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21 TRACE ELEMENT EMISSIONS21.1 Introduction

Coal and oil fuels, and also most waste and low grade fuels, contain trace quantities of a number of elements that are potentially harmful to man and other living organisms. Also further trace quantities of potentially harmful compounds such as carcinogenic hydrocarbons may be generated during the combustion process. The fate of such trace elements and compounds during fluidised bed combustion must, therefore, be considered and may be particularly important for coal firing because of the large tonnages of coal burnt.

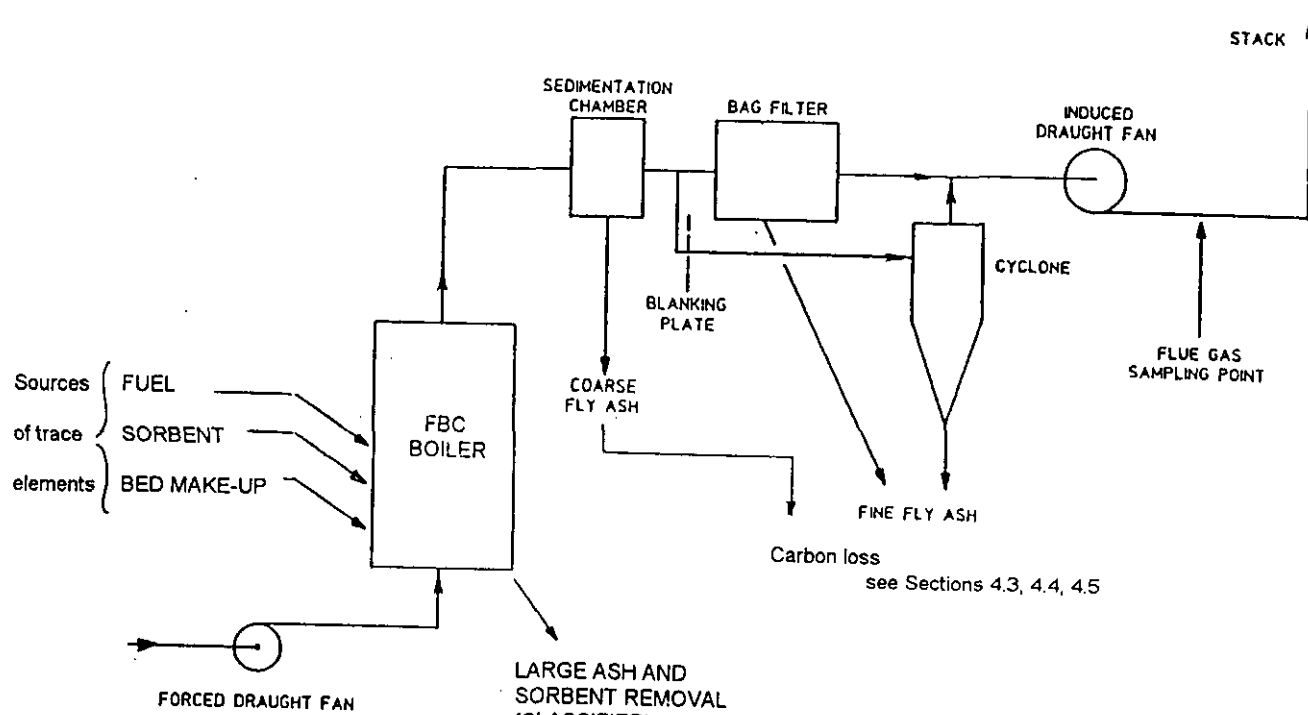
Figure 21.1 shows diagrammatically the trace element flows in a typical atmospheric pressure fluidised bed combustion installation. Trace elements may enter the combustor not only with the fuel but also with the bed solids make-up and with limestone or other sorbents for sulphur retention. Some of the more volatile trace elements may leave the combustor in vapour form in the off gases. The remainder leaves in solid form, either in the bed solids overflow stream with the large ash and/or sorbent, or with the elutriated solids in the off gas stream. When gas cleaning equipment is provided much of the elutriated trace elements in solid form leave the system with the coarse and fine fly ash; the remainder of the elutriated solids leave with the stack gases.

Potential uses and disposal methods for the bed solids overflow and fly ash streams are discussed in Section 16. However, detectable amounts of trace elements and compounds are emitted in the stack gases and it is these emissions that are discussed in the present Section.

The composition of the stack gases is complex, they generally contain most or all of the following classes of compounds.

1. Primary combustion products - CO_2 , water vapour.
2. Secondary combustion products due to incomplete combustion - solid C, CO , CH_4 , H_2 .
3. Sulphur oxides - SO_2 , SO_3 .
4. Nitrogen oxides - NO_x , N_2O .

Figure 21.1
Diagram of a Typical AFBC Boiler Installation



LARGE ASH AND SORBENT REMOVAL (CLASSIFIER)
For amount and size

see Section 9

For retention by bed of Na, V, P, Ba, Pb, Zn

see Section 3.5.2 and Section 14.2.3.3

Use and disposal

see Section 16

Sulphur retention

see Section 11

FLUE GAS

For	see Section
CO in oil firing	5.3.9
SO ₂ , SO ₃	11
NO _x , N ₂ O	12
Na, K on turbine blading	14.2.4

Heavy metals	} 21
Toxic elements	
Halogens	
Alkali metals	
Hydrocarbons	
Radioactivity	
H ₂ , CH ₄ , CO	

5. Trace elements as vapours or on elutriated dust - heavy and/or toxic metals, halogens, alkali and alkali earth elements.
6. Complex hydrocarbons and organic compounds - e.g. dioxin, carcinogens.
7. Radioactive compounds.

It has been found convenient to consider some of these classes of material separately in other sections of this Manual as indicated in Figure 21.1. The present Section, therefore, contains information only on compounds and elements in classes 2, 5, 6, and 7. Most of the information available on these classes appertains to coal firing since coals contain more trace elements than other premium fuels. Section 16 should be consulted for information on trace elements in either the spent bed solids or the coarse and fine fly ash streams.

The effects and significance of trace elements emissions are varied. With heavy metal elements and toxic or radioactive materials there is concern to avoid a build-up in the environment of materials that could be potentially harmful to the environment and to life, including man. With Cl, Na and V the interest is in a possible increase in corrosion rates on heat transfer surfaces while with Ca, Cl, K, and Na the possible effect of these elements on the fouling of heat transfer surfaces is the principal concern.

The following discussion in this Section is sub-divided to consider all the above mentioned effects.

21.2 Toxic and Heavy Metal Emissions

The emission of toxic and heavy metal elements in the stack gases is principally of interest during coal firing since coal fuels contain a greater variety of trace elements than other premium fuels. Low grade and waste fuels may also contain a variety of trace elements but they are not discussed in this section as it is not possible to generalise on account of their variability and each application must be considered individually.

Although these elements are present in coals only in very low concentrations nevertheless the large amounts of coal fired might conceivably cause environmental and health problems.

21.2.1 Sampling and analysis

The occurrence of trace elements in coal has been known for at least 45 years but the possibility of the release during coal combustion of potentially harmful trace elements has not been generally recognised until the development of physical techniques of analysis increased the sensitivity of detection to the range 10^{-10} - 10^{-12} g/m³.

At such low concentrations it has been found that normal analytical accuracy cannot be expected when measuring trace elements (21.1). Mass balance closures to within $\pm 25\%$ should be regarded as good, for a survey (21.2) showed that the scatter in mass balance closures varies with the concentration of the species being measured. A comparison made in that survey between theoretical and actual trace element mass balance closures showed that the limits given in the Table 21.1 below are acceptable.

Table 21.1

Variation of Trace Element Mass Balance Closures with the
Concentration of the Elements Measured

Element concentration ppm	Scatter in mass balance closures, \pm %	
	theoretical	actual
100	16	22
10	22.5	30
1	32.5	30

21.2.1.1 Sampling techniques

To obtain even the analytical accuracies shown in Table 21.1 careful attention is necessary both in the sampling procedure and in any pre-analytical treatment of the sample. The majority of trace elements are found in the elutriated solids in the stack gases but some volatile elements occur also in the gas phase. Obtaining a representative sample for analyses therefore requires both adequate scrubbing of gases to recover trace element vapours and isokinetic sampling to ensure

the correct concentration and size distribution of solids. This latter requirement is particularly important because there may be a relationship between particle size and trace element concentration. To comply with these requirements it is recommended that the sampling train used should be based on equipment specified by the US Environmental Protection Agency (EPA). A commercial version of the EPA train known as the Source Assessment Sampling System (SASS) is available and is illustrated diagrammatically in Figure 21.2.

When the SASS apparatus is used it is further recommended that prior to any testwork all glassware and PTFE parts be thoroughly leached in three changes of 0.5 M nitric acid while stainless steel components should be passivated by immersion in a 1:1 solution of concentrated nitric acid and water (21.3). For field testwork using the SASS apparatus it has been found preferable to use 0.5 M nitric acid as the oxidising agent in place of that specified by the SASS manufacturer (21.3). The use of 0.5 M nitric acid is not only safer under field conditions but also allows mercury to be determined by atomic absorption spectrometry along with the other elements.

On completion of sampling, and in cases where mercury is to be determined, a representative sub-sample (circa 100 ml) should be obtained of all solutions collected in the impingers and washings of the sample train. This sub-sample should then be stabilised to avoid the loss of mercury prior to analysis by the addition of around 1 ml of potassium dichromate.

21.2.1.2 Sample pre-treatment

Solid samples will require pre-treatment before analysis. Most of the methods of analysis sufficiently sensitive to measure trace element concentrations need either or both,

- a) the removal of carbon, as this element causes interference
- b) a sample in liquid form.

Carbon can be removed by ashing the sample in air at 500 or 800°C. However, even at the lower temperature this procedure may result in the loss of some of the more volatile trace elements (21.1, 21.4). A preferred method is to heat the sample to about 100°C in oxygen at a reduced pressure of 1.3 - 2.6 Pa

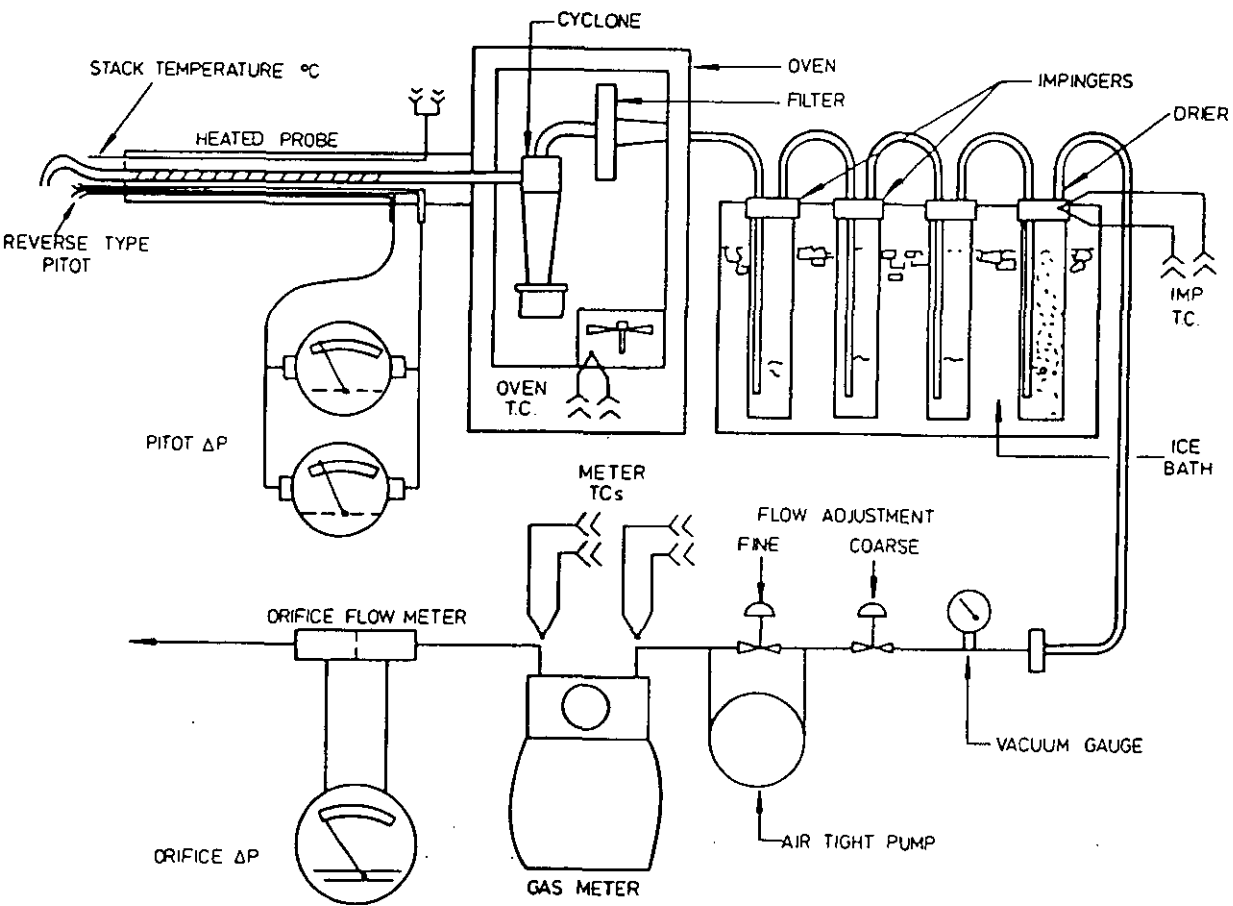


Figure 21.2
EPA Source Assessment Sampling System

(0.01 - 0.02 mm Hg) while applying an electrodeless radio-frequency discharge to generate active oxygen atoms (21.4).

Alternatively, when the analytical method requires a liquid sample, wet oxidation with fuming nitric acid can be used followed by solution of the inorganic residue in hydrofluoric acid, boric acid and aqua regia.

21.2.1.3 Analytical methods

All the methods in current use for trace element analysis measure some physical characteristic that differs for each element. Detection limits of 10^{-9} to 10^{-12} g are reported (21.1). The main features of each method are as follows.

Nuclear activation analysis (NAA) measures emissions from unstable isotopes generated by nuclear irradiation. Several grams of sample are used, which reduces the risk of inhomogeneity, and sample processing is minimal since carbon does not interfere - both advantages when dealing with coal. However, several potentially dangerous elements, e.g. Cd, Cu, Hg, Pb, Ni, and Zn, are not readily determined.

X-ray fluorescence spectroscopy (XRF) also requires minimal preparation of solid samples. The quantities used, about 250 mg, through less than for NAA, are larger than for other methods and hence at less risk of error. Bombardment by means of X-rays ejects electrons from the inner shells of some atoms which then emit secondary X-rays of characteristic frequency as outer shell electrons move to fill the gaps. Self absorption, enhancement and effects of particle size all interfere with the quantitative emission of secondary X-rays but can be corrected by calculation. These corrections become large for the lighter elements, such as B, F, Na, Mg and Al, so that for them XRF is not the most suitable analytical method.

Spark source mass spectrometry (SSMS) ionizes the sample and then separates the ions according to their mass/charge ratios. It is rapid and covers a wide range of elements but is liable to interference by multiple charged and complex ions. The sample weight is very small with consequent risk of errors when dealing with non-homogenous materials. Coal samples require preliminary treatment to remove carbon and hydrogen.

Atomic emission spectroscopy (AES) measures the intensity of light emitted at wavelengths characteristic of individual elements when atoms are excited in a flame. It is rapid and sensitive but liable to spectral interference both from 'overcrowding' of lines when many elements are present and from broad molecular bands. Samples need to be dissolved, which ensures that they are homogeneous but also involves eliminating carbon from coals. Care is also needed to avoid changes in the concentration of excited atoms due to changes in flame temperature.

Atomic absorption spectrometry (AAS) vaporizes samples in a flame, a graphite furnace or by conversion to volatile hydrides. Light from a succession of lamps, each consisting of a single element, passes through the vapour and the degree of absorption is measured. Absorption, which depends on the concentration of ground-state atoms present, is much less sensitive to flame temperature than the emission from excited species used for AES; it is, however, still liable to spectral interference. Sample preparation, including elimination of carbon from coals, is needed before all three methods of injection. For the commonest, flame vaporization, this involves solution of the samples, which has the advantage of ensuring homogeneity but at some risk of contamination.

Other physical analytical methods, photo-electron spectrometry, ion-microprobe mass spectrometry, auger electron spectrometry, etc., can be used to determine trace element distribution within individual particles but these are more specialized than is necessary for examining emissions from industrial combustion.

None of the available techniques determines all the elements and none can be considered absolutely accurate. Choice between them is generally based on convenience or utility. The recommended approach (21.1) is to use a combination of two techniques; SSMS for rapid and relatively inexpensive semi-quantitative measurement of the maximum possible number of elements and AAS for more accurate determination of any potentially hazardous elements revealed by the SSMS analysis.

21.2.2 Trace element content of coals

Two sets of analyses giving the trace element content of British coals have been issued by the British Coal Corporation. The earlier (21.9) included only eight elements that were considered as potentially harmful but covered a total of 234 coals from all UK coalfields. However, values for the more volatile trace elements

could be low as the measurements were made on ashes prepared at 500°C. (See section 21.2.1.2). The second investigation (21.10) made measurements on untreated coals but only covered 23 samples, although a much wider range of elements, 52 per sample, was measured.

As an illustration of the results obtained Table 21.2 shows the analyses from a recent investigation (21.1) of four UK coals from different regions of the country and Table 21.3 gives the trace element concentrations of a further 14 UK coals to illustrate the variations encountered. Table 21.3 also includes values for typical sands and sulphur retention sorbents as trace elements can also enter the combustor with the bed solids.

Mean values of trace element concentrations for the 18 coals of both Tables 21.2 and 21.3 are also given in Table 21.3. In spite of wide individual variations most measurements for all the elements examined fall between 4 times and one quarter of the mean value for a particular element. Similar results are recorded for an extensive range of US coals (21.1). Consequently US experience can be taken into account when considering trace element emissions from coal combustion in the UK.

Table 21.2
Analysis and Trace Element Content of Four UK
Coals from Various Regions. (ref 21.1)

Region Test	Nottinghamshire		Scotland		Yorkshire	South Wales	
	1	2	3	4	5	6	7
<u>Proximate Analysis (as received basis)</u>							
Moisture %	9.3	9.2	5.1	4.9	9.1	2.3	2.1
Ash %	19.9	15.8	14.2	15.2	17.6	19.9	22.4
Volatile matter %	32.1	33.2	30.6	30.6	31.4	12.0	10.5
Fixed carbon %	38.7	41.8	50.1	49.3	41.9	65.8	65.0
<u>Ultimate Analysis (dry basis)</u>							
C %	62.50	66.90	69.90	68.80	63.80	69.40	69.30
H %	4.50	4.80	4.70	4.60	4.50	3.10	3.10
O %	9.20	9.40	8.50	8.30	10.30	3.90	3.80
N %	1.47	1.57	1.50	1.37	1.72	1.22	1.17
S %	0.80	0.79	0.66	0.81	2.07	1.76	1.80
Cl %	0.34	0.32	0.22	0.22	0.22	0.03	0.01
<u>Calorific value (dry basis)</u>							
kJ/kg	25280	27280	28580	28200	26240	27440	25880
<u>Trace element concentration (mg/kg)</u>							
As	*		*		*	*	
	7	2	2	2	16	26	7
Cd	< 0.6	0.1	< 0.6	0.2	< 0.6	< 0.6	0.2
Cr	31	41	49	37	29	27	43
Co	13	10	14	14	8	11	10
Cu	30	24	21	23	45	45	28
Pb	18	10	22	16	19	16	23
Mn	190	96	88	51	125	100	69
Hg	0.03	0.2	<0.02	< 0.1	<0.02	<0.02	0.2
Ni	48	43	45	46	29	31	31
V	55	50	50	56	70	70	74
Zn	66	34	39	46	18	23	27

* Analysis by independent specialist laboratory; remainder by CRE.
 See ref (21.1).

Table 21.3

Trace Element Concentrations in UK Coals and Bed Materials

Reference	Coal tested	Trace element concentration (ug/kg)															
		As	Ba	B	Cd	Cr	Co	Cu	F	Pb	Mn	Hg	Mo	Ni	Se	V	Zn
(21.1)	Bersham	6			0.05	28	10	50		33	27	0.2		35		60	36
	Hem Heath	5			0.5	50	6	35		22	100	0.1		28		43	45
	Linby	7			0.1	22	10	33		15	95	0.2		36		27	22
	Seafield	3			0.03	55	5	21		9	70	0.2		29		38	43
	Calverton	14			<0.1	10	9	21		14	68	0.3		29		21	13
	Allerton Bywater	2			0.2	10	10	31		23	95	<0.01		55		30	23
	Daw Mill	2			0.06	11	3	13		9	140	0.1		10		12	7
	Blidworth	6			<0.05	7	7	19		11	63	0.2		24		16	9
(21.5)	Nottinghamshire	9				9	11	22	22	18	19	0.2		39		19	6
	Derbyshire	6				11	9	27	77	10	80	0.1		23		18	10
	Staffordshire	2				6	5	24	62	18	70	0.1		15		14	44
	Yorkshire	5				7	6	23	26	10	21	0.1		17		25	7
(21.6)	Baddesley	5			<0.5	25	6	18		9	47	<0.05		14		20	9
(21.7)	Daw Mill	7	304	50	<0.1	10		13		3	107	0.4	<1	15	2.3	15	12
(21.8)	Kiverton Park	20	52	35	<0.7	29	12	32		21	190	0.3	<2	29	1.1	60	20
(21.1)	Linby	<0.5			<0.3	16	5	30		28	150	<0.5		33		37	25
Mean values for coals of Tables 21.2 and 21.3		5			0.17	25	8	27		15	81	0.17		28		33	24
(21.1)	Bed Materials																
	1-1.2 mm sand	2			0.3	10	2	4		0.8	30	0.2		5		18	7
	Sand	3			0.1	3	0.1	15		0.6	26	0.1		3		14	5
(21.1)	Limestone, Shap Beck Penrith,	<0.5			1	<0.3	0.9	2		6	230	<0.5		4		5	11
(21.8)	Middleton	0.5	1050	<2	3	13	1.8	8		37	51	<0.05	<2	1	<0.5	5	24
(21.7)	Bauxite, RASC grade Guyanan	0.9	425	12	<1	74		7		<3	311	0.1	<1	20	<0.5	175	6

21.2.3 Distribution of trace elements in combustor outlet streams

Table 21.4 illustrates how the trace elements are distributed between the outlet streams from a typical fluidised bed combustion boiler installation (21.1). The installation was similar to that outlined in Figure 21.1 and was fitted with a bag filter. The trace element content of each outlet stream has been expressed as a percentage of the total recovery for each element analyzed.

Two trends are apparent in the data of Table 12.4. Firstly, most of the trace elements remain with the solid products and, secondly, the trace elements tend to be more concentrated in the finer sized material. Nevertheless, significant proportions of some elements, in particular As, Cd, Cr and Ni, do leave with the stack gases.

Approximate emission concentrations of trace elements in the stack gases can be evaluated for estimation purposes when experimental data is lacking by multiplying mean stack gas percentage recoveries obtained from Table 21.4 by the average concentration of the required trace element in a UK coal obtained from Table 21.3. An estimate of the volume of stack gases per unit of coal burnt will also be required. The results of such a calculation are shown in Table 21.5.

Table 21.4
Percentage Total Recovery of Trace Elements in
Discharge Streams from a Fluidised Bed Combustion Boiler (21.1)

Trace element	Coal *	Bed solids	Large ash	Fly ash		Stack	
				Coarse	Fine	Solids	Gas
Arsenic	1	26.7	1.5	9.8	16.6	0.4	0.03
	3	23.1	1.6	14.9	59.9	0.003	0.5
	5	7.0	11.7	3.8	75.9	0.1	1.5
	6	5.2	4.5	4.3	85.8	0.1	0.05
Cadmium	1	26.3	0.3	8.9	61.1	0.04	3.3
	3	58.1	2.7	5.4	22.6	0.1	10.8
	5	44.3	2.1	4.3	32.0	0.1	17.2
	6	31.6	0.2	2.7	65.4	0.1	-
Chromium	1	43.8	1.4	9.0	43.8	0.3	1.7
	3	31.2	1.2	5.4	49.3	0.02	12.9
	5	26.0	15.3	3.3	52.4	0.1	2.9
	6	41.2	20.6	8.4	9.4	0.2	20.5
Cobalt	1	73.3	1.9	14.3	9.9	0.6	-
	3	28.2	0.6	10.5	60.6	0.2	-
	5	17.8	10.1	4.1	67.8	0.1	-
	6	13.7	3.9	5.0	77.4	0.01	-
Copper	1	61.3	0.4	9.5	28.6	0.2	0.05
	3	44.9	0.5	9.9	44.5	0.01	0.2
	5	26.2	4.5	4.8	64.3	0.1	0.02
	6	25.1	4.4	4.7	65.7	0.1	0.04
Lead	1	47.6	0.3	6.5	45.2	0.3	-
	3	36.2	0.2	8.6	55.0	0.02	-
	5	18.2	1.7	2.4	77.6	0.1	-
	6	17.0	0.6	5.5	76.7	0.1	-
Manganese	1	48.1	1.0	17.3	33.4	0.2	0.02
	3	67.2	1.3	9.5	21.4	0.006	0.5
	5	25.9	29.8	7.2	37.0	0.1	-
	6	28.8	8.1	5.2	57.6	0.1	0.2
Mercury	1	56.9	0.1	10.2	32.5	0.2	-
	3	51.3	0.1	6.8	41.6	0.1	-
	5	21.2	0.5	0.7	77.6	0.1	-
	6	17.4	0.2	11.9	70.4	0.1	-
Nickel	1	36.9	0.6	8.1	52.9	0.3	1.1
	3	28.8	0.4	9.7	53.4	0.02	8.3
	5	17.9	6.4	4.0	68.7	0.1	2.8
	6	21.6	3.6	3.9	65.0	0.1	5.7
Vanadium	1	40.6	1.4	7.6	50.1	0.3	-
	3	31.8	1.1	7.3	59.4	0.02	0.4
	5	18.4	9.3	4.1	68.1	0.1	-
	6	26.7	7.7	3.1	61.8	0.1	-
Zinc	1	52.6	0.5	12.1	34.5	0.2	0.08
	3	41.6	0.3	8.2	49.2	0.01	0.6
	5	24.4	16.0	4.1	55.8	0.1	-
	6	27.4	3.8	3.4	65.4	0.1	-

* Coal analysis as for Tests 1,3,5 and 6 in Table 21.2

Table 21.5
Prediction of Trace Element Emission Concentrations from Tables 21.3 and 21.4

Trace element	As	Cd	Cr	Co	Cu	Pb	Mn	Hg	Ni	V	Zn
Mean percentage recovery in stack gases, Table 21.4	0.67	11.1	9.6	0.23	0.18	0.13	0.28	0.12	4.6	0.23	0.27
Mean percentage in coal. Table 21.3, mg/kg	5	0.17	25	8	27	15	81	0.17	28	33	24
Mean predicted stack gas concentrations, $\mu\text{g}/\text{m}^3$ †	3	1.7	2.23	1.7	4.5	1.8	21	0.02	120	7	6

† Assuming 16.7 kg stoichiometric air per kg coal, combustion using 30% excess air and a gas density of 1.293 kg/m³ at NTP.

21.2.4 Emission levels

Table 21.6 shows the results of measurements by CRE of the concentration of trace elements in the stack gases from a number of coal burning industrial units (21.1, 21.3, 21.5). The type of unit and the method of gas cleaning are also indicated in Table 21.6.

The general level of concentrations range from 4 - 4500 $\mu\text{g}/\text{m}^3$ for Cr, the highest, down to 0.001 - 11.7 $\mu\text{g}/\text{m}^3$ for Hg, which gave the lowest concentrations measured. The variability in the results reflects not only the difference between coals but also the difficulties of analysis and sampling. See Section 21.2.1.

The main trend in the results appears to correlate with the efficiency of the gas cleaning equipment, with the highest concentrations being emitted from installations with the least efficient gas cleaning. Such a trend would be anticipated for compounds associated with the fine solids entrained in the gas stream; see Table 21.4. For a given type of gas cleaning equipment the emission levels are generally similar for both fluidised bed combustion and conventional firing.

An exception to the above statement seems probable in the case of arsenic; see Table 21.7. The results for three coals, burnt in both fluidised bed combustion and stoker fired installations, showed that the emissions of As from the fluidised bed combustion unit were approximately one tenth that from the stoker fired unit. This trend was reversed, however, when a further pair of fluidised bed combustion and stoker fired boilers were connected, in turn, to a single highly efficient bag filter gas cleaning installation. The lower emission levels were regained in a final test when the fluidised bed combustion boiler was connected to a less efficient gas cleaning system but operating with a lower stack gas temperature; see Table 21.7. These observations suggest that As is released in the form of As_2O_3 , which sublimates at 193°C (379°F).

Table 21.6
Concentration of Trace Elements in Boiler Stack Gases

Type	Unit			Coal	Trace element concentration, Mg/m ³										
	Output MW(th)	Firing method	Gas cleaning method		As	Cd	Cr	Co	Cu	Pb	Mn	Hg	Ni	V	Zn
0.6m square pilot plant		FBC	2-stage cyclone plus scrubber	Bersham	260	0.4	440	170	870	870	260	0.9	440	1310	870
				Hem Heath	80	4	4	160	360	360	400	1	410	400	1020
Vertical shell	2.3	FBC	Bag filter	Limby	200	0.4	360	160	280	360	360	1.2	800	800	320
				Seafield	40	0.4	780	230	310	310	780 45	1.2	780	780	1170
				Quarter	9.5	1.2	106	4	11.4	7.2	30	0.007	105	17	20
				Scottish	5.6	0.3	304	0.5	6	0.7	3	0.003	242	14	13
Vertical shell	4.3	FBC	Bag filter	Yorkshire	31	0.8	44	0.6	1.5	1.4	16	0.007	56	6	1
Vertical shell	4.0	FBC	Cyclone with vortex collector packets	S. Wales	6	0.01	250	0.1	4.4	1.7	-	0.001	120	6	2
Double locomotive	10.0	FBC	Multicell cyclone	Calverton	93	-	19	-	0.8	-	430	0.8	13	-	-
				Calverton	8.5	0.4	4500	110	440	550	1.5	2700	220	140	
				Bag filter								300			
Segmented bed coil	30.0	FBC	Multicell cyclone	Hem Heath	3.4	0.4	170	85	240	160	1300	0.6	290	240	550
Composite water tube horizontal shell	15.0	FBC	with blowdown	Allerton Bywater	43	8.3	420	310	830	650	1350	2.0	1000	930	720
Composite water tube horizontal shell	10.0	FBC	Multicell cyclone	Daw Hill	140	1.6	270	130	320	120	120	0.5	770	300	90
Horizontal shell	2.2	Chain grate stoker	Skimmer	Blidworth	-	3.8	110	90	460	440	-	-	290	280	110
				Quarter	88.7	0.2	397	2	27	9	104	11.7	217	26	22
				Scottish	52	0.01	24	9	28	13	37	1.8	31	37	22
				Yorkshire	336	0.06	40	1.5	60	15	52	1.2	60	75	45
Horizontal shell	2.0	Vibrating gratestoker	Bagfilter	Calverton	8.4	-	39	-	1.7	-	66	0.1	24	-	1
Vertical shell grass drier	2* 2.5	FBC	Cyclone	Quarter	32	-	425	45	87	2.5	174	4.9	452	131	289
				Derbyshire	-	-	521	69	120	26	1136	1.3	279	34	347
				Staffordshire	-	-	278	34	89	790	1707	1.5	236	40	461
				Yorkshire	7.8	-	294	46	91	33	64	1.0	281	135	72

Table 21.7

Arsenic Concentration in Boiler Stack Gases

Firing method	AFBC			Grate stoker		
	Arsenic concentration $\mu\text{g}/\text{m}^3$	Gas cleaning method	Stack gas temperature $^{\circ}\text{C}$	Arsenic concentration $\mu\text{g}/\text{m}^3$	Gas cleaning method	Stack gas temperature $^{\circ}\text{C}$
Coal						
Nottinghamshire	9.5	bag filter	-	88.7	skimmer	-
Scottish	5.6	bag filter	-	52	skimmer	
Yorkshire	31	bag filter	-	336	skimmer	
Calverton	93	bag filter	210	8.4	bag filter	180
Calverton	8.5	cyclone	180			

21.2.5 Assessment of health hazard potential

The concentrations for trace elements shown in Table 21.6 are those in the gases leaving the top of the stack. The entrained solids that are carrying much of the trace elements are so fine that they will remain in suspension and not become deposited on the ground around the stack. Also the gases will become diluted before they reach ground level. Because of varying atmospheric winds the point of maximum ground level concentration will vary continually and the mean ground level concentration should be based on a time averaged sample. Daily averages are generally recommended (21.1) and for these the dilution factor has been calculated as 1 in 68 000(21.11) for chimneys conforming to the Chimney Height Regulations (21.12). Table 21.8 shows ground level concentrations calculated using this dilution factor for the data of Table 21.6.

Currently, there are no statutory controls on ambient concentrations of trace elements in the UK. Assessment of pollution hazards has been based, therefore, on the threshold limit value for each element published by the American Conference of Governmental and Industrial Hygienists (21.13). For continuous exposure of the general public a limit of 1/30 of the threshold limit value is advised (21.13). Table 21.9 shows the maximum ground level concentration, irrespective of source, for each of the eleven trace elements measured. The second column shows 1/30 of the threshold limit value recommended for each element.

For all eleven elements the highest estimated daily mean ground level concentration is lower than the corresponding recommended limit for continuous exposure of whole populations by a factor of at least 10^2 , sometimes 10^4 . Consequently the possibility of danger to health seems remote.

Table 21.8

Estimated Trace Element Concentrations at Ground Level Emitted by FBC Boilers and Driers

Type	Unit Gas cleaning method	Coal	Estimated trace element ground level concentration mg/m ³										
			As	Cd	Cr	Co	Cu	Pb	Mn	Hg	Ni	V	Zn
0.6m square pilot plant	Cyclone and scrubber	Bersham	3.8	0.006	6.5	2.5	12.8	12.8	3.8	0.01	6.5	19	12.8
		Hem Heath	1.2	0.06	0.06	2.3	5.3	5.3	5.9	0.01	6.0	5.9	15
		Limby	2.9	0.006	5.3	2.3	4.1	5.3	5.3	0.02	11.8	11.8	4.7
		Seafield	0.6	0.006	11.5	3.4	4.5	4.5	11.5	0.02	11.5	11.5	17.2
Vertical shell	Bag filter	Nottinghamshire	0.14	0.015	1.6	0.06	0.16	0.37	0.67	0.0001	1.6	0.25	0.3
		Scottish	0.08	0.05	4.5	0.007	0.09	0.01	0.44	0.0004	4.6	0.02	0.02
		Yorkshire	0.46	0.01	0.65	0.009	0.02	0.02	0.04	0.0001	0.8	0.09	0.02
		S.Wales	0.09	0.001	3.7	0.001	0.06	0.02	0.23	0.0001	1.8	0.09	0.03
Vertical shell	Bag filter	Calverton	1.4	-	0.3	-	0.01	-	-	0.01	0.2	-	-
Vertical shell	Cyclone with vortex collector	Calverton	0.13	0.007	-	1.6	6.5	8.1	6.3	0.02	-	3.2	2.1
Double locomotive	Bag filter	Hem Heath	0.05	0.005	2.5	1.3	3.5	2.4	4.8	0.08	4.3	3.5	8.1
Segmented bed coil	Multicell cyclone	Allerton Bywater	0.63	0.12	6.2	4.6	12	9.6	19	0.03	15	14	11
Composite water-tube and horizontal shell	Multicell cyclone	Daw Mill	2.0	0.02	3.9	1.9	4.7	1.8	20	0.007	4.0	4.4	1.3
Composite water-tube and horizontal shell	Multicell cyclone	Blidworth	-	0.06	1.6	1.3	6.8	6.5	1.3	-	4.3	4.1	1.6
Grass drier	Cyclone	Nottinghamshire	0.47	-	6.2	0.7	1.3	0.04	2.6	0.17	6.6	1.9	4.4
		Derbyshire	-	-	7.7	1.0	1.8	0.38	16.7	0.02	4.1	0.5	5.1
		Staffordshire -	-	4.1	0.5	1.3	1.2	25.1	0.02	3.5	0.6	6.5	
		Yorkshire	0.1	-	4.3	0.7	1.3	0.5	0.9	0.01	4.1	2.0	1.1

Table 21.9

Assessment of Possible Health Hazard due to Trace Elements

Element	Estimated ground level concentration for maximum emission shown in Table 21.8 ng/m ³	Occupational exposure limit * (1/30) mg/m ³
As	3.8	6700
Cd	0.12	3400
Cr	11.5	17000
Co	4.6	3300
Cu	12.8	67000
Pb	12.8	5000
Mn	25.1	170000
Hg	0.17	1700
Ni	15	3300
V	19	17000
Zn	17.2	170000

21.2.6 Effects of limestone addition and staged combustion

In view of ever more stringent Environmental Regulations there will be an increasing need for limestone addition for sulphur retention and the use of staged combustion for NO_x control. The 0.6m (2ft) square pilot plant unit at CRE has been used to quantify the effect of these measures on trace element emissions (21.1). The trace element concentrations obtained during tests on that unit with and without air staging and limestone addition are given in Table 21.10.

Table 21.10 shows that both the dust loadings of the stack gases and the trace element emission concentrations are increased by both limestone addition and air staging. The increased rates of trace element emission are mainly caused by the increased dust loading as is shown by scaling the trace element concentrations to a common dust loading of 0.7 g/m³; see table 21.10 lines 7-9. For the results with limestone addition the values so scaled for some trace elements are lower than would be expected. This could be because limestone itself, which is deficient in some trace elements (see Table 21.3), has contributed to the increased dust loading.

The trace element emission rates could be reduced when either limestone addition or staged combustion are used through the use of more efficient gas cleaning equipment. The pilot plant used to obtain the above result used only a two stage cyclone for gas cleaning (21.1). However, even at the increased emissions rates the ground level trace element concentrations are at least 100 times less than the recommended maximum exposure rates of 1/30 times the threshold limit values. Consequently the possibility of a health hazard seems remote.

21.2.7 Emissions in direct contact driers

In some types of drying application such as grass driers the combustion gases give up their heat to the product by direct contact. A diagram of a typical unit of this type a coal fired fluidised bed combustion grass drier - is shown in Figure 21.3. It was clearly of interest to ascertain with such units whether the resulting contamination of the product with trace elements could be in any way a health or environmental hazard.

Table 21.10

Trace Element Concentration in the Stack Gases during Operation with Staged Combustion and Limestone Addition

Line No.	Unit	Stack gas dust loading g/m ³	material	Bed Ca:S Ratio	Static depth m	Secondary air %	Trace element concentration mg/m ³										
							As	Cd	Cr	Co	Cu	Pb	Mn	Hg	Ni	V	Zn
1 *	0.6m (2 ft) square combustor #		sand		-	0	200	0.4	360	160	280	360	360	1.2	800	800	320
2		1.0	sand		1	0	360	0.45	560	180	360	180	300	-	780	890	330
3		0.7	sand		0.5	0	-	0.37	330	130	270	90	150	-	740	570	170
4		0.9	sand		0.5	25	-	0.47	250	210	400	150	290	-	690	670	350
5		2.5	limestone	3:1	0.6	0	-	1.9	850	340	740	470	900	0.8	1150	1040	410
6		2.0	limestone	3:1	0.6	25	-	1.7	600	250	590	310	710	0.6	990	850	320
7 \$	Conditions as lines	0.7	sand		0.5	25	-	0.36	194	163	311	116	225	-	537	443	272
8 \$	4 - 6 but scaled to	0.7	limestone	3:1	0.6	0	-	0.5	238	95	207	132	252	0.2	322	291	115
9 \$	0.7 g/m ³ dust loading	0.7	limestone	3:1	0.6	25	-	0.6	210	97	206	108	248	0.2	346	297	112

* Line 1 is the entry for Linby coal taken from Table 21.6 for comparison.

Fired on Linby coal; bed temperature 850 °C (1560 °F); fluidising velocity 0.6 m/s (2 ft/s).

\$ Compare with line 3 for effect of use of secondary air and/or use of limestone.

A series of tests was carried out by CRE to measure the extent of such contamination in a 5 MW (17×10^6 Btu/h) grass drier similar to that illustrated in Figure 21.3 (21.5). The findings are summarised in Table 21.11. The dried grass product was analyzed for eleven trace elements. Significant enrichment occurred only for the elements As and Co. In Table 21.12 the highest trace element concentration found for any combination of grass or coal is compared with that level considered to be toxic to cattle. Precise data on the minimum levels of each element likely to prove harmful to animals are not easy to obtain. Many elements interact, the presence of one affecting the uptake, utilisation, tissue storage, excretion, etc. of another. The estimates given in Table 21.12 are considered to be the best available currently (21.14, 21.15).

All the elements measured were present in both the feed grass and the coals fired (Table 21.11). The ratios of toxic level concentration in product, given in the last column of Table 21.12 show that, with the exception of lead, all the other trace element concentrations in the dried grass are lower than any likely to put livestock at risk. The evidence for the toxic levels of lead is vague (21.5) but any danger suggested by Table 21.12 is almost certainly exaggerated as the usual range for lead in pasture grass is in the ranges 2 - 30 mg/kg d.b. worldwide and 2 - 7.5 mg/kg d.b. in the UK (21.5).

The trace element concentration in the stack gases from the drier at stack height and at ground level are given in Tables 21.6 and 21.8 respectively. The concentration of all the elements were at least 200 times less than any concentration considered harmful and therefore posed no problems.

From the testwork described above it follows, therefore, that coal firing can be recommended for the operation of fluidised bed combustion direct contact driers as it is most unlikely to create any health or environmental hazard with respect to trace element emissions.

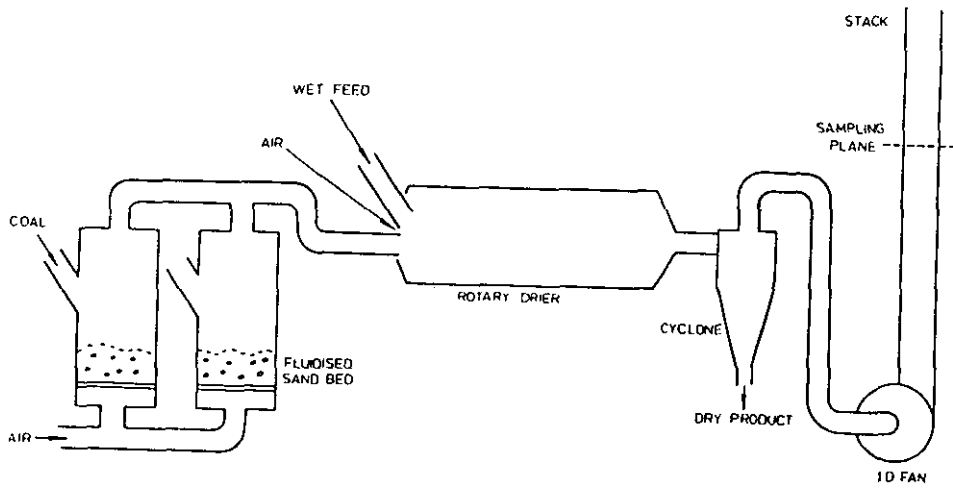


Figure 21.3
Schematic Diagram of a Coal-fired Crop Drier

Table 21.11

Trace Element Concentrations in a Grass Drier

Coal type	Stream sampled	Element concentration (mg/kg dry basis)										
		As	Cr	Co	Cu	F	Pb	Mn	Hg	Ni	V	Zn
Nottinghamshire	Coal	9	9	11	22	-	18	19	0.2	39	19	6
	Feed grass	0.1	2	0.06	10	-	2	37	0.06	2	1	28
	Dried product	3	3	1	12	-	5	40	0.05	9	6	25
	Enrichment ¹	30	1.5	16.7	1.2	-	2.5	1.1	0.8	4.5	6	0.9
Derbyshire	Coal	6	11	9	27	77	10	80	0.1	23	18	10
	Feed grass	0.1	2	0.09	8	7	3	90	0.05	1	1	33
	Dried product	2	2	0.6	12	12	5	80	0.04	3	4	26
	Enrichment ¹	20	1	6.7	1.5	1.7	1.7	0.9	0.8	3	4	0.8
Staffordshire	Coal	2	6	5	24	-	18	70	0.1	15	14	44
	Feed grass	0.1	2	0.07	7	-	2	100	0.04	1	1	25
	Dried product	0.5	1	0.4	10	-	4	80	0.03	2	3	25
	Enrichment ¹	5	0.5	5.7	1.4	-	2	0.8	0.8	2	3	1
Yorkshire	Coal	5	7	6	23	-	10	21	0.1	17	25	7
	Feed grass	0.2	2	0.08	4	-	1	90	0.02	1	1	30
	Dried product	2	3	0.7	10	-	4	90	0.02	6	6	30
	Enrichment ¹	10	1.5	8.7	2.5	-	4	1	1	6	6	1

Note 1 Enrichment = Concentration in Product / Concentration in feed gas

Table 21.12

Assessment of Health Risk through Product Contamination

Trace element	Maximum concentration in dried product mg/kg	Concentration toxic to cattle mg/kg	Concentration ratio toxic/product
As	3.0	>65 ¹	22
Cr	3.0	500 ²	167
Co	1.0	150	150
Cu	12	100	8.3
F	12	30-50 ⁴	2.5
Pb	5	>3 ³	0.6
Mn	90	820	9.1
Hg	0.05	5-10 ²	100
Ni	9	>250	28
V	6	25 ²	4.2
Zn	30	900	30

Note 1 Level likely to cause excessive As in milk; no evidence of harm to beast.

2 From laboratory studies with rats; no data for cattle.

3 Level at which excretion = ingestion. No evidence about toxic level but lead content of pasture ranges from 2 to 30 mg/kg (dry basis).

4 Reference (21.14).

21.3 Emissions of Alkali, Alkali Earth and Halogen Elements

21.3.1 Importance

Emissions of sodium, potassium, calcium, magnesium and chlorine from fluidised bed combustors are important as they are associated with fouling deposits on downstream heat transfer surfaces. Additionally, emissions of chlorine may exacerbate corrosion on such surfaces. Emissions of fluorine are also of interest in direct contact drying applications because of the poisonous nature of this element. Such emissions have been discussed in Section 21.2.7 above. All these elements under discussion originate in the mineral matter of the feed fuel. Coal fuels are an obvious source as such fuels may contain 5-50%, or more, of inorganic matter and emissions from coal fired combustors are discussed below. However, oil fuels also contain some sodium, chlorine and vanadium which can give rise to downstream corrosion problems. These aspects are discussed in Section 5 on oil firing.

21.3.2 Size of emissions during coal firing

The greater part of the inorganic matter of feed coals either remains in the bed or is recovered as coarse and fine grits in the gas cleaning system; see Figure 21.1. That part remaining in the stack gases is made up of very fine entrained solids with a still smaller proportion as inorganic salts in the vapour phase. Table 21.13 shows results of mass balance tests carried out using a laboratory, 70 mm (2.7 in.) diameter fluidised bed combustor operated at a bed temperature of 850°C (1560°F) and fluidising velocity of 0.5 m/s (1.6 ft/s). Three typical UK coals of varying fouling properties (21.17) were burnt; their analysis is given in Table 21.14. The Table 21.13 results indicate the proportions of the alkali elements and chlorine in the feed that left in the stack gases. For comparative estimating purposes it is suggested that this data may be used, in conjunction with a coal analysis and stack gas flow rate, to predict the alkali and halogen concentration in the stack gases. For example, at the operating conditions used in the combustor the sodium emissions were in the range of 0.7 - 18 ppm, according to the coal fired.

Table 21.13

Alkali and Halogen Mass Balances for Three Typical UK Coals

(% of element in feed coal, normalised to 100% balance)

Element	Coal *	Emitted from bed		Retained in
		Vapour	Fly ash	Bed Ash
Na	1	10.2	4.7	85.1
	2	2.8	22.5	74.7
	3	0.7	37.6	61.7
K	1	-	-	-
	2	1.8	79.4	18.8
	3	0.6	83.2	16.2
Ca	1	2.9	16.7	80.4
	2	0.6	28.6	70.8
	3	1.0	38.9	60.1
Mg	1	1.8	16.6	81.6
	2	0.3	25.1	74.6
	3	-	65.3	34.7
Cl	1	97.0	3.0	0
	2	98.1	1.9	0
	3	97.6	2.4	0

* For analysis see Table 21.14

Table 21.14
Analysis of Three Typical UK Coals

Coal		1	2	3
Proximate analysis (%w/w,ad)	Moisture	8.0	6.1	4.7
	Ash	3.1	4.9	5.2
	Volatile matter	35.5	35.7	34.6
	Fixed carbon	53.4	53.3	55.5
Calorific value	(kj/kg, db)	32220	31980	32220
Coking properties	BS Swelling number	1	1	3½
	Gray-King coke type	D	D	E
Ultimate analysis	C (%w/w, dmmf)	82.6	82.9	83.2
	H (")	5.3	5.2	5.4
	O (")	9.1	8.9	8.0
	N (")	1.6	1.6	1.7
	S (" db)	0.84	1.09	1.65
	Cl (" dmmf)	0.83	0.67	0.34
	Na (", db)	0.18	0.10	0.11
	K (")	0.01	0.08	0.10
	Ca (")	0.47	0.38	0.13
	Mg (")	0.08	0.10	0.04
Mineral content (%w/w,ad)	Kaolinite	1.17	2.04	2.74
	Mica	0.08	0.73	1.02
	Calcite	0.49	0.20	<0.02
	Ankerite	0.73	0.94	0.46
	Siderite	<0.01	0.24	<0.01
	Dolomite	0.25	0.29	0.05
	Pyrite	0.30	0.60	1.16
	Quartz	<0.01	0.26	0.43
	Gypsum	0.11	0.11	0.16
	Rutile	0.02	0.03	0.05
	Apatite	0.04	0.10	0.03
Sodium(as Na ₂ SO ₄)	0.51	0.30	0.35	

ad air dried.

db dry basis.

dmmf dry mineral matter free

21.3.3 Fouling assessment of coals

It is clearly of interest to predict the severity of fouling from the analysis of a coal. Since the fouling occurs in the freeboard, correlations used for conventional combustion may be applicable. The most widely accepted indices for this purpose are the slagging factor, R_s , and the fouling factors, R_f and R_f' .†(21.17,21.18).

The slagging factor, R_s , has been developed empirically to relate ash analysis to the fused slag deposits that form on furnace walls and other surfaces exposed predominantly to radiant heat. R_s is defined by,

$$R_s = (B_a/A_c) S \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad 21.1$$

where B_a = wt% of ($Fe_2O_3 + CaO + MgO + K_2O + Na_2O$) in the high temperature ash*

A_c = wt% of ($SiO_2 + Al_2O_3 + TiO_2$) in the high temperature ash.

S = wt% of total sulphur in the dry coal.

Equation 21.1 is valid when,

$$\text{wt\% of } (CaO + MgO) < \text{wt\% of } Fe_2O_3$$

Thus R_s is applicable to bituminous type ash but not to lignitic types.

The total sulphur, S , gives an indication of the amount of pyritic iron present which influences the state of oxidation of the iron in the slag and thus its plastic range. The parameter, R_s , has no theoretical basis but provides an indication of the melting point and viscosity of the slag.

† Symbols are defined in Section 1 of this Manual

* High temperature ash is the residual inorganic material produced when coal is raised in temperature in air to 815°C (1500°F) according to the British Standards procedures (21.19).

Equations 21.1 to 21.3 have been used to make a predicted assessment of the fouling and slagging properties of the three typical UK coals having the analysis given in Table 21.14. The predicted assessment is given in Table 21.16. These predictions correspond with the reported behaviour of these coals in industrial combustion trials (21.17). However, the extent of fouling and slagging during coal combustion is governed by the combustor design and operating conditions as well as by the nature of the fuel (the coal analysis and ash characteristics). Thus the use of such indices for fluidised bed combustion can only attempt to establish a broad ranking of coal ash deposition performance. Further insight may be gained from the next section where the underlying mechanism of fouling is discussed.

21.3.4 Mechanism of fouling

Detailed studies have been carried out at CRE to analyse fouling deposits and elucidate possible mechanisms of deposit formation (21.17). The deposits have been shown to be predominantly mixtures of sodium chloride and sodium sulphate with smaller proportions of compounds of potassium, calcium and magnesium and chloride and sulphate ions. Such mixtures form viscous liquids at fluidised bed combustion temperatures which quickly trap any entrained dust particles to build up layers of solid material.

Three typical UK coals were selected for the studies to give varying degrees of fouling and slagging; see section 21.3.3 above and Table 21.16. The coal analyses are given in Table 21.14. The sodium and chlorine occur in the coals as ions spread throughout the coal matrix (21.17) while sulphur is present mainly as iron pyrites. The potassium is predominantly in association with the insoluble micaceous clays and calcium and magnesium occur mainly as carbonates.

During the combustion process, tests on a 4.3 MW (1.4×10^6 Btu/h) industrial fluidised bed combustion boiler have shown that virtually all the chlorine in the coal is released into the gas stream as hydrochloric acid (21.20). At the same time sulphur is released as sulphur oxides except for a small proportion trapped as sulphate by calcined alkali earth carbonates in the coal ash; see also section 11. The hydrochloric acid evolved can react with Na, K, Mg and Ca compounds or their decomposition products to form volatile chlorides. These latter, in turn, can undergo chemical reactions with gaseous sulphur oxides to form sulphates. Such

Table 21.16

Fouling Property Assessment for Typical UK Coals and
their Ionisable Salt Content

Coal	1	2	3
Slagging factor, R_s	N/A	0.7	0.6
Predicted extent of slagging	-	medium	low/medium
Fouling factor, R_f	N/A	1.6	1.0
R_f'	7.1	N/A	N/A
Predicted extent of fouling	severe	severe	high
Ionisable salt content			
Na, % extracted ^{*1}	100	77	62
K, "	28	4	2
Ca, "	51	42	66
Mg, "	48	40	26
Cl, "	90	65	63
SO ₄ , "	9	44	100
Total ionisable salt removal, % of coal; af basis ^{*2}	1.4	1.1	0.7

^{*1} % extracted by boiling a - 212 μ m coal sample under reflux for 6 hours.

^{*2} extracted after 3 cycles of wet grinding in a high speed ball mill (2hr) and refluxing with boiling water (2hr).

changes can occur by gaseous reactions in the freeboard or at convenient surfaces, for example, on particles of fly ash or on tube banks, etc. Laboratory work has suggested that such gas phase reactions, with subsequent direct condensation of crystals from the gas phase onto cooled heat transfer surfaces may be the major cause of fouling with subsequent trapping of solids by the viscous salt mixture building up a deposit with a layered structure.

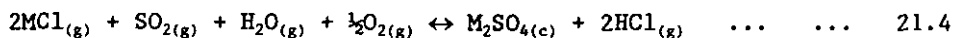
The factors affecting the build up of initial deposits have been studied on both the laboratory and plant scale, using a 0.2 MW (6.3×10^4 Btu/h) fluidised bed combustion furnace at CRE (21.17). The results are summarised briefly below and may assist in the selection of an optimum choice of operating conditions and tube bank location. The effect of deposits on the corrosion of metal components is discussed in Section 14.

21.3.4.1 Surface Temperature

The influence of surface temperature on the initial deposition of inorganic salt minerals from the combustion of coals is illustrated by Figure 21.4 for two typical UK coals. The deposits of all ionic species are at a maximum in the temperature range 550 - 650 °C (1020 -1200 °F) although the concentration of the deposits varies considerably from coal to coal. Electron photomicrographs at 600 °C (1110 °F) show that, although the deposits are predominantly crystalline, many crystals have rounded edges, which suggests that the salt mixture is in the semi-fluid state necessary for deposit build-up in the above temperature range.

21.3.4.2 Proximity to bed surface

Chemical reactions of the type,



where M = Na, K, $\frac{1}{2}$ Ca or $\frac{1}{2}$ Mg

(g) = gas phase

(c) = condensed (deposit) phase

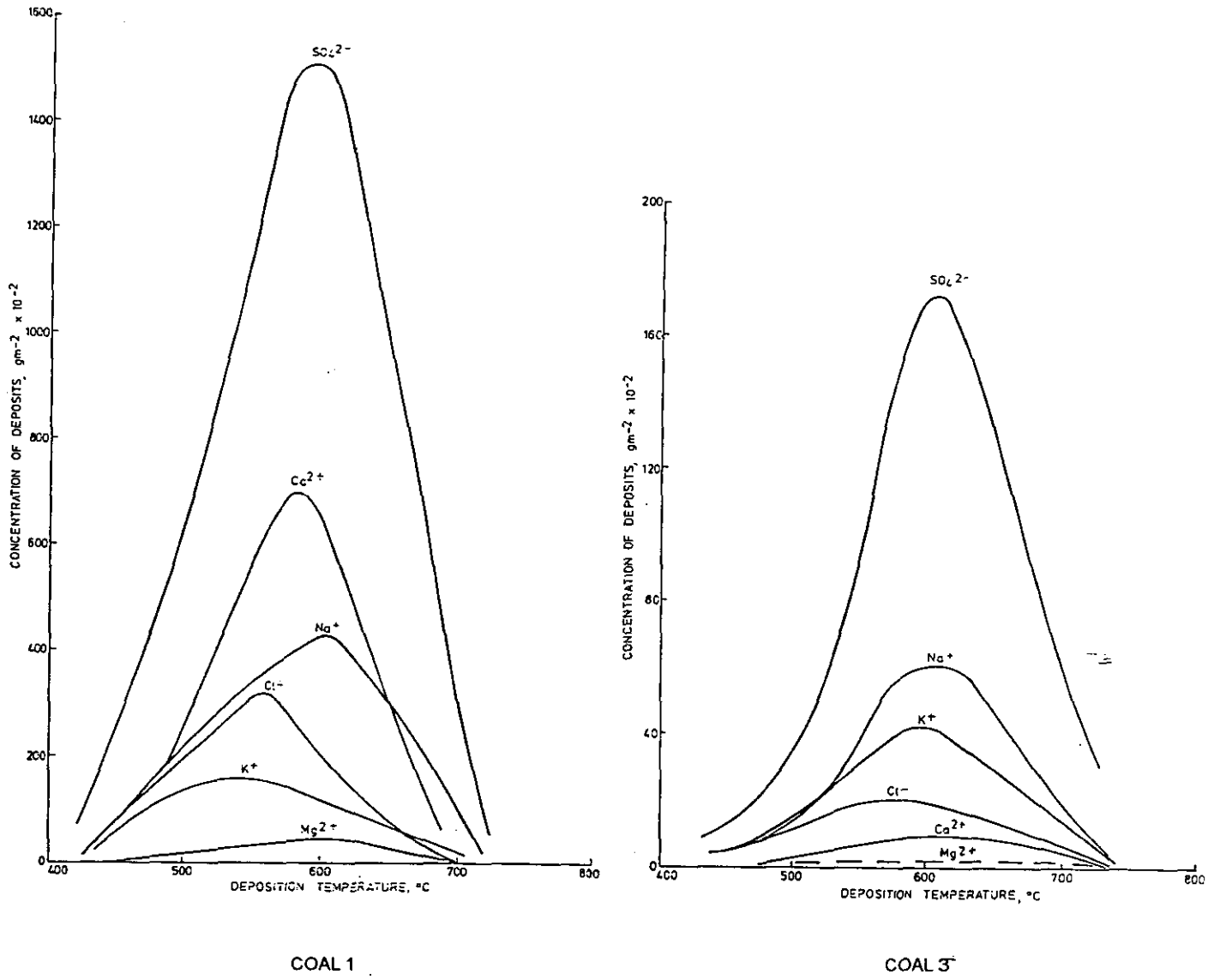


Figure 21.4
Influence of Surface Temperature on Initial Salt Deposition Rates

can occur in the freeboard. As the bed surface is approached the reaction time for such reactions is reduced. As a result the deposits become richer in chlorides, which have melting point eutectics lower than those of sulphates, and maximum deposition rates occur at lower temperatures in the range 500 - 600 °C (930 - 1110 °F). The calcium and sulphate concentrations are also reduced in the deposits.

21.3.4.3 Freeboard oxygen concentration

A reduction in the oxygen concentration of the freeboard gases will tend to suppress reactions of the type shown in equation 21.4 and will have the same effects on the deposits as placing surfaces closer to the fluidised bed.

21.3.4.4 Bed solids composition

Figure 21.5 illustrates the change in the concentration of sodium, chloride and sulphate ions in the initial deposits when the sulphur sorbents limestone and dolomite are used in place of silica sand as the bed solids material. Because of sulphur retention by the sorbents the partial pressure of sulphur dioxide in the freeboard is much reduced which, in turn, results in a reduction in alkali sulphate according to equation 21.4. As a result there is a marked increase in sodium and chloride ions in the deposits when sorbents are used. The increased proportions of alkali chlorides will enhance initial and ensuing deposition.

21.3.4.5 Coal composition

As the coal chlorine content is reduced lower concentrations of alkalis are deposited with the temperature of maximum deposition occurring 50 - 90 °C (90 - 160 °F) higher; see Figure 21.6. This temperature change is consistent with the hypothesis that alkali and alkali earth metals are mainly released as their chlorides during combustion.

The extent to which the elements Na, K, Ca, Mg and the chloride ion may become available in the gas stream is indicated by the ionisable salt content of the coal. The ionisable salt content is the proportion of those elements and ions that can be extracted from a finely ground coal sample by refluxing with water. Values for the most important elements are given in Table 21.16 for the three typical coals

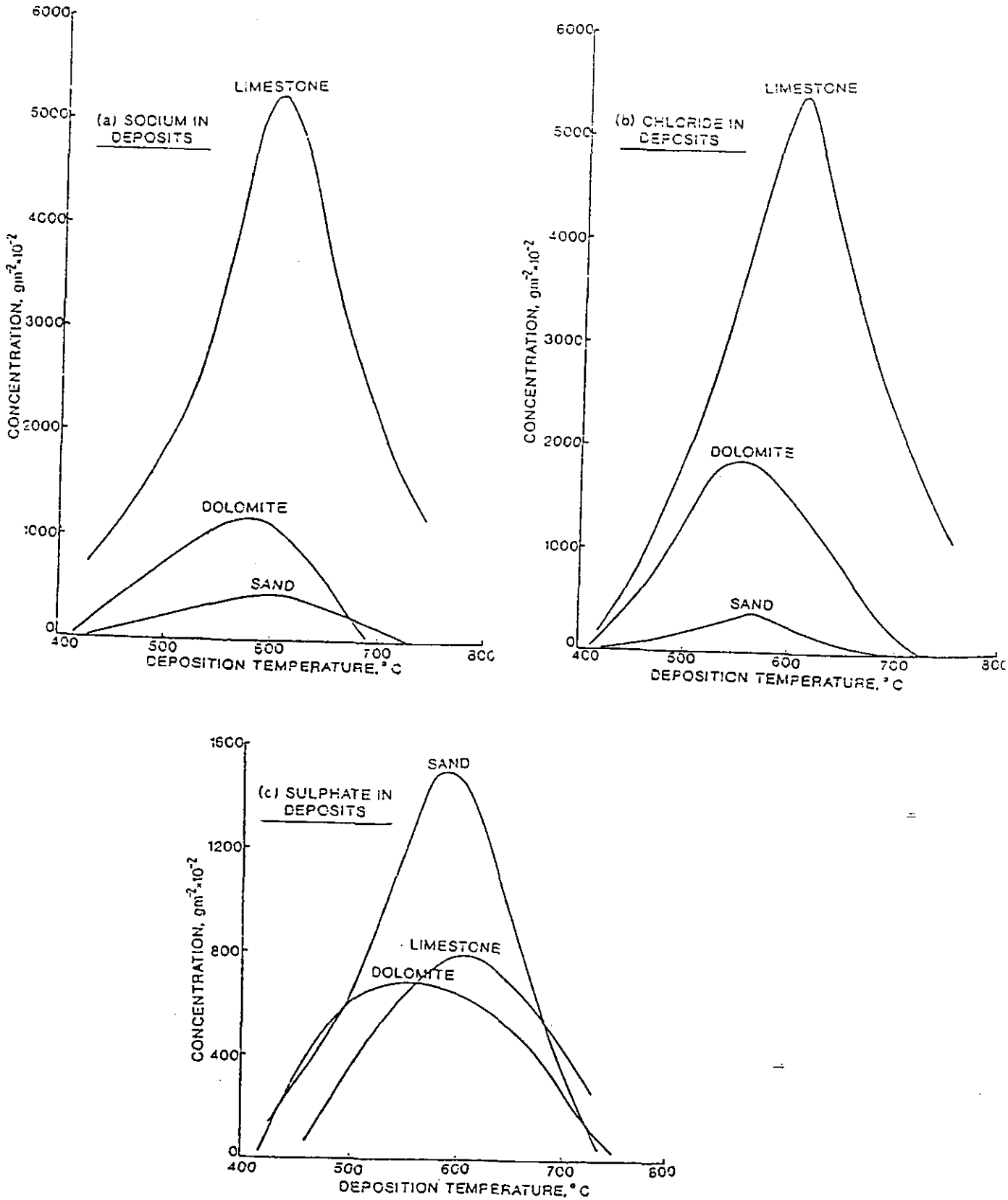


Figure 21.5
Effect of Bed Material on Deposit Composition
using Coal 1

SODIUM IN DEPOSITS

POTASSIUM IN DEPOSITS

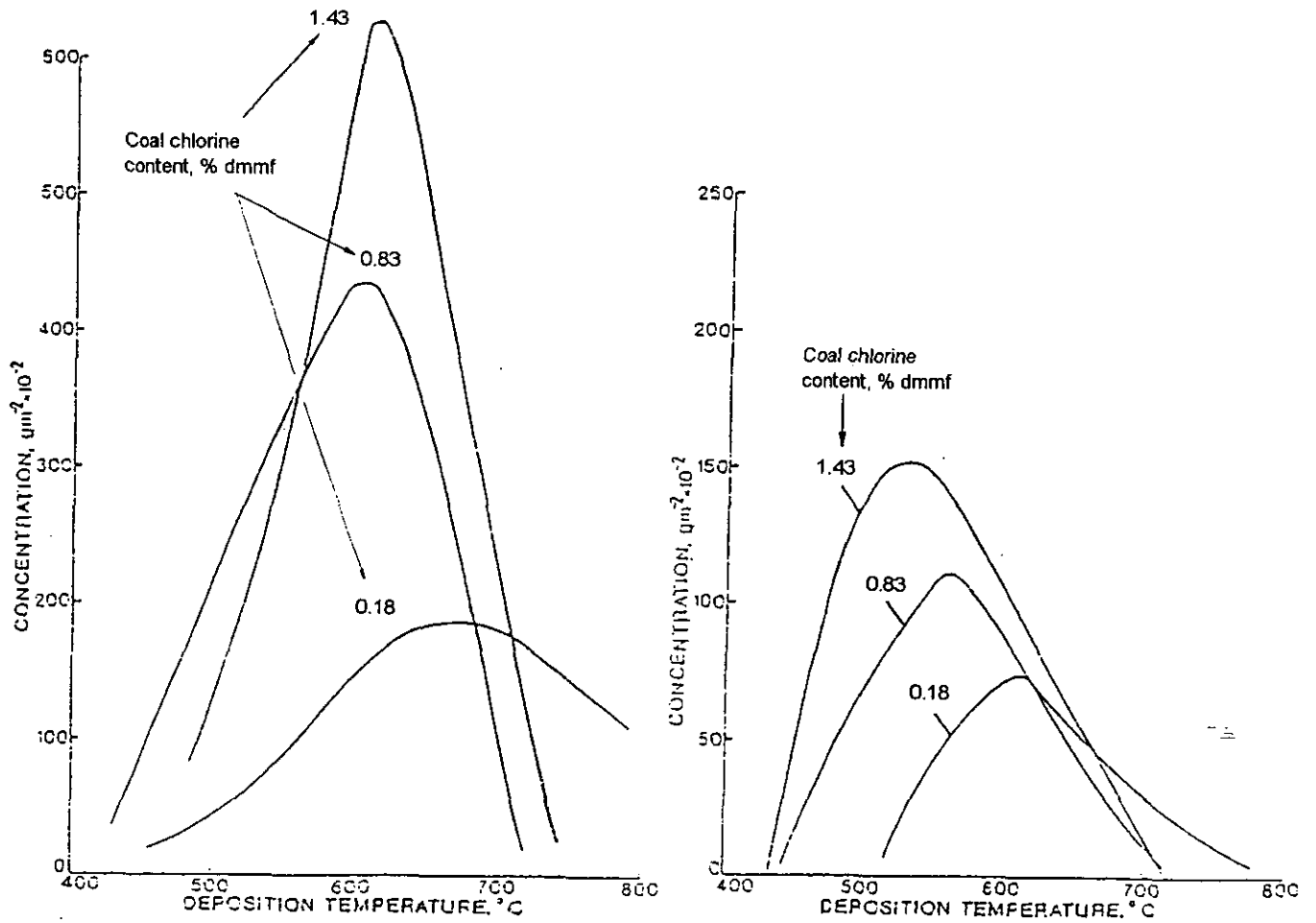


Figure 21.6
Effect of Coal Chlorine Content on the Deposition of Mineral Salts
using Coal 1

together with a total value expressed as a percentage of the total coal (as fired basis).

From the above discussion it is clear that the volatility of sodium and chlorine during fluidised bed combustion and the extent to which alkali halides are converted to sulphates in the freeboard are both important factors in the formation and subsequent build-up of fouling deposits. The ionisable salt content of a coal is a measure of the extent to which elements may be released during combustion. Table 21.16 shows that as the ionisable salt content falls so do the fouling tendencies of coals. However, insufficient data is yet available for the development of a quantifiable correlation.

21.3.5 Methods of reducing fouling

In the preceding section it is shown that fouling is caused by alkalis, principally sodium, and chlorine becoming volatilised during combustion with subsequent reaction in the freeboard with sulphur dioxide to form sulphates. Not all the alkalis in the coal feed are released; a proportion can be held back as non-volatile compounds in the ash. Most of the potassium is normally retained in this way and some sodium. The ionisable salt content of the coal is regarded as an indicator of the alkali and chlorine retention and hence of the fouling propensities of a coal (see Section 21.3.3) although no quantitative correlation is yet available.

Two approaches to the reduction of fouling are, therefore, possible:

- 1) To burn coals containing less sodium and chlorine; i.e. those having a lower ionisable salt content.
- 2) To treat coals with an additive that will assist in retaining more sodium in a non-volatile form.

Approach 1 has been discussed in Section 21.3.4.5 above and Figure 21.6 illustrates the fouling reduction that is achievable. Approach 2 has been studied using commercially available additives (21.21). Sodium appears to be retained in non-volatile form through reaction with the clay mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) during combustion, forming compounds such as nepheline (NaAlSiO_4) and hauyne ($(\text{Na,Ca})_8(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4)_2$). During conventional (stoker feed) coal combustion the addition of kaolinite as a fuel additive has been shown to have considerable potential in reducing fouling. Unfortunately at the lower temperatures of fluidised

bed combustion, 850 °C (1560 °F) compared with 1100 -1200 °C (2010 -2190 °F), the reaction rate of sodium with kaolinite is negligible. However, some compounds may be able to promote a significant reaction rate of sodium or magnesium with kaolinite at fluidised bed combustion temperatures. Potassium nitrate appears promising for this purpose even though its addition increases the total alkali to be "fixed". No firm recommendations can yet be made as the subject is an area of on-going research.

21.4 Emissions of Secondary Combustion Products

The principal secondary combustion product occurring in the freeboard of a coal-fired fluidised bed combustor is unburnt carbon, which is normally retained with the fly ash. Section 4.5.3, Issue 002, should be consulted for details on re-firing carbon rich fly ash to increase the overall combustion efficiency. However, traces of hydrogen, carbon monoxide and methane can also occur in the freeboard gas at concentrations which increase rapidly at low excess air levels. The effect is illustrated by Figure 21.7 which shows the change in concentration of these gases with freeboard excess air level for a typical medium sized industrial boiler (3MW (1×10^7 Btu/h)) (21.22).

An interesting feature of the results shown in Figure 21.7 is that over the entire excess air range the ratio of methane to hydrogen remains close to unity and that of carbon monoxide to methane is approximately 4.0.

21.5 Emissions of Complex Organic Compounds

During the combustion of low grade and waste fuels the possibility of the emission of complex organic compounds such as dioxins should always be considered. No generalised data is available because of the variable nature of such fuels.

During coal combustion minute traces of polycyclic hydrocarbons have been detected in the freeboard gases of the CURL pressurised combustor (21.23) as shown in Table 21.17. The National Academy of Sciences classification for carcinogenicity (21.24) is included in Table 21.17 for reference.

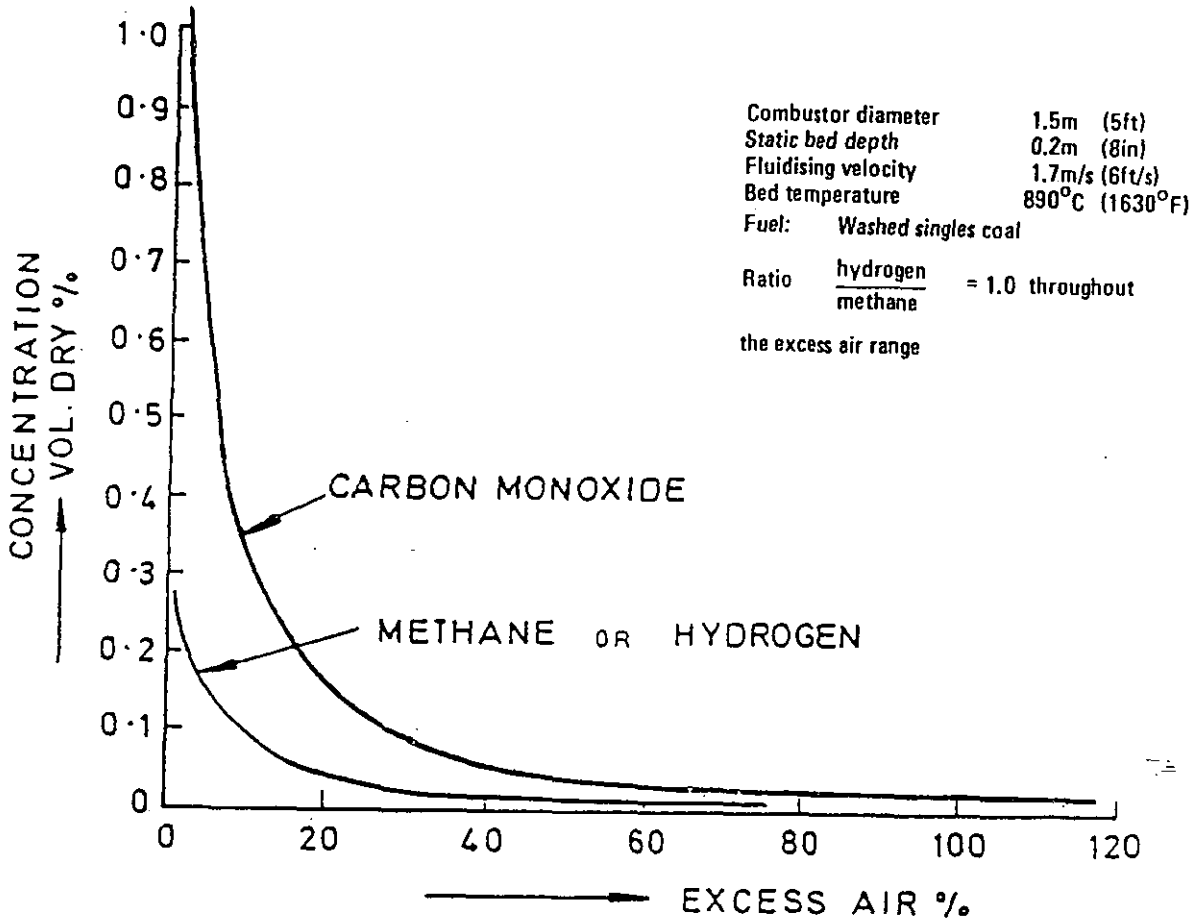


Figure 21.7
Variations of CO, CH₄, and H₂ Concentrations in Flue Gases with the Excess Air Level

Table 21.17
Polycyclic Organic Material Analyses

Component	NAS Notation	Concentration		
		in exhaust duct ppb (10^{-9})	in flue gas alone ppt (10^{-12})	in total flue gas ppt (10^{-12})
Anthracene/Phenanthrene	-	<0.2	93	93
Methyl anthracenes	*	<0.2	10	10
Flouranthene	-	<0.2	21	21
Pyrene	-	<0.2	9	9
Methyl Pyrene/ Flouranthene	-	<0.2	7	7
Benzo (c) phenanthrene	***	<0.2	3	3
Chrysene/Benz (a) anthracene	*	<0.2	3	3
Methyl chrysenes	*	<0.2	<0.7	0.8
7,12-Dimethylbenz (a) anthracene	****	<0.2	<0.1	<0.15
Benzo fluoranthenes	**	<0.2	<0.1	<0.15
Benz (a) pyrene	***	<0.2	<0.1	<0.15
Benz (e) pyrene	-	<0.2	<0.1	<0.15
Perylene	-	<0.2	<0.1	<0.15
Methylbenzopyrenes	-	<0.2	<0.1	<0.15
3-Methylcholanthrene	****	<0.2	<0.1	<0.15
Indeno (1,2,3-cd) pyrene	*	<0.2	<0.1	<0.15
Benzo (ghi) perylene	-	<0.2	<0.1	<0.15
Dibenzo (a,h) anthracene	***	<0.2	<0.1	<0.15
Dibenzo (a,h) carbazole	***	<0.2	<0.1	<0.15
Dibenz (ai and ah) pyrenes	***	<0.2	<0.1	<0.15
Coronene	-	<0.2	<0.1	<0.15

Note: NAS notation: the greater the number of * the more carcinogenic the compound
 thus, - : not carcinogenic
 * : weakly carcinogenic
 , *, **** : strongly carcinogenic (in ascending order)

21.6 Emissions of Radioactive Compounds

Table 21.18 shows, for information without comment, the results of radioactivity measurements on samples of bed solids and freeboard gases from two tests using the CURL pressurised combustor (21.23).

Table 21.18
Radioactivity Measurements

Sample Description	Radioactivity pico Curies/gm	
	α	β
<u>first test</u>		
Bed material	18.8 ± 4.0	46.8 ± 6.0
Coal	5.0 ± 2.4	9.0 ± 5.2
Dolomite	5.8 ± 2.4	8.2 ± 5.2
Primary cyclone dust	8.2 ± 3.2	44.4 ± 6.0
Secondary cyclone dust	14.8 ± 4.0	69.4 ± 6.6
<u>second test</u>		
Bed material	8.2 ± 3.2	24.6 ± 5.4
Coal	10.6 ± 3.2	16.0 ± 5.4
Dolomite	2.4 ± 2.4	27.4 ± 5.4
Primary cyclone dust - coarse	19.6 ± 4.0	55.0 ± 6.4
- fine	9.0 ± 3.2	61.2 ± 6.4
- total	19.4 ± 4.0	55.1 ± 6.4
Secondary cyclone dust - coarse	14.0 ± 4.0	84.6 ± 7.0
- fine	5.0 ± 2.4	94.8 ± 7.2
- total	11.3 ± 3.5	87.7 ± 7.1
Flue gas dust - coarse	22.2 ± 5.0	111.8 ± 7.2
- fine	7.0 ± 7.0	78.9 ± 23.7
Total in flue gas dust	20.7 ± 5.2	108.5 ± 8.9
Total in flue gas pico Curies/kg of gas	4.9	25.1

* Limits are estimates of the 2 σ counting error

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