are ~0.5 kg/MW<sub>elec</sub> plant size per year (Podolski et al., 1995).



**Figure 8.9** Most probable mercury-species transformations during pulverised coal combustion (picture from Brown et al., 1999)

An overview of the most important Hg-species transformations in the gases from coal firing is shown in Figure 8.9. For waste incineration this will be similar, with Cl and Hg concentrations being significantly higher.

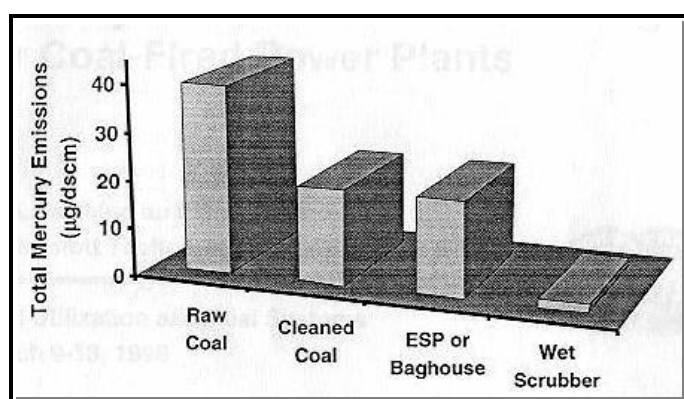
(Mukherjee et al., 2000), i.e. the concentrations leaving the furnace, entering the flue gas duct are of the order 5-50 µg/m<sup>3</sup><sub>STP</sub>. For a waste incineration processes the raw flue gas concentration of Hg is at least one order of magnitude higher, say, up to 1 mg/m<sup>3</sup><sub>STP</sub> (Krishnan et al., 1997, Saenger et al., 1999b). Thus, an emission regulation

An estimation for Hg emissions from a coal-fired power plant is 1-10 µg/m<sup>3</sup><sub>STP</sub>

of  $0.05 \text{ mg/m}^3_{\text{STP}}$  (at 11% oxygen, dry) enforces a removal efficiency of  $\sim 90\%$ . This task is further complicated by the fact that three Hg species must be considered: 1) gaseous HgE which is not soluble in water, 2) gaseous oxidised mercury, mainly  $\text{HgCl}_2$  which is very well soluble in water and 3) particle-bound mercury, Hg-p.

Fuel cleaning is a first step in Hg emissions control. Processing household wastes and municipal solid waste into refuse-derived fuel will lower the mercury content (removing batteries, electric and electronic equipment, lamps *etc.*). Coal cleaning efforts resulted in a decrease of  $\sim 37\%$  on average in the Hg concentration of US coals (Brown *et al.*, 1999).

Dust control systems reduce Hg emissions to some extent, with further removal by the control system for  $\text{SO}_2$ . The vast majority of pulverised coal combustion plants have a cold-side electrostatic precipitator, ESP (7 chapter 5) as the only emissions control device, although there is a trend to install more baghouse filter systems. Typical Hg removal efficiencies for emission control equipment at US coal fired power plants are 4% for a particulate control scrubber, 32% for an ESP and 44% for a fabric filter baghouse. Comparing wet and dry FGD shows typical numbers of 34% Hg removal for a wet scrubber FGD and 30% for dry FGD with injected sorbent collection on a fabric filter (Brown *et al.*, 1999).



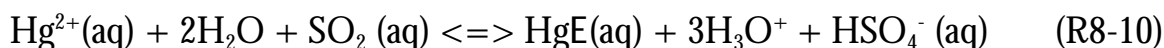
**Figure 8.10** Mercury emissions control for a coal-fired flue has with dust control and wet FGD scrubber (dscm=dry standard cubic feet per minute) (picture from Farthing and Holmes, 1998)

In some cases, such as shown in Figure 8.10, no Hg reduction of any significance is obtained with an ESP or a baghouse filter. The somewhat higher Hg removal efficiency of a filter system as compared to an ESP is the result of interactions between gas phase mercury and particulate matter such as fly ash dust cakes in filter systems.

In wet FGD systems the low temperature may condense Hg from the volatile phase and thus remove it from the gas stream - see Figure 8.10. The most important form of oxidised mercury,  $\text{HgCl}_2$ , is well soluble in water. At the same time, concentrations of HgE vapor were found to increase when passing a wet FGD scrubber. This may be due to the reduction of  $\text{Hg}^{2+}$  in dissolved  $\text{HgCl}_2$  to the less



soluble HgE by SO<sub>2</sub> oxidation, which is inhibited by very strong acidic solutions (pH < 3) (Krissmann *et al.*, 1998):



Several methods for the removal of oxidised and elemental gas-phase Hg, downstream of an ESP for particulate control, are being applied in Germany at several fluidised bed incinerators for sewage sludge containing 1-4 mg/kg (dry) Hg (Saenger *et al.*, 1999a,b). At these plants, Hg is trapped in scrubbers and adsorbers. Oxidised Hg is effectively removed by dissolving in a wet scrubber (operated at pH ~ 1) liquid that is basically used for the removal of HCl, or in the FGD scrubber by using a Hg precipitation agent such as TMT (trimercapto-s-triazine) or Na<sub>2</sub>S<sub>4</sub>. In those cases where the removal of oxidised Hg is not sufficient and elemental Hg has to be removed as well, the elemental Hg is oxidised by an oxidising agent such as sodium chlorite, or (again) Na<sub>2</sub>S<sub>4</sub>. The principles of these processes are summarised in Table 8.9.

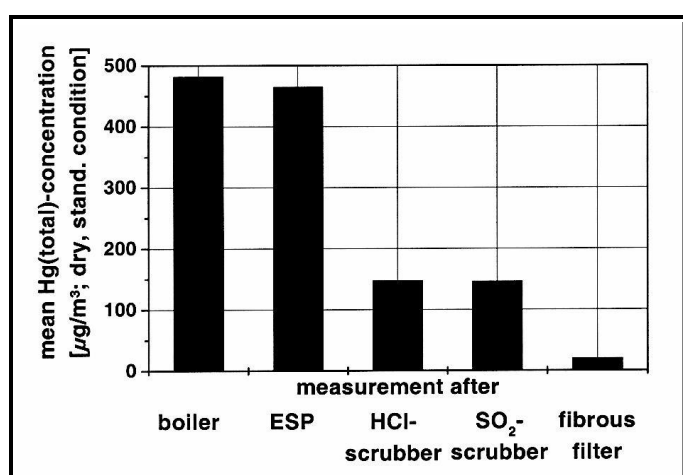


Figure 8.11 Hg removal in ESP, HCl scrubber and fibrous filter for sewage sludge incineration flue gas (picture from Saenger *et al.*, 1999b)

Also listed in Table 8.9 are processes based on trapping elemental carbon on activated carbons that are saturated with sulphuric acid, H<sub>2</sub>SO<sub>4</sub>. In these cases oxidised Hg is captured also: it dissolves in the sulphuric acid (Saenger *et al.*, 1999a,b).

A typical result of Hg removal from sewage sludge incineration is shown in Figure 8.11. Hg is controlled by Na<sub>2</sub>S<sub>4</sub> injection between the ESP and the HCl scrubber, in addition a mixture of

activated carbon (5-15%-wt) and hydrated lime (85-95%-wt) is injected between the SO<sub>2</sub> scrubber and a fibrous filter. In this process, the Hg concentration is reduced from 0.5 - 0.95 mg/m<sup>3</sup><sub>STP</sub> to 0.035-0.2 mg/m<sup>3</sup><sub>STP</sub> after the first scrubber and finally 0.007-0.04 mg/m<sup>3</sup><sub>STP</sub> after the fibrous filter, giving a total Hg removal efficiency of ~ 97%. The removal efficiency of the ESP for Hg is only ~ 4%. A small problem with this process set-up is that some H<sub>2</sub>S is carried over from the HCl scrubber to the SO<sub>2</sub> scrubber that cause precipitation of Hg and some other heavy metals.

**Table 8.9 Options for removal of oxidised and/or elemental mercury from flue gases (from sewage sludge incineration) downstream of an ESP (data from Saenger et al., 1999a,b)**

Hg/ Hg <sup>2+</sup>	Agent / sorbent	Equipment	Chemistry	R8 -
Hg <sup>2+</sup>	water / HCl	Acid wet scrubber for HCl	HgCl <sub>2</sub> is dissolved in HCl scrubber liquid	
Hg <sup>2+</sup>	TMT	Wet scrubber for SO <sub>2</sub>	$3 \text{Hg}^{2+} + 2 \text{TMT}^{3-} \Rightarrow \text{Hg}_3(\text{TMT})_2 (\text{s})$	11
Hg	Sodium chlorite	Acid wet scrubber for HCl	$4\text{HCl} + 5\text{NaClO}_2 \Rightarrow 4\text{ClO}_2 + 5\text{NaCl} + 2\text{H}_2\text{O}$ $2\text{ClO}_2 + 5\text{HgE} + 8\text{HCl} \Rightarrow 5\text{HgCl}_2 + 4\text{H}_2\text{O}$	12 13
Hg & Hg <sup>2+</sup>	Na <sub>2</sub> S <sub>4</sub>	Acid wet scrubber for HCl	$\text{HgCl}_2 + \text{Na}_2\text{S}_4 \Rightarrow \text{HgS} + 3 \text{S} + 2 \text{NaCl}$ $\text{HgE} + \text{Na}_2\text{S}_4 \Rightarrow \text{HgS} + \text{Na}_2\text{S}_3$ $\text{Na}_2\text{S}_4 + 2 \text{HCl} \Rightarrow \text{H}_2\text{S} + 3 \text{S} + 2 \text{NaCl}$ $\text{HgCl}_2 + \text{H}_2\text{S} \Rightarrow \text{HgS} + 2 \text{HCl}$ $\text{HgE} + \text{S} \Rightarrow \text{HgS}$	14 15 16 17 18
Hg & Hg <sup>2+</sup>	SO <sub>2</sub> + activated carbon for HgE  TMT for Hg <sup>2+</sup>	Carbon injection, spray dryer for TMT, second ESP, acid wet scrubber	On activated carbon: $\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{SO}_4 (\text{ads})$ $\text{H}_2\text{SO}_4(\text{ads}) + 2\text{Hg} \Rightarrow$ $\text{Hg}_2\text{SO}_4(\text{ads}) + 2\text{H}_2\text{O} + \text{SO}_2$ $\text{Hg}_2\text{SO}_4(\text{ads}) + \text{H}_2\text{SO}_4(\text{ads}) \Rightarrow$ $\text{HgSO}_4(\text{ads}) + 2 \text{H}_2\text{O} + \text{SO}_2$	19 20 21
Hg	sulphur impregnated carbon	Carbon injection after acid wet scrubber, baghouse filter	see above	
Hg & Hg <sup>2+</sup>	selenium impregnated mineral	Fixed bed adsorber after acid wet scrubber	$\text{Hg} + \text{Se} \Rightarrow \text{HgSe}$ $\text{Hg}^{2+} + \text{Se}^{2-} \Rightarrow \text{HgSe}$	22 23

In short, the three most important methods used for mercury capture from waste incinerator flue gases are 1) the acid scrubber for HCl, 2) addition of an oxidising agent and wet scrubbing and 3) addition of an oxidising agent and adsorption on an impregnated activated carbon. Some other processes use modified zeolites as a sorbent; in the MercOx process oxidation of HgE with H<sub>2</sub>O<sub>2</sub> is applied.

For power plant firing coal, lignite or peat, the control of mercury may present a serious and expensive problem for the near future. Implementation of Hg regulations for coal-fired power plants as of 2003 - 2004 by the USA EPA (CCT, 2001) will certainly be followed by the rest of the (developed) world. When compared

to Hg emission control for the waste handling sector several disadvantages have to be dealt with by the heat and power sector. First, flue gas streams are much larger and Hg concentrations are much lower, being of the order of 0.01 ppmw. Secondly, due to a lower Cl/Hg ratio the fraction of oxidised Hg is smaller, emphasising the problem of trapping elemental Hg. Similar to waste-derived Hg also for coal it was found that > 50 % of the Hg is in the HgE form when the chlorine content of the fuel or waste is < 0.1 %-wt, whilst less than 20% of the Hg is found as HgE in the flue gas when the chlorine content of the incoming material is above ~ 0.2 %-wt (Kema, 1997, Zaenger *et al.*, 1999b). Third, there is no acid scrubber for HCl control at power plants. As a fourth factor, due to the large gas volumes and flue gas velocities the residence time in flue gas clean-up equipment is very short, for example ~ 1 second for an ESP operated at ~ 150EC. As a result, the removal of Hg from power plant flue gases will have to depend mainly on activated carbons that will have to be injected in flue gas ducts or used in packed beds (7 Figure 6.4) at C/Hg mass ratios of the order of 5000 - 100000, depending mainly on the temperature (Brown *et al.*, 1999, Meserole *et al.*, 1999, Krishnan *et al.*, 1997). As will be shown below, also this suffers from some disadvantages specific for flue gases from fossil fuel fired power plants, such as the presence of SO<sub>2</sub> and NO<sub>2</sub>.

Experiences with MSW incineration have shown that activated carbon (AC) injection allows for Hg emission reductions above 90 %. For the much lower concentrations of Hg in flue gases from power plants the adsorption of Hg by ACs suffers from mass

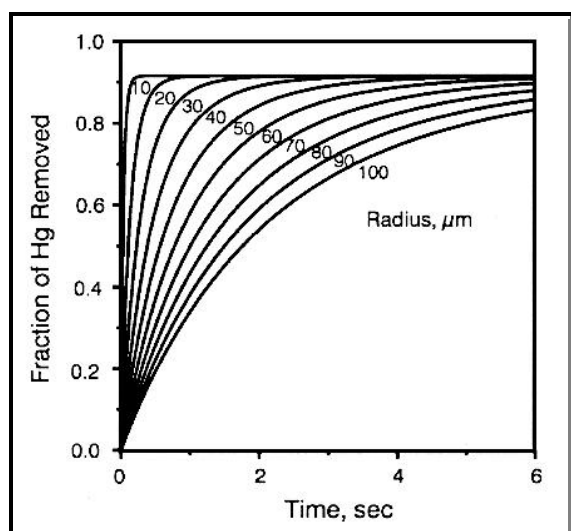


Figure 8.12 Removal of mercury (inlet 20  $\mu\text{g}/\text{m}^3$ ) with activated carbon at 140EC: effect of particle size and residence time (picture from Brown *et al.*, 1999)

transfer limitations and/or a low capacity of the AC as a result of low Hg concentration or low AC reactivity (Chen *et al.*, 1996, Meserole *et al.*, 1999). As for the mass transfer, it can be shown that at ~ 140EC it shows a minimum value for AC particle size sizes of ~200  $\mu\text{m}$  due to the combined effects of diffusion and forced convection (Brown *et al.*, 1999). For AC sorbent particles ranging from 1 to 100  $\mu\text{m}$ , the removal of Hg from a flue gas at 140EC is illustrated by Figures 8.12 and 8.13. Sorbent particles larger than ~20  $\mu\text{m}$  may be too large, presenting too little outer surface for mass transfer. Typical contact times needed are 1-2 seconds.

At high temperatures ( $> 180\text{EC}$ ) the capacity or reactivity of the AC may become limiting (Chen *et al.*, 1996). When the AC is injected upstream of an ESP the Hg removal efficiency is much lower than with injection upstream of a baghouse filter because of 1) a shorter contact time between the particles (collection can continue in the filter cake) and 2) carbon particles may not be removed from the flue gases by an ESP due to a too low particle resistivity (7 chapter 5) (Krishnan *et al.*, 1999).

There are large differences as to how elemental and oxidised Hg are bound on ACs. It is assumed that the elemental Hg is eventually oxidised after adsorption. The fact that the removal of Hg increases with decreasing temperature indicates physisorption as the capture mechanism. For example, at  $\sim 180\text{EC}$ ,  $\sim 150\text{EC}$  and  $\sim 130\text{EC}$  typical C/Hg mass ratios needed for 50-80% Hg removal are  $\sim 50000$ ,  $\sim 10000$  and  $\sim 4000$  kg/kg, respectively.

For power plant flue gases one problem is that many other species are adsorbed by the AC as well, such as  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , HCl, dioxins/furans, PAHs, and other trace elements. The combination  $\text{NO}_2 + \text{SO}_2$  has a very negative effect on mercury adsorption, whilst absorbed HCl supports the transition from physisorbed elemental Hg to stronger bound chemisorbed Hg.

Much higher Hg removal is achieved with ACs that are impregnated with sulphur, iodide or chlorine. In sulphur-impregnated ACs, Hg is strongly bound as  $\text{HgS}$ . Sorption capacities may be 2-3 orders of magnitude higher than those of "virgin" ACs, especially when the sulphur impregnation is carried out at high temperatures. (Vidic *et al.*, 1998). Iodide-impregnated ACs show the best performance, forming stable Hg-I complexes (Brown *et al.*, 1999).

The many disadvantages related to the use of ACs has led to the development of Hg sorbents based on metal oxides, silicates, fly ashes *etc.* Metal oxides such as  $\text{MnO}_2$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{MoS}_2$  showed moderate capacities, making them possible alternatives for

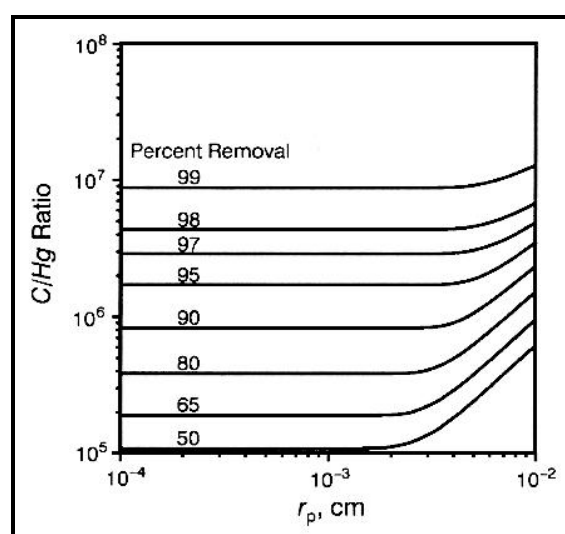


Figure 8.13 Removal of mercury (inlet  $20 \mu\text{g}/\text{m}^3$ ) with activated carbon at  $140\text{EC}$ : effect of particle size and C/Hg ratio (picture from Brown *et al.*, 1999)

activated carbons (Granite *et al.*, 2000, 1998). The latter explains recent findings on Hg emissions from a Finnish cement plant: replacing ~10% of the coal/petcoke fuel with the alternative fuel car tyre scrap showed a reduction of Hg emissions with ~90%, apparently due to the Mn and Cr that is introduced to the system with the car tyres (Mukherjee *et al.*, 2001).

Fly ashes may also absorb or adsorb Hg, at very small amounts, though, when considering the amount of carbon in fly ashes. There is no simple relation between the Hg-sorbing capacity and the carbon content of ashes (Hassett and Eylands, 1999, Sakupitakphon *et al.*, 2000). Temperature, gas phase composition and the original fuel have a large effect on Hg sorption.

Recently, Reed *et al.* (2001) reported that carbonaceous dust from a coal gasifier showed “substantial capacity” for Hg capture in a hot gas filter operated below 200EC. Hg was found to be chemisorbed as HgS. Loadings of ~ 0.03 mg/g filter fines were obtained, meaning that ~ 10% of the hot gas filter fines would suffice to absorb all of the HgE from the gasifier fuel gas in a low temperature mercury filter/adsorber. In gasifier product gas oxidised Hg is present as HgS (after reaction with H<sub>2</sub>S) and HgCl<sub>2</sub>; CO and H<sub>2</sub> reduce significant amounts of oxidised Hg to HgE.

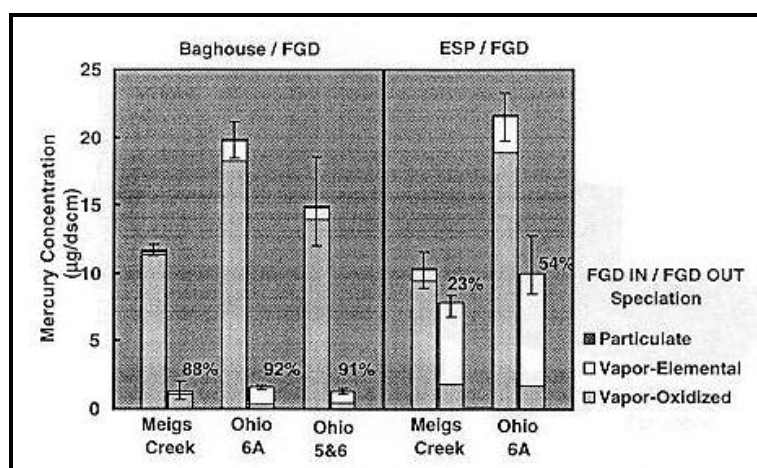


Figure 8.14 Mercury speciation and removal by a baghouse/FGD or ESP/FGD from several facilities (dscm=dry standard cubic feet per minute) (picture from Farthing and Holmes, 1998)

A last feature is related to the removal of Hg in FGD systems that are operated downstream of baghouse filters or ESPs, for particulate control, respectively. Figure 8.14 shows that Hg removal efficiencies of 88-92% were obtained at coal-fired power plants with a baghouse/FGD combination, against 23-54% when operating with an ESP/FGD combination. It is also seen that concentrations

of HgEvapour are higher at the exit of the combination ESP/FGD. Apparently, in the ESP oxidised Hg is reduced to HgE, which cannot be trapped in the FGD downstream (Farthing and Holmes, 1998).

## 8.7 Alkali in fuels

Alkali is found in fossil fuels as organically bound sodium (Na) and potassium (K) and salts such as chlorides and (alumino)silicates, dispersed in the mineral. In wood and other biomasses potassium is found especially in fast growing parts of trees and in grasses. Sodium is often incorporated as sandy inclusions or as NaCl from seawater. Much of this alkali is present in water-soluble or ion-exchangable forms. Straw harvested after a wet summer contains significantly lower alkali. Typical levels of K in biomasses such as straw are five times those found in coal, Na concentrations are usually higher in coal than in biomass (Bryers, 1996, Davidson, 1997). RDF contains some alkali as salts and wood particles, alkali in sewage sludge is related to salts, fertilisers *etc.* Surprisingly high concentrations of alkali are found in auto shredder residue (ASR). Black liquor is a very high alkali fuel owing to the paper pulping process it derives from. Recovery of sodium salts as  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$  is a primary objective of black liquor recovery boilers.

**Table 8.10 Alkali concentrations in some fossil fuels and waste-derived fuels (in mg/kg, i.e. ppmw, dry)**

	Coal	Lignite	Peat	Orimul-sion™	Wood saw dust	Straw	RDF	Auto shredder res.	Scrap tyres	Sew. sludge	Black liquor solids
Na	100 - 1500	100 - 300	~ 400	~ 2000	~ 40	100 - 5000	3000 - 5000	~ 10000	200 - 600	~ 2000	15 - 20 %
K	50 - 3000	100 - 1000	~ 700	~ 300	~ 500	5000 - 10000	2000 - 3000	~ 3000	200 - 600	~ 6000	~ 1 %

Alkali compound vapors may cause hot corrosion on the surfaces of expansion turbine blades, which resulted in a concentration limit of 0.024 ppmw, later 0.1 ppmw Na+K. In biomass-fired plants, relatively large amounts of alkali cause problems such as slagging (formation of sintered deposits on heat transfer surfaces or refractories subjected to radiative heat transfer), fouling (deposition of ash on the convective heat transfer section of the steam generator at temperatures below the melting point of the ash) and corrosion (Andersen *et al.*, 2000, Bryers, 1996).

## 8.8 Alkali in flue gases and fuel gases

According to Lee *et al.*, (1993, 1992), studying PFBC of Illinois coal, sodium vapours result from direct vaporisation of NaCl at PFBC conditions (900-950EC, ~ 10 atm).

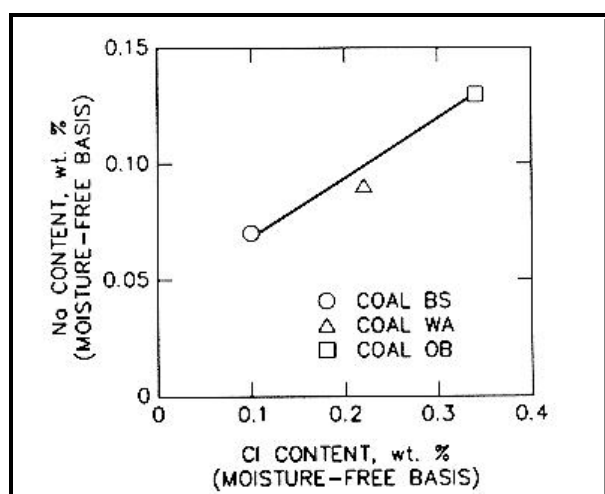


Figure 8.15 Relation between Na and Cl in Illinois coals (picture from Lee *et al.*, 1992)

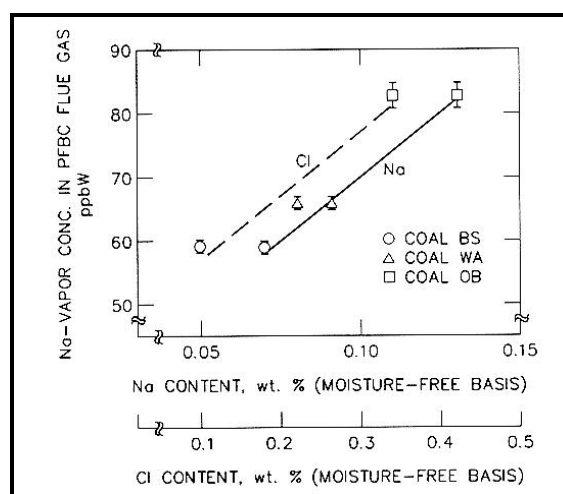


Figure 8.16 Na vapor in PFBC flue gas versus Na and Cl in Illinois coal (picture from Lee *et al.*, 1992)

The correlation between Na and Cl is shown in Figure 8.15, being the result of the salinity of the ground water at the coal seam. Since K is present mainly as non-volatile aluminosilicates, Na was found to be the major alkali species in the gas phase (Na/K mass ratio = 6 - 40). Measured values for alkali vapour in PFBC flue gases show values of 67-90 ppb Na+K (Lee *et al.*, 1992). Later work showed that alkali vapour concentrations are negligible at temperatures below 700°C (Lee *et al.*, 1993).

According to Srinivasachar *et al.* (1990), NaOH and NaCl are the most important vapor phase species whilst silicates and sulphate will dominate the solid phase in an oxygen-rich post-combustion zone. Under the high temperature, reducing conditions

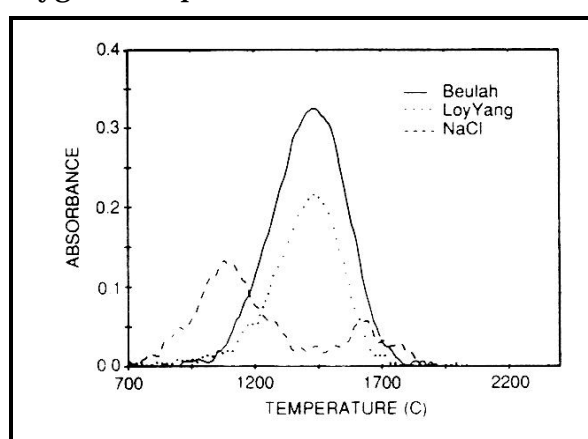


Figure 8.17 Na release from NaCl and from two coals during heat-up (picture from Srinivasachar *et al.*, 1990)

in a flame, elemental Na is the most common species, except for high chlorine coal. They also analysed the release of Na from two types of coal during heat-up, and compared it to Na release from NaCl, as shown in Figure 8.17. Clearly (and in disagreement with the work of Lee *et al.* discussed above) Na was not released as NaCl but as atomic Na as a decomposition product of clay minerals.

A summary of sodium behaviour during coal combustion is given in Figure 8.18.

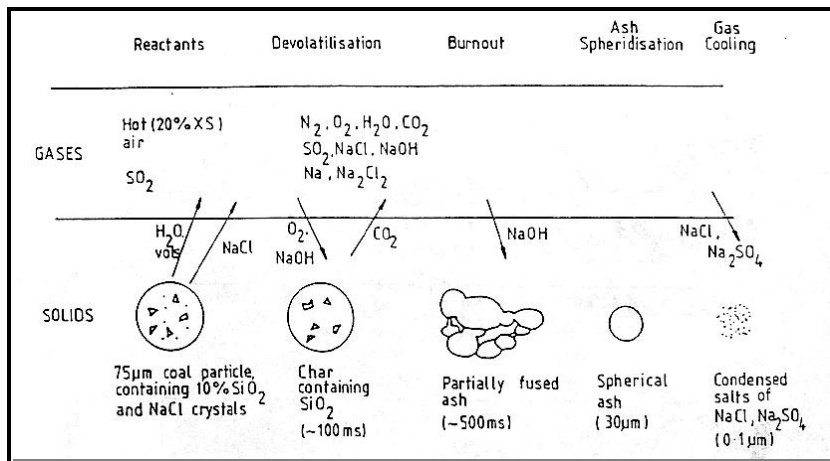


Figure 8.18 Sodium behaviour during pulverised coal combustion (picture from Bryers, 1996)

After release as NaOH, Na or NaCl it may react with char and ash-forming matter to form silicates and sulphur compounds, and later NaCl and Na<sub>2</sub>SO<sub>4</sub> will form. Slagging and fouling will result from low-melting point silicates and sulphate. K may form low-melting silicates as well (Bryers,

1996). Recent coal/straw co-combustion tests indicated that K from straw is released as KCl, which reacts to form potassium aluminum silicate and sulphate. Upon cooling, this sulphate is deposited on *e.g.* superheater surfaces, where it may give increased corrosion (Andersen *et al.*, 2000). Another co-firing study (coal/straw, coal/wood) showed gas phase KCl and NaCl concentrations lower than expected, which was explained by binding of the alkali from the biomass by clay minerals in the coal, as aluminum silicates (Dayton *et al.*, 1999).

**Table 8.11 Saturated vapour pressure of alkali chlorides (from Scott and Carpenter, 1996)**

Gas temperature, °C	Saturated vapour pressure, parts per billion metal	
	Na	K
400	0	0
500	1	10
550	15	70
600	100	400
900	160,000	620,000

Table 8.11 shows that the concentration limit of 100 ppbw = 0.1 ppmw for expansion turbines will be exceeded by alkali (chloride) vapors at ~ 550 EC. For fuel gases, this will be diluted by a factor, say, 2.5 by combustion in a gas turbine combustion chamber, increasing the allowable concentration (and temperature) at the expansion turbine inlet.

For the Shell/Demkolec coal IGCC project, it was calculated that for fuel gas clean-up temperature levels 600EC and 350EC the concentrations of Na+K would be 100+800 ppbw (as NaCl + KCl) and 0.0007+0.004 ppbw, respectively. For a gasification temperature of ~ 1230EC calculations predict Na/K > NaCl/KCl > NaBO<sub>2</sub> /KBO<sub>2</sub> as the most important gaseous alkali species. Lowering the fuel gas



temperature below 530-570EC should bring alkali vapour concentrations below turbine inlet specification limits (Alderliesten *et al.*, 1990).

**Table 8.12 Alkali saturation in coal-derived gas (from Scott and Carpenter, 1996)**

Species	Saturation vapour pressure, Pa at 900°C	Concentration of Na or K, ppm wt in gas at 1 MPa, 900°C*
Na <sub>2</sub> SO <sub>4</sub>	0.0029	0.004
K <sub>2</sub> SO <sub>4</sub>	0.023	0.06
NaCl	210	160
KCl	480	620
NaOH	1400	1000
KOH	2300	3000

\* based on a mean gas molecular weight of 30

Under oxidising conditions at temperatures below 1000EC part of the alkali could be converted to less volatile sulphates (provided that sulphur is present), given the vapour pressure data listed in Table 8.12.

Experimental data on alkali concentrations in flue gases from PFBC combustion of several grades of coal, peat and lignite were presented by Laatikainen *et al.* (1993), as collected in Table 8.13. PFBC bed temperature varied from 770 to 910 EC, pressure was 10 bar in most cases. Although temperature had a clear effect, correlations between alkali emissions and fuel type could not be found. Alkali vapour concentrations lie almost an order of magnitude above the current turbine manufacturers' limit of ~ 0.1 ppmw.

**Table 8.13 Vapour-phase alkali concentrations during PFB combustion, in ppmw (table from Laatikainen et al., 1993)**

	T, °C	Sodium		Potassium		Total average
		Range	Average	Range	Average	
Peat A <sup>1)</sup>						
freeboard	730 - 771	0.09-0.48	0.21	0.10 - 0.60	0.32	0.53
after cyclones	691 - 739	0.17-0.51	0.28	0.14 - 0.56	0.30	0.58
Peat B <sup>1)</sup>						
freeboard	704	0.29	0.29	0.29	0.29	0.58
after cyclones	649 - 735	0.10 - 0.25	0.16	0.09 - 0.31	0.20	0.36
Coal B <sup>2)</sup>						
after cyclones	788 - 816	0.08 - 0.19	0.12	0.11 - 0.34	0.21	0.33
Coal B <sup>3)</sup>						
after cyclones	673 - 833	0.07 - 0.45	0.19	0.10 - 0.20	0.15	0.34
<i>Measurements before the cyclones:</i>						
Peat A <sup>1)</sup>	705 - 810	4)	4)	0.21 - 0.38	0.29	>0.29
Peat A	674 - 745	0.11 - 0.20	0.16	0.07 - 0.32	0.17	0.33
Coal A	747 - 799	0.06 - 0.28	0.15	0.10 - 0.25	0.16	0.31
Brown coal	677 - 689	0.06 - 0.10	0.08	0.10 - 0.14	0.12	0.20

1) without any additives  
 2) with dolomite  
 3) with limestone  
 4) results are not used because of contaminations

From the discussion above it may be concluded that two routes exist for protecting an expansion turbine or gas turbine from vapour phase alkali: 1) lowering the temperature to below 600EC where the alkali will form condensed-phase chlorides and sulphates that can be removed with the fly ash or 2) removal of the alkali at temperatures above 600EC using a sorbent material. This last option will be discussed below.

### 8.9 Alkali control in hot gases: aluminosilicate sorbents

Since the 1980s several aluminosilicate, clay-like materials have been tested for the removal of alkali from gases at high temperatures. Materials such as emathlite and kaolinite can be used in two ways for this purpose: 1) by injection as powdered sorbent into the combustion or gasification zone, or 2) in a separate, fixed bed reactor with the sorbent through which the gas stream is forced (Uberoi *et al.*, 1990). An interesting option would be to combine alkali trapping with particulate control in a moving granular bed filter GBF (7 chapter 5.11.7) (Wilson *et al.*, 1996, McDaniel *et al.*, 1995). One drawback for this is that the maximum alkali uptake of < 5% for typical moving GBF granules would require large amounts of fresh granules. For emathlite, one feature was that the clay became sticky after alkali sorption, making it problematic for a GBF (McDaniel, 1995).

**Table 8.14 Typical compositions of aluminosilicate sorbents for alkali removal from gases at 600-1000EC (data from Wilson *et al.*, 1996)**

	SiO <sub>2</sub> %-wt	Al <sub>2</sub> O <sub>3</sub> %-wt	(Na,K) <sub>2</sub> O %-wt	(Ca,Mg)O %-wt	P <sub>2</sub> O <sub>5</sub> %-wt	Others %-wt
Emathlite	~ 69	~ 8	~ 1	~ 9	~ 3	~ 10
Kaolinite	~ 51	~ 44	~ 0	~ 0	~ 0	~ 5
Bauxitic kaolinite	~ 36	~ 58	~ 0	~ 0	~ 0	~ 6
Attapulgit	~ 62	~ 10	~ 1	~ 10, ~ 5	~ 1	~ 2
Ca-montmorillonite	~ 54	~ 18	~ 2	~5, ~ 13	~ 0	~ 8

Table 8.14 gives some averaged compositions of various materials that have proven to remove alkali from hot coal conversion gas streams. Maximum sorption capacities are ~ 25% alkali for kaolinite and ~ 15% for bauxites and emathlite.

The alkali removal is supported by water but hindered (except for kaolinite) by HCl (Schulz *et al.*, 1995, Uberoi *et al.*, 1990) (Alk = Na or K):



Calcium montmorillonite ("Fuller's Earth") has the benefit that strong pellets can be produced, the other sorbents show better alkali sorption performance (McDaniel *et al.*, 1995, Wilson *et al.*, 1996). Rieger *et al.* (1999) analysed the effect pellet formation and pellet structure on alkali removal from coal gasification fuel gas at 800-900EC.

## 8.10 References

- Agnihotri, R., Chauk, S., Jadhav, R. Gupta, H., Mahuli, S., Fan, L.-S. (1998) "Multifunctional sorbents for trace metal capture: fundamental sorption characteristics" in: Proc. of the 15<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., Pittsburgh (PA), Sept. 1998 (CD-ROM)
- Alderliesten, P.T. *et al.* (1990) "Systeemstudie hoge temperatuur gasreiniging bij KV-STEG systemen", ECN/KEMA/TNO-M&E/TU Delft, report ref. nr. 90-310 NOVEM Sittard (the Netherlands)
- Andersen, K.H. *et al.* (2000) "Deposit formation in a 150 MWe utility PF boiler during co-combustion of coal and straw" *Energy & Fuels* 14 765-780
- Benson, S.A. *et al.* (1996) "Trace element transformations in gasification" Adv. coal-fired power systems Review meeting '96, Morgantown, (WV), July 1996
- Biswas, P., Wu, C.Y. (1998) "Control of toxic metal emissions from combustors using sorbents: A review" *J. Air & Waste Manage. Assoc.* 48 113-127
- Brown, T.D., Smith, D.N., Hargis Jr., R.A., O'Dowd, W.J. (1999) "Mercury measurement and its control: what we know, have learned and need to further investigate" *J. Air & Waste Manage. Assoc.* June 1999, 1-97
- Bryers, R.W. (1996) "Fireside slagging, fouling and high temperature corrosion of heat-transfer surfaces due to impurities in steam-raising fuels", *Prog. Energy Combust. Sci.*, 22 29-120
- Brüggendick, H., Gilgen, R. (1996) "Adsorption technology brings waste incinerators into compliance - STEAG's /a/c/t<sup>TM</sup> process in European facilities" ACS Division of Fuel chemistry, Vol. 41 No. 1 (211<sup>th</sup> ACS National Meeting, New Orleans (LA), March 1996) pp. 399-403
- CCT (2001) Clean Coal Today, US DOE No. 44 / Spring 2001
- CCT (1997) Clean Coal Today, US DOE No. 25 / Spring 1997
- Chen, S., Rostam-Adabi, M., Chang, R. (1996) "Mercury removal from combustion flue gas by activated carbon injection: mass transfer effects" in: Preprints. of the papers presented at the 211<sup>th</sup> ACS National Meeting, New Orleans (LA), March 1996, Vol. 41(1) pp. 442-446
- CIEMAT (1998?) "Flue gas cleaning" European Commission DG XVII Clean Coal Technology Handbook, Section 5, Madrid/Brussels
- Couch, G.R. (1995) "Power from coal - where to remove impurities" IEA Coal Research, report IEACR/82, London

- Davidson, R.M. (1997) "Coproprocessing waste with coal" IEA Coal Research, Report IEAPER/36 London
- Dayton, D.C., Belle-Oudry, D., Nordin, A. (1999) "Effect of coal minerals on chlorine and alkali metals released during biomass/coal cofiring" *Energy & Fuels* 13 1203-1211
- Erickson, T.A., Brekke, D.W., Botros, P.E. (1996) "Assessment of HAPs emissions from advanced power systems" in: Adv. coal-fired power systems Review meeting '96, Morgantown, (WV), July 1996
- Farthing, G., Holmes (1998) "Mercury emissions control strategies for coal-fired power plants", presented at the 23rd. Int. Techn. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 1998 *Handout material not included in conference proceedings.*
- Finland (1994) Government decision 626/1994 (1.8.1994)
- Foster Wheeler (1997) Heat Engineering, Spring 1997
- Frandsen, F.F., Dam-Johansen, K., Rasmussen, P. (1994) "Trace elements from combustion and gasification of coal - an equilibrium approach" *Progr. Energy Combust. Sci.* 20 115-138
- Galbreath, K.C., Toman, D.L., Zygarlicke, C.J., Pavlish (2000) "Trace element partitioning and transformations during combustion of bituminous and subbituminous US coals in a 7 kW combustion system" *Energy & Fuels* 14 1265-1279
- Galbreath, K.C., Zygarlicke, C.J. (1996) "Mercury speciation in coal combustion and gasification flue gases", *Environm. Sci. Technol.* 38(8) 2421-2426
- Gosh-Dastibar, A., Mahuli, S., Agnihotri, R., Chauk, S., Fan, L.-S. (1996) "High reactivity sorbents for simulateous removal of trace heavy metals and SO<sub>2</sub>" in: Proc. of the 12<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., S.-H. Chiang (Ed.), Pittsburgh (PA), Sept 1996
- Granite, E.J., Pennline, H.W., Hargis, R.A. (2000) "Novel sorbents for mercury removal from flue gas" *Ind. & Eng. Chem. Res.* 39 1020-1029
- Granite, E.J., Pennline, H.W., Haddad, G.J., Hargis, R.A. (1998) "An investigation of sorbents for mercury removal from flue gas" in: Proc. of the 15<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., Pittsburgh (PA), Sept. 1998 (CD-ROM)
- Hassett, D.J., Eylands, K.E. (1999) "Mercury capture on coal combustion fly ash" *Fuel* 78 243-248
- Helble, J.J. (1996) "Air toxics in combustion and gasification systems: formation and removal", in: High temperature gas cleaning, R. Schmidt *et al.*, (Eds.), Karlsruhe, Germany, pp. 367-382
- Helsen, L., van de Bulck, E. (2000) "Metal behaviour during the low-temperature pyrolysis of chromated copper arsenate-treated wood waste" *Environm. Sci. Technol.* 34 2931-2936
- Huotari, J., Vesterinen, R. (1995) "Muut polton päästöt", Chapter 11 in: "Poltto ja palaminen", R. Raiko, *et al.*, (Eds.), IFRF Finland, Gummerus, Jyväskylä, Finland
- Kema (1997) "Behaviour, control and emissions of trace species by coal-fired power plants in Europe" Report 83428.SP.08 97P01.07B KEMA, Arnhem, the Netherlands
- Klensch, S., Reimert, R. (1999) "Behaviour of heavy metals during the thermal conversion of sawdust in an entrained flow reactor" in: "High temperature gas cleaning", Vol. II, 1999, A. Dittler, G. Hemmler, G. Kasper (Eds.), University of Karlsruhe, Germany, pp. 772-783
- Krishnan, S.V., Gullett, B.K., Jozewicz, W. (1997) "Mercury control in municipal waste combustors and coal-fired utilities" *Environm. Progr.* 16(1) 47-53

- Krissmann, J., Siddiqi, M.A., Peters-Gerth, P., Ripke, M., Lucas, K. (1998) "A study on the thermodynamic behaviour of mercury in a wet flue gas cleaning process" *Ind. & Eng. Chem. Res.* **37** (8) 3288-3294
- Laatikainen, J., Nieminen, M. Hippiainen, I. (1993) "Release of sodium and potassium in the PFB combustion of peat and coal", *Proc. of the 12th Int. Conf. on FBC, San Diego (CA), 1993*, L.N. Rubow (Ed.), ASME, New York, 1369 - 1374
- Lee, S.H.D., Teats, F.G., Swift, W.M., Banerjee, D.D. (1992) "Alkali-vapor emissions from PFBC of Illinois Coals", *Comb. Sci. and Technol.* **86** 327-336
- Lee, S.H.D., Swift, W.M., Kassman, H. (1993) "Measurement of alkali vapor/aerosol in PFBC exhaust gas at the ABB Carbon 15 MWth component test facility" in: *Measurement of ammonia and trace metals in fluidised bed combustion*, H. Kassman, Report OOK 95:02, Chalmers University of Technology, Gothenburg, Sweden
- McDaniel, H.M., Haas, J.C., Wilson, K.B., Gupta, R.P. (1995) "Moving granular-bed filter for multi-contaminant control" *Proc. of the 12<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., Sept. 1995*, S.-H. Chiang (Ed.) Pittsburgh (PA) pp. 237-242
- Meij, R. (1989) "Tracking trace elements at a coal fired plant equipped with a wet flue gas desulphurisation facility" *Kema Sci. & Technol. Rep., Special Issue 7(5)* pp. 269-355
- Merdes, A.C., Keener, T.C., Khang, S.-J, Jenkins, R.G. (1998) "Investigation inot the fate of mercury in bituminous coal during mild pyrolysis" *Fuel* **77(15)** 1783-1792
- Meserole, F.B., Chang, R., Caery, T.R., Machac, J., Richardson, C.F. (1999) "Modelling mercury removal by sorbent injection" *J. Air & Waste Manage. Assoc.* **49** 694-704
- Miller, S.F., Wincek, R.T., Miller, B.G., Scaroni, A.W. (1998) "Trace elements emissions when firing pulverised coal in a pilot-scale combustion facility" in: *Proc. of the 23rd. Int. Techn. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 1998*, pp. 953-964
- Mukherjee, A.B., Kääntee, U., Zevenhoven, R. (2001) "The effects of switching from coal to alternative fuels on heavy metals emissions from cement manufacturing" accepted for the 6<sup>th</sup> Int. Conf. on the Biogeochemistry of Trace Elements, Guelph (ON), Canada, Jul. 29-Aug. 2, 2001.
- Mukherjee, A.B., Melanen, M., Ekqvist, M., Verta, M. (2000) "Assessment of atmospheric mercury emissions in Finland" *The Science of the Total Environment* **259** 73-83
- Podolski, W.F., Swift, W.M., Miller, S.A. (1995) "Air emissions from pressurized fluidised bed combustors", in: "Pressurized Fluidized Bed Combustion", M. Alavarez Cuenca, E.J. Anthony (Eds.) Blackie Academic & Professional, London
- Reed, G.P. *et al.*, (2001) "Control of gasifier mercury emissions in a hot gas filter: the effect of temperature" *Fuel* **80** 623-634
- Rieger, M., Mönter, D., Schulz, R.A. (1999) "Removal of alkali from high temperature gases: sorbent reactivity and capacity" , in: *High temperature gas cleaning, Vol. II*, A. Dittler *et al.*, (Eds.), Karlsruhe, Germany, pp. 760-771
- Ruth, L.A. (1998) "Energy from municipal solid waste: a comparison with coal combustion technology" *Progr. Energy Combust. Sci.* **24** 545-564
- Saenger, M., Werther, J., Hanâen, H. (1999) "Concentrations and mass balance of mercury in a fluidised bed sewage sludge incineration plant" in: *Proc. of the 15<sup>th</sup> Int. Conf. on FBC, may 1999, Savannah (GA) (CD-ROM) paper FBC99-0041*

- Saenger, M., Werther, J., Lungwitz, H. (1999) "Mercury emissions from German fluidised bed sludge incinerators - a status report" in: Proc. of the 15<sup>th</sup> Int. Conf. on FBC, may 1999, Savannah (GA) (CD-ROM) paper FBC99-0042
- Sakulpitakphon, T., Hower, J.C., Trimble, A.S., Schram, W.H., Thomas, G.A. (2000) "Mercury capture by fly ash: study of the combustion of a high-mercury coal at a utility boiler" *Energy & Fuels* 14 727-733
- Schager, P. (1990) "The behaviour of mercury in flue gases", Lic. tech. thesis, Chalmers University of Technology, Gothenburg, Sweden
- Scott, D.H., Carpenter, A.M. (1996) "Advanced power systems and coal quality", IEA Coal Research, Report IEACR/87, London, UK
- Schulz, R.A., Kirkby, N.F., Chrysohoidou (1995) "Fixed bed sorption studies of alkali vapour by aluminosilicates at 600-950°C", Proc. of the 12th Ann. Int. Pittsburgh Coal Conf., S.-H. Chiang (Ed.), Pittsburgh (PA) 1213-1218
- Seeker, Wm. R. (1990) "Waste incineration", Proc. of the Combustion Institute, The Combustion Institute, Pittsburgh (PA) 867-885
- Senior, C.L. *et al.* (1998) "Toxic emissions from coal combustion" in: Proc. of the 15<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., Pittsburgh (PA), Sept. 1998 (CD-ROM)
- Sheu, G.-R., Mason, R.P. (2001) "An examination of methods for the measurements of reactive gaseous mercury in the atmosphere" *Environm. Sci. Technol.* 35 1209-1216
- Srinivasachar, S., Helble, J.J., Ham, D.O., Domazetis, G. (1990) "A kinetic description of vapor phase alkali transformations in combustion systems" *Progr. Energy Combust. Sci.* 16 303-309
- Takeshita, M. (1994) "Environmental performance of coal-fired FBC", Report IEACR/75, IEA coal research, London
- Tsuji, T., Moritomi, H., Yoshiie, R., Fujiwara, N., Fujita, Y. (2000) "A study on mercury behaviour on coal combustion using a thermo-balance and a drop-tube furnace and a bench-scale coal combustion furnace" in: Proc. of the 6<sup>th</sup> SCEJ Symp. on Fluidisation, Dec. 2000, Maebashi, Japan pp. 225-230
- Uberoi, M., Punjak, W.A., Shadman, F. (1990) "The kinetics and mechanism of alkali removal from flue gases by solid sorbents", *Prog. Energy Combust. Sci.* 16 205-211
- Vassilev, S.V., Braekman-Danheux, C., Laurent, Ph., Thiemann, T., Fontana, A. (1999) "Behaviour, capture and inertisation of some trace elements during combustion of refuse-derived char from municipal solid waste" *Fuel* 78 1131-1145
- Vidic, R.D., Liu, W., Brown, T.D. (1998) "Application of sulphur impregnated activated carbons for the control of mercury emissions" in: Proc. of the 15<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., Pittsburgh (PA), Sept. 1998 (CD-ROM)
- Werther, J. (1999) "Legal requirements on gaseous emissions from waste combustion and are these fulfilled?" lecture at 1999 Finnish Waste-to-Energy course, Part 2, Turku, Oct. 1999
- Wilson, K.B., Haas, J.C., Gupta, R.P., Turk, B.S. "Moving granular bed filter development program", Advanced coal-fired systems '96 Review meeting, Morgantown (WV) July 1996
- Yan, R., Gauthier, D., Flamant, G., Peraudeau, G., Lu, J., Zheng, J. (2001) "Fate of selenium in coal combustion: volatilisation and speciation in the flue gas" *Environm. Sci. Technol.* 35 1406-1410