

The Oslo Commission was established by the Convention for the Prevention of Marine Pollution by Dumping from Ships and Aircraft (the “Oslo Convention”) which was opened for signature in Oslo on 15 February 1972. The Convention entered into force on 6 April 1974. It has been ratified by the following European States: Belgium, Denmark, Finland, France, Federal Republic of Germany, Iceland, Ireland, Netherlands, Norway, Portugal, Spain, Sweden and the United Kingdom.

The Convention for the Prevention of Marine Pollution from Land-Based Sources (the “Paris Convention”) was opened for signature in Paris on 4 June 1974. The Convention entered into force on 6 May 1978. It has been signed by Luxembourg. It has been ratified by the following: Belgium, Denmark, the European Economic Community, France, Federal Republic of Germany, Iceland, Ireland, Netherlands, Norway, Portugal, Spain, Sweden and the United Kingdom.

*La Commission d’Oslo a été créée par la Convention pour la Prévention de la Pollution Marine par les Opérations d’Immersion Effectuées par les Navires et Aéronefs, dite Convention d’Oslo, qui a été ouverte à la signature à Oslo le 15 février 1972. La Convention est entrée en vigueur le 6 avril 1974 et a été ratifiée par les Etats suivants: la Belgique, le Danemark, l’Espagne, la Finlande, la France, l’Irlande, l’Islande, la Norvège, les Pays-Bas, le Portugal, la République fédérale d’Allemagne, le Royaume-Uni de Grande Bretagne et d’Irlande du Nord et la Suède.*

*La Commission de Paris a été créée par la Convention pour la Prévention de la Pollution Marine d’Origine Tellurique, dite Convention de Paris, qui a été ouverte à la signature à Paris le 4 juin 1974. La Convention est entrée en vigueur le 6 mai 1978. Le Luxembourg est Signataire de la Convention. La Convention a été ratifiée par: la Belgique, la Communauté économique européenne, le Danemark, l’Espagne, la France, l’Irlande, l’Islande, la Norvège, les Pays-Bas, le Portugal, la République fédérale d’Allemagne, le Royaume-Uni de Grande Bretagne et d’Irlande du Nord et la Suède.*

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*Pour tout renseignement sur les activités et les publications des Commissions d'Oslo et de Paris, ou pour tout exemplaire supplémentaire de ce rapport contacter:*

The Secretary  
Oslo and Paris Commissions  
New Court  
48 Carey Street  
London WC2A 2JQ  
United Kingdom

Tel: +44 (0)171 242 9927

Fax: +44 (0)171 831 7427

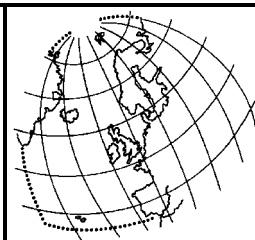
E-mail: [Secretariat@ospar.org](mailto:Secretariat@ospar.org)

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# Oslo and Paris Commissions 1997



## Large Combustion Installations ( $\geq 50$ MWth)

### Emissions and reduction in emissions of heavy metals and persistent organic compounds

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## **Introduction<sup>1</sup>**

Because of their many uses in electricity generation, industrial processes, transport, domestic heating, etc., fossil fuels are a significant cause of environmental pollution.

The combustion of fossil fuels leads to atmospheric emissions which contribute directly to the degradation in air quality. The most familiar of these emissions are those of sulphur dioxide and the oxides of nitrogen.

The atmosphere is also a far from insignificant path for the transfer of pollutants to other compartments of the environment. Thus, it has been clearly established that soils and aquatic media are affected by the transfer, sometimes over long distances, of heavy metals or persistent organic compounds released into the air.

The circulation of toxic metals and persistent organic compounds through the soil, water and atmosphere, as well as their inevitable passage into the food chain, is a source of concern for the environment in general and for humans in particular.

However, there are many problems that make an environmental approach to anthropogenic emissions of trace elements very tricky, and that only rarely allow definite conclusions to be drawn.

It is important to review these problems, even if only briefly:

- Trace element analyses always imply laborious and difficult investigations. The search for often minute concentrations of heavy metals or persistent organic compounds requires the use of analytical methods which have both a high sensitivity and a high degree of discrimination. The results obtained are subject to uncertainties that are generally quite significant;
- Heavy metals are liable to be encountered in various forms. In the environment, some of these forms are relatively soluble, mobile and potentially bioavailable, while others are insoluble and biologically inert. The form in which a metallic compound occurs can change with time after reactions with other components of the environment;

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<sup>1</sup> Whilst Germany appreciates the amount of work that has gone into this document and the valuable information that it provides, Germany holds a reservation on this document since it lists “sea water scrubbing”, which is accompanied by a direct transfer of pollutants to the marine environment, as a best available technique (BAT) for flue gas desulphurisation. Germany considers such a qualification as inappropriate and incompatible with the spirit of the Convention for the Prevention of Marine Pollution from Land-Based Sources.

- Some families of persistent organic compounds cover a multitude of molecular forms with physical, chemical and biological properties that vary according to the substance in question. This is particularly the case with polycyclic aromatic hydrocarbons and polychlorinated dibenzodioxins and dibenzofurans. There are numerous compounds corresponding to these whose environmental impact differs from one to another;
- Inventories of trace element emissions are still scarce and uncertain. This is both because of the difficulties with the sampling and analyses mentioned above and because of the lack of measurements that are frequent enough and systematically applied to all possible sources of emission.

Having said that, the frequent absence of accurate data should in no way mean that we cease to examine possible preventive and curative measures as soon as a human activity is a potential source of emission. This is particularly the case with the combustion of fossil fuels.

This study attempts to detail the contribution of the consumption of fossil fuels to atmospheric pollution and, in the special case of large combustion installations (with a capacity of at least 50 MWth), to investigate the problem of the emissions of heavy metals and persistent organic compounds capable of directly or indirectly affecting the aquatic environment that the Oslo and Paris Commissions have set themselves the objective of protecting.

Peat, regarded as a semi-fossil fuel, and plant-derived non-fossil fuels, such as wood, are also used in a few large combustion installations. Within the limits of the available data on this subject, environmental aspects relating to the use of these types of fuel have also been studied.

Although this document is more particularly concerned with trace elements, an integrated approach to environmental problems related to the running of large combustion installations has been undertaken with the idea of optimising the fight against pollution and strictly limiting the risks of transferring pollution from one part of the environment to another. This approach is in keeping with the spirit of Directive 96/61/EC of 24 September 1996 on the integrated prevention and reduction of pollution.

This approach has also been made necessary by the many interfaces which in fact exist between the various techniques for reducing polluting emissions.

For, although there are actually only a few methods specifically for the prevention or reduction of trace element emissions into the environment, the objectives being pursued in this field will also very often be attained by the use and optimisation of methods intended to reduce or prevent emissions of other pollutants.

In particular, methods for controlling dust emissions are of considerable importance to atmospheric emissions, while methods for controlling the release of sulphur dioxide and nitrogen oxides may, to various extents, have some effect on the releases of certain heavy metals and persistent organic compounds.

This document take into account work in progress in other authorities, such as the European Commission and the UN Economic Commission for Europe.

In particular, however, the intrinsic performances of the methods for controlling emissions of dust, sulphur dioxide and nitrogen oxides are only reported here in part and for information.

Neither are economic considerations discussed.

For these two aspects, reference should be made to the work of the above-mentioned organisations, particularly that relating to the draft amendment of Directive 88/609/EEC of 24 November 1988 on the limitation of emissions of certain pollutants into the air from large combustion plants.

## **1. Levels of consumption of fossil fuels**

[(1), (2)]

The growth in the world consumption of commercial primary energy (coal, oil, gas) was very buoyant in the 1960s with a mean annual increase of 5% from 1960 to 1973. However, it experienced a distinct slowdown after the first oil crisis (+3,1% per year from 1973 to 1979) and even a fall after the second oil crisis (-0,7% per year from 1979 to 1982).

From 1983, and particularly after 1986, with the recovery from the oil crisis (reflected in a reduction of oil prices by a half) and with the return to a stronger economic growth in industrialised countries, the increase in energy consumption was resumed with higher growth rates (+3% from 1983 to 1989).

After stagnating in 1990 and increasing by about 0,5% in 1991, the world energy demand remained roughly constant in 1992, but with considerable regional contrasts: a moderate growth in the USA (+1,8%), strong growth in Asia (+5%), a substantial reduction in Eastern Europe (-8%) and virtual stagnation in Western Europe.

**Table 1: Changes in world primary energy consumption [IEA, OECD]**

	1973		1979		1991	
	Mtoe	%	Mtoe	%	Mtoe	%
North America	1 876	34,6	2 060	31,7	2 145	27,3
South America	208	3,8	292	4,5	398	5,1
Western Europe	1 223	22,6	1 333	20,5	1 452	18,5
EU (12 countries)	1 079	19,9	1 168	18,0	1 242	15,8
Germany	338	6,2	37	5,7	347	4,4
Spain	52	1,0	67	1,0	92	1,2
France	177	3,3	190	2,9	232	3,0
United Kingdom	221	4,1	220	3,4	218	2,8
Eastern Europe	1 113	20,5	1 440	22,2	1 613	20,5
Africa	90	1,7	127	1,9	217	2,8
Asia	837	15,5	1 172	18,0	1 922	24,5
Oceania	68	1,3	80	1,2	107	1,3
Total	5 415	100	6 503	100	7 854	100

## 1.1 Oil

In 1992, with a demand of 3,1 Gtoe, oil was the main world energy source since it accounted for nearly 40% of commercial energy requirements (50% in 1973).

**Table 2: Changes in consumption of oil products (in million tonnes) for the European Union and some of its Member States [EUROSTAT, SOEC]**

	1973	1990	1991	1992
EU (12 countries)	n.a.	459,0	487,2	493,8
Germany (*)	136,9	106,4	126,5	127,5
France	111,2	79,5	84,5	84,2
The Netherlands	25,4	20,3	20,6	21,5
Belgium	25,8	17,3	18,6	19,2
Denmark	17,1	8,1	8,3	8,1
Spain	n.a.	40,5	40,5	41,8
Portugal	n.a.	11,3	11,3	12,4
United Kingdom	99,4	73,2	74,4	74,4

(\*) Former West Germany until 1990; Germany after reunification from 1991

**Table 3: Changes in consumption of heavy fuel oil (in million tonnes) for the European Union and some of its Member States [IEA, OECD]**

	1973	1980	1985	1990	1991
EU (12 countries)	221,7	179,2	93,1	82,1	85,7
Germany (*)	42,6	30,4	14,3	10,1	10,6
France	37,5	28,6	9,3	7,8	9,1
United Kingdom	43,4	22,7	18,2	14,0	14,5

(\*) Germany after reunification



The main countries within the boundaries covered by the Paris Convention with oil reserves are Norway and the United Kingdom.

## 1.2 Natural Gas

In 1992, natural gas accounted for about 22% of commercial world energy demand (1,7 Gtoe).

**Table 4: Changes in consumption of natural gas (in Mtoe) for the European Union and some of its Member States [IEA, OECD]**

	1973	1979	1989	1990	1991
EU (12 countries)	118	179	210	215	231
Germany	29	51	55	55	58
France	14	21	24	25	28
The Netherlands	29	33	31	31	34
United Kingdom	25	40	46	47	51

In 1991, the consumption of natural gas as a proportion of total energy consumption was 18,6% for the European Union, 16,6% for Germany, 12,1% for France, 49,2% for the Netherlands and 23,3% for the United Kingdom.

The main countries within the boundaries covered by the Paris Convention with reserves of natural gas are Norway, the Netherlands and the United Kingdom.

## 1.3 Coal

In 1992, coal (hard coal, lignite, coke, briquettes) represented approximately 28% of commercial world energy demand (2,2 Gtoe), almost identical with that in 1973.

**Table 5: Changes in coal consumption (in million of toe) for the European Union and some of its Member States [IEA, OECD]**

	1973	1979	1989	1990	1991
EU (12 countries)	284	291	291	286	274
Germany	139	138	136	129	115
France	29	32	21	20	21
United Kingdom	76	74	63	64	64

**Table 6: Changes in gross internal consumption of hard coal (in millions of tonnes) for the European Union and some of its Member States [EUROSTAT, SOEC]**

	<b>1973</b>	<b>1990</b>	<b>1991</b>	<b>1992</b>
EU (12 countries)	n.a.	320,9	328,8	308,8
Germany (*)	98,5	82,6	86,0	81,8
France	40,3	29,2	31,2	28,6
The Netherlands	4,8	14,2	13,0	12,1
Belgium	17,0	16,0	15,4	14,3
Denmark	3,5	10,0	13,5	11,0
Spain	n.a.	31,3	32,2	33,0
Portugal	n.a.	4,5	4,7	4,7
United Kingdom	133,6	106,9	108,2	100,4

(\*) Former West Germany until 1990; Germany after reunification from 1991.

Among the countries within the boundaries covered by the Paris Convention with coal reserves, Germany is broadly the leader with estimated reserves (1991) of 80 billion tonnes.

## **1.4 Particular case of electricity generation**

From 1950 to the present, the world consumption of electricity has increased 12-fold. The OECD countries (covering 16% of the world population) consume 60% of the world production of electricity.

The generation of electricity by thermal power stations running on fossil fuels has doubled worldwide over the last 20 years (this trend is mainly due to developing countries, whose production has increased by a factor of 5). In spite of this increase, the relative contribution of thermal power stations to the total production of electricity has fallen off, faced with the rise in nuclear generation and has decreased from 74% in 1970 to 64% today.

At present, coal accounts for about 60% of the world production of electricity by thermal power stations, while oil accounts for nearly 19% and natural gas for something of the order of 20%.

**Table 7: Net installed power (GW) of power stations at 31/12/1991 by type of production [UNO]**

	<b>Thermal</b>	<b>Hydroelectric</b>	<b>Nuclear</b>	<b>Geothermal</b>
North America	614,6	151,7	121,1	5,5
South America	65,1	98,8	2,3	0,9
Western Europe	306,2	159,5	123,7	1,4
EU (12 countries)	271,9	82,2	108,9	0,9
Germany	89,2	8,9	25,0	-
Spain	20,3	16,3	7,0	-
France	22,6	24,9	59,2	0,2
The Netherlands	16,9	-	0,5	0,1
United Kingdom	54,5	4,2	11,3	-
Sweden	7,9	16,2	10,0	-
Eastern Europe	324,1	86,9	46,6	-
Africa	54,6	19,5	1,0	-
Asia	445,2	124,4	47,8	1,3
Oceania	31,9	12,3	-	0,3
<b>Total</b>	1 841,7	653,1	342,5	9,4

## 1.5 The future

It is quite difficult to make projections about the consumption of fossil fuels in the decades to come.

However, unless we are very much mistaken, it is possible to predict a continual growth of consumption in developing countries or the probable continuation of the current stagnation in Western Europe.

As far as predictions of the distribution of consumption between the different types of fuel are concerned, an analysis of the size of proved reserves throws some useful light on the matter.

The following table gives the state of world reserves of energy.

**Table 8: State of proved world reserves of fossil fuels [(1)]**

Type of fuel	Date of estimate	Reserves (Mtoe)	Location of reserves	Estimated duration of production ( )
Coal (including lignite)	1/1/1991	532 451	Asia (21,3%) Eastern Europe (29,5%) North America (23,7%) Western Europe (8,5%) Africa (7,2%) Australia, Oceania (8,7%) Latin America (1,1%)	250 years
Oil	1/1/1993	137 898	Middle East (65,5%) Latin America (13,6%) Eastern Europe (5,8%) Africa (6,1%) North America (3%) China (2,4%) Eastern Europe, Oceania (2%) Western Europe (1,6%)	45 years
Natural gas	1/1/1993	131 326	Former-USSR (38,4%) Middle East (30,7%) Asia apart from Middle East (7,4%) North America (5%) Africa (6,7%) Latin America (5,3%) Western Europe (4,3%)	65 years

(\*) duration of production of proved reserves expressed in years of production 1991

As we shall see later, the choice of the type of fuel has a direct effect on the releases into the environment that its combustion is capable of producing. In particular, natural gas has considerable advantages because of its relatively low potential for emission compared with coal or oil.

However, the choice of fuel is made on the basis not only of technical factors but of economic and geopolitical ones as well. For this reason, it would not be realistic to recommend the preferential use of such and such a fuel solely on environmental grounds.

Not only that, but the state of world reserves clearly shows the need to envisage the use of all available fossil fuels. The measures taken to prevent or reduce emissions into the environment should then be proportional to the potential emissions from the fuel in question.

In this connection, the large amount of work carried out into the use of clean technologies (particularly gasification) for the combustion of coal in large combustion installations is of great importance.

## **2. Emissions due to the combustion of fossil fuels**

The combustion of fossil fuels is a source of atmospheric emissions contributing significantly to the degradation of air quality. Depending on the type of use, releases into the aquatic environment are also liable to be involved. Waste is also produced.

The last two aspects of the integrated approach to pollution will not be dealt with in this chapter, which is concerned with emissions due to the combustion of fossil fuels in general, but will be the subject of developments in the chapter on the particular case of large combustion installations ( $\geq 50$  MWth).

Whether it is at the domestic level (heating of dwellings) or the industrial level (production of steam or electricity), the combustion of fossil fuels contributes to atmospheric releases of carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ), which are direct greenhouse effect gases.

The various uses to which fossil fuels are put are also the source of emissions of sulphur dioxide ( $\text{SO}_2$ ), nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide ( $\text{CO}$ ), dust, hydrochloric acid, volatile non-methanic organic compounds (VNMOC), heavy metals, etc. in variable quantities depending on the use, the fuel and the processes involved. It is estimated that the main global responsibility for the emissions of sulphur into the atmosphere lies at the door of thermal power stations.

Tables 9 and 10 show the changes in the total emissions of  $\text{SO}_2$  and  $\text{NO}_x$  in all the countries that are signatories to the 1992 OSPAR Convention. Tables 11 to 13 give details of the emissions into the air of various pollutants as a result of the combustion of fossil fuels in several of these countries.

Note: it should be stressed that the methods of measurement, the definitions and the estimates made of the emissions of atmospheric pollutants are liable to be inconsistent between one country and another. The data that follow therefore require a certain amount of caution in their interpretation.

**Table 9: Change between 1980 and 1993 in the total SO<sub>2</sub> emissions (in kt/year) for countries that are signatories to the 1992 OSPAR Convention [(3)]**

	1980	1987	1990	1993	Change 1980/1993 (in %)
Belgium	828	367	317	294	-64
Denmark	451	251	180	157	-65
Finland	584	328	260	123	-79
France	3 338	1 290	1 298	1 121	-66
Germany (*)	7 517	7 351	5 331	3 153	-58
Iceland	6	23	24	24	300
Ireland	222	174	178	157	-29
The Netherlands	490	263	205	157	-67
Norway	141	74	54	36	-74
Portugal	266	232	283	300	13
Spain	3 319	1 903	2 266	2 071	-38
Sweden	508	228	136	101	-80
Switzerland	116	63	43	34	-71
United Kingdom	4 903	3 897	3 752	3 184	-35
<b>Total</b>	<b>22 689</b>	<b>16 444</b>	<b>14 327</b>	<b>10 912</b>	<b>-52</b>

(\*) Germany after reunification

**Table 10: Change between 1980 and 1993 in the total NO<sub>x</sub> emissions (in kt/year) for countries that are signatories to the 1992 OSPAR Convention [(3)]**

	1980	1987	1990	1993	Change 1980/1993 (in %)
Belgium	442	331	352	340	-23
Denmark	274	302	269	267	-3
Finland	295	288	300	280	-5
France	1 823	1 630	1 585	1 544	-15
Germany (*)	3 657	3 598	3 071	2 274	-38
Iceland	13	18	20	23	77
Ireland	73	115	115	122	67
The Netherlands	583	599	575	552	-5
Norway	184	237	230	229	24
Portugal	96	146	215	246	156
Spain	950	892	1 188	1 227	29
Sweden	454	437	411	398	-12
Switzerland	170	174	165	145	-15
United Kingdom	2 319	2 558	2 702	2 339	1
<b>Total</b>	<b>11 333</b>	<b>11 315</b>	<b>11 198</b>	<b>9 986</b>	<b>-12</b>

(\*) Germany after reunification

**Table 11: Changes in the emissions (in kt/year) of SO<sub>2</sub> and NO<sub>x</sub> due to the combustion of fossil fuels in Member States of the European Union [(4)](\*)**

	1980		1986		1990		1995		2000		2010	
	SO <sub>2</sub>	Nox	SO <sub>2</sub>	NOx	SO <sub>2</sub>	NOx	SO <sub>2</sub>	NOx	SO <sub>2</sub>	NOx	SO <sub>2</sub>	NOx
<b>Production of electricity</b>	<b>9 946</b>	<b>2 578</b>	<b>8 610</b>	<b>2 395</b>	<b>8 301</b>	<b>2 513</b>	<b>6 495</b>	<b>2 303</b>	<b>3 855</b>	<b>1 735</b>	<b>552</b>	<b>1 298</b>
using solid fuels	5 896	1 782	6 508	1 894	6 012	1 927	4 410	1 746	2 561	1 383	487	1 085
using oil	4 022	607	2 081	337	2 270	429	2 072	392	1 287	213	61	45
using gas	29	189	21	164	19	157	13	165	7	139	4	169
<b>Energy sector</b>	<b>1 495</b>	<b>270</b>	<b>819</b>	<b>210</b>	<b>714</b>	<b>214</b>	<b>752</b>	<b>229</b>	<b>760</b>	<b>231</b>	<b>721</b>	<b>247</b>
solid fuels	39	8	23	5	15	4	13	3	12	3	9	2
oil	1 400	228	758	172	699	198	739	213	748	213	712	231
gas	55	34	39	32	0	12	0	15	0	15	0	14
<b>Industry</b>	<b>4 243</b>	<b>904</b>	<b>2 116</b>	<b>718</b>	<b>2 473</b>	<b>772</b>	<b>2 516</b>	<b>795</b>	<b>2 415</b>	<b>797</b>	<b>2 394</b>	<b>846</b>
solid fuels	457	106	657	164	544	149	584	160	620	170	732	201
oil	3 743	550	1 404	314	1 871	333	1 879	331	1 746	309	1 616	290
gas	43	248	55	241	58	290	52	304	49	318	46	356
<b>Domestic and commercial use</b>	<b>2 307</b>	<b>662</b>	<b>1 296</b>	<b>611</b>	<b>1 131</b>	<b>539</b>	<b>1 064</b>	<b>545</b>	<b>925</b>	<b>528</b>	<b>775</b>	<b>504</b>
Solid fuels	571	76	501	69	447	52	390	45	309	35	248	28
oil	1 735	426	794	345	685	263	675	259	616	237	526	204
gas	1	160	1	197	0	223	0	241	0	255	0	273
<b>Transport</b>	<b>615</b>	<b>5 488</b>	<b>559</b>	<b>5 621</b>	<b>669</b>	<b>6 580</b>	<b>719</b>	<b>5 716</b>	<b>750</b>	<b>4 595</b>	<b>790</b>	<b>4 804</b>
Solid fuels	1	0	0	0	0	0	0	0	0	0	0	0
oil	614	5 488	559	5 621	669	6 580	719	5 716	750	4 595	790	4 804
gas	0	0	0	0	0	0	0	0	0	0	0	0

(\*) The data for 1980 to 1986 are for measured or estimated actual emissions. The data for 1990 to 2010 were provisional at the time of their publication

Data on emissions of dust, CO, CO<sub>2</sub> and hydrocarbons (HCs) are given in the table below for several European countries (1986).

**Table 12: Estimated emission in 1986 of particles, carbon monoxide, carbon dioxide and hydrocarbons in a few Member States of the European Union [(4)]**

	Particles (kt)	CO (kt)	CO <sub>2</sub> (mt)	HCs (kt)
Germany (West)	562	8 926	204 308	2 436
Belgium	NI	NI	28 678	NI
Spain	NI	NI	49 837	NI
France	271	6 431	98 748	NI
Italy	413	5 571	94 149	767
The Netherlands	153	1 229	42 320	470
Portugal	NI	NI	7 844	NI
United Kingdom	270	5 076	157 228	2 321

In France, dust has been subjected to measurement since 1980 by distinguishing between the following 5 sectors:

- residential and service sector (including urban heating);
- industry and agriculture;
- thermal power stations (excluding industries producing their own power supplies);

- energy conversion (oil refining and treatment of natural gas);
- transport.

The table and graph below show the changes in dust emissions in France.

**Table 13: Emissions of dust (in kt) in France by sector [CITEPA]**  
(\*)

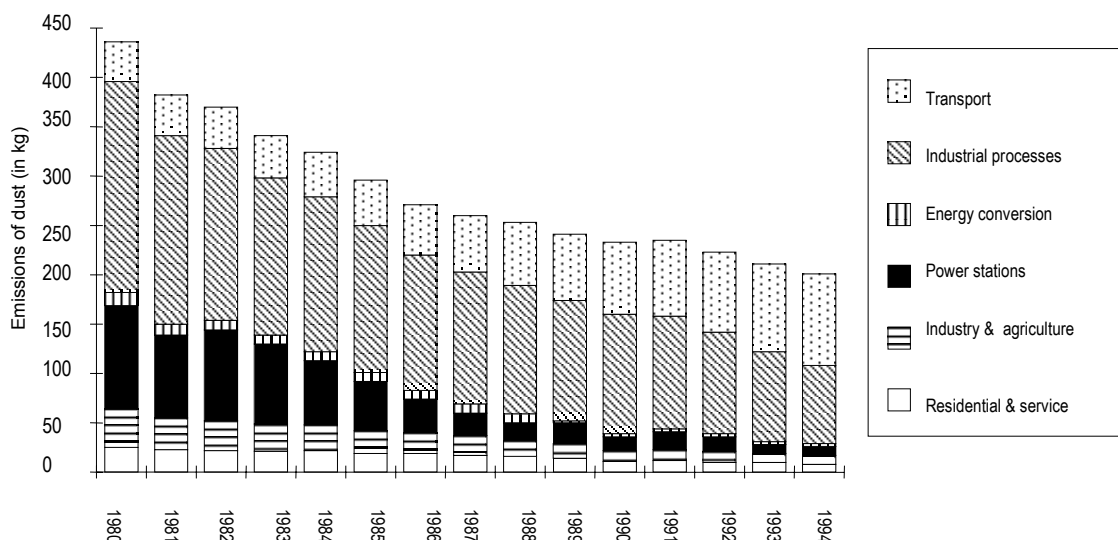
	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Residential and service	25	23	22	21	22	19	19	17	16	14	11	12	10	10	8
Industry and agriculture	39	32	30	28	26	23	21	20	16	15	11	11	11	9	9
Power stations	105	84	92	81	65	50	34	23	18	21	14	18	15	9	9
Energy conversion	13	11	10	9	9	9	9	9	9	2	3	3	3	3	3
Total combustion	182	151	154	140	123	101	82	69	59	52	39	44	39	31	29
Industrial processes	214	191	174	159	157	149	137	134	130	122	121	114	103	91	79
Transport (**)	40	41	42	43	45	46	51	57	64	67	73	77	81	89	93
Total	436	382	370	342	325	296	271	260	253	240	233	236	224	210	202

(\*) These data are estimates made in the light of current knowledge. They may be corrected retrospectively.

(\*\*) Emissions due to transport have been estimated by using the COPERT software of the CORINAIR programme.



**Figure 1: Dust emissions by sector in France [CITEPA]**



In France, dust emissions due to combustion in boilers decreased by 27% during the period between 1980 and 1993, changing from 42% in 1980 to 15% in 1993 [(5)].

## 2.1 Particular case of emissions of heavy metals and persistent organic compounds

There is at present no detailed inventory of the emissions of heavy metals and persistent organic compounds in general, or for the combustion of fossil fuels in particular. There is, nevertheless, a great deal of work in progress with the set objective of drawing up such inventories as soon as possible.

In particular, the next CORINAIR inventory for the year 1994 should deal with 27 pollutants, amongst which are:

- 9 heavy metals: As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn;
- 10 compounds or families of persistent organic compounds: hexachlorocyclohexane (HCH), pentachlorophenol (PCP), hexachlorobenzene (HCB), tetrachloromethane (TCM), trichloroethylene (TRI), perchloroethylene (PER), trichlorobenzene (TCB), trichloroethane (TCE), dioxins and furans, polycyclic aromatic hydrocarbons (PAHs).

Amongst the persistent organic compounds liable to be emitted during the combustion of fossil fuels, the most frequently cited are the PAHs, the polychlorodibenzodioxins (PCDDs) and the polychlorodibenzofurans (PCDFs).

## **“Heavy Metals [(6), (7), (8)]**

Nriagu *et al.* [(6), (7), (8)] have attempted to quantify the total emissions of heavy metals worldwide for 1983. The assessments made for releases into the air are given in Table 14.

**Table 14: Evaluation of world atmospheric emissions of heavy metals from anthropogenic sources in 1983 (tonnes) - from Nriagu *et al.* (1988)**

Source category	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
1-Coal combustion: -electric utilities -industry and domestic	232-1 550 198-1 980	77-387 99-495	1 240-7 750 1 680-11 880	930-3 100 1 390-4 950	155-542 495-2 970	1 080-6 980 1 485-11 880	1 395-9 300 1 980-14 850	775-4 650 990-9 900	108-775 792-1 980	1 085-7 750 1 485-11 880
2-Oil combustion: -electric utilities -industry and domestic	5,8-29 7,2-72	23-174 18-72	87-580 358-1 790	348-2 320 179-1 070	-	58-580 358-1 790	3 840-14 500 7 160-28 640	232-1 740 716-2 150	35-290 107-537	174-1 280 358-2 506
3-Wood combustion	60-300	60-180	-	600-1 200	60-300	-	600-1 800	1 200-3 000	-	1 200-6 000
4-Mobil sources	-	-	-	-	-	-	-	248 030	-	-
5-Non-ferrous metal industry	9 550-15 080	2 662-8 202	-	15 129- 32 567	44,8-223	2 330-33 480	8 781	30 060-69 640	735,8-2 095	51 025- 93 828
6-Steel and iron manufacturing	355-2 480	28-284	2 840-28 400	142-2 840	-	-	36-7 100	1 065-14 200	0,8-2,2	7 100-31 950
7-Cement production	178-890	8,9-534	890-1 780	-	-	-	89-890	18-14 240	-	1 780-17 800
8-Other anthropogenic sources	1 420-3 250	124-1 712	245-1 430	1 142-2 823	155-2 160	5 249-11 260	269-1 289	5 614-8 450	31,4-100,8	6 043-20 506
Total emissions	12 000- 25 630	3 100-12 040	7 340-53 610	19 860- 50 870	910-6 195	10 560- 65 970	24 150- 87 150	288 700-376 000	1 810-5 780	70 50- 193 500
Median value	18 820	7 570	30 480	35 370	3 553	38 270	55 650	332 350	3 790	131 880
Percentage of atmospheric emissions due to fossil fuel combustion ( $\Sigma$ 1 to 4)	11,8 %	10,5 %	41,6%	22,7 %	63,6 %	31,6 %	75,5 %	78,4 %	61,0 %	12,8 %

It is important to note that evaluations published since these estimates were made do not, *a priori*, enable us to consider them as still valid for the current period.

For example, the increasing introduction of unleaded fuels has led to a reduction in emissions from mobile sources. Pacyna [(7)] thus estimates that world atmospheric emission of lead from mobile sources would have been 129 000 tonnes in 1989, or virtually 50% of that estimated in 1983.

From a comparison of results obtained from various independent estimates in Europe, Pacyna also reckons that these evaluations could have uncertainties of less than 25% for lead, but of the order of 50% for mercury and cadmium and about 100% for the other heavy metals.

Estimates have also been made for the region within the European geographical boundaries (UN/ECE) [(7)].

**Table 15: Evaluation of atmospheric emissions of anthropogenic origin of five heavy metals in Europe (tonnes)**

Source category	As (1982)	Cd (1982)	Hg (1987)	Pb (1985)	Zn (1982)
Fossil combustion:					
-utility boilers	330	125	189	1 300	1 510
-industrial, commercial and residential units	380	145	216	1 600	1 780
Gasoline combustion	-	-	-	64 000	-
Non-ferrous metal industry	3 660	730	29	13 040	26 700
Iron and steel industry	230	53	2	3 900	9 410
Waste incineration	10	37	35	540	650
Other anthropogenic sources	360	30	255	1 120	4 540
<b>Total</b>	<b>4 970</b>	<b>1 120</b>	<b>726</b>	<b>85 500</b>	<b>44 590</b>

Finally, quantitative assessments covering a wider range of 16 trace elements have also been carried out [(6)].

According to these, the combustion of coal in thermal power stations and for industrial or domestic uses is a major source of atmospheric emission for Hg, Mo and Se, and a substantial source for As, Cr, Mn, Sb and Ti.

Similarly, the combustion of liquid fossil fuels would apparently be the largest source of emission for V and Ni and an important source for Sn.

**Table 16: Principal sources of atmospheric emissions of heavy metals**

Source category	Trace metals	
	Major source	Substantial source
Fossil fuel combustion	Hg, Mo, Se	As, Cr, Mn, Sb, Tl
Combustion of oil in stationary sources	V, Ni	Sn
Combustion of gasoline	Pb	
Non-ferrous metal industry	As, Cd, Cu, Zn, In, Sn, Sb, Tl	Pb, Se
Iron and steel industry	Cr, Mn	Zn

### “PAHs [(9), (10)]

PAHs are produced during pyrolysis type reactions that occur not only during the combustion of fossil fuels but also during waste incineration, or during the utilisation of specific industrial processes (coking plant, metallurgical industries, etc.). Thus, to various extents and not always by known processes, industry, domestic heating and motor vehicles, etc. all constitute sources of PAH emissions into the atmosphere.

Several different types of polycyclic hydrocarbons are in fact grouped together under the designation PAH:

- polycyclic hydrocarbons having only aromatic rings;
- mixed polycyclic hydrocarbons with both aromatic and non-aromatic rings;
- heterocyclic polycyclic hydrocarbons having at least one ring with a nitrogen or oxygen atom in place of a carbon atom.

PAHs occur in both the solid and the gaseous state. The proportions of the two phases depends on the temperature and on the processes and fuels in question.

The concern over PAH emissions is justified by the fact that several of them, of which the best known is benzo(a)pyrene or BaP, have powerful carcinogenic and/or mutagenic effects which have long been the subject of investigation [(9), (10)].

These compounds biodegrade with difficulty and are liable to accumulate in sediments and the flesh of aquatic organisms, and are thus of a kind to have long term effects.

Nevertheless, the differences in structure between the various PAHs lead to highly variable degrees of risk and the level of concern about these emissions is therefore greatly dependent on the nature of the compounds revealed in different cases. Table 17 summarises the carcinogenic potential of the main PAHs.

**Table 17: Carcinogenic potential of the main PAHs [(9)]**

Compound	Carcinogenic potential	Compound	Carcinogenic potential
Anthracene	-	Dibenz(a,h)anthracene	+++ /++++
Benz(a)anthracene	+	Dibenz(a,j)anthracene	++
Benzo(b)fluoranthene	++ /+++	Dibenzo(a,e)pyrene	++ /+++
Benzo(g,h,i)fluoranthene	-	Dibenzo(a,h)pyrene	++++
Benzo(j)fluoranthene	++ /+++	Dibenzo(a,i)pyrene	+++
Benzo(k)fluoranthene	+	Dibenzo(a,l)pyrene	+++
Benzo(a)fluorene	-	Dibenzo(cd,jk)pyrene	+ /++
Benzo(b)fluorene	-	7,12-Dimethylbenz(a)anthracene	++++
Benzo(c)fluorene	-	Fluoranthene	-
Benzo(g,h,i)perylene	±	Fluorene	-
Benzo(a)pyrene	++++	Indeno(1,2,3-cd)pyrene	++
Benzo(e)pyrene	-	3-Methylcholanthrene	++++
Chrysene	±	Perylene	-
Coronene	-	Phenanthrene	-
Cyclopenta(c,d)pyrene	+ /++	Pyrene	-
Dibenz(a,c)anthracene	±		

- : non carcinogenic
- ± : carcinogenic potential uncertain or very weakly carcinogenic
- +
- ++ : moderately carcinogenic
- +++ : strongly carcinogenic
- ++++ : very strongly carcinogenic

Since the formation of PAHs is related to incomplete combustion, domestic heating installations and motor vehicles are potentially very much involved in their production. If only for economic reasons, the combustion conditions in large combustion installations are significantly better controlled.

The table below, taken from the work of Truesdale and Cleland (1982), gives the emission factors for different fuels burnt in a domestic wood stove.

Emissions measured for several large combustion installations are also listed in section 4.1.4.

**Table 18: PAH emission factors (mg/GJ) for different fuels in a conventional wood stove [(9)]**

	Bituminous coal	Peat	Wood
Heating values (MJ/kg)	29,6	20,2	17,0
Anthracene	138	427	353
Benz(a)anthracene	67,5 (*)	159	3,5
Benzo(b,k)fluoranthene	<1	4,9	<1
Benzo(g,h,i)perylene	<1	34,7	2,4
Benzo(a)pyrene	16,9	149	35,3
Benzo(e)pyrene	27,0	99	29,4
Chrysene	145	69,4	94,1
Coronene	<1	<1	<1
Dibenz(a,h)anthracene	<1	<1	<1
7,12-Dimethylbenz(a)anthracene	40,5	2,0	88
Fluoranthene	192	501	218
Fluorene	209	516	276
9-Methylanthracene	<1	337	129
7-Methylbenz(a)anthracene	6,8 (*)	14,9 (*)	29,4 (*)
12-Methylbenz(a)anthracene	<1	<1	3,5 (*)
3-Methylcholanthrene	3,4	2,0	17,6
1-Methylphenanthrene	247	451	865
Naphthalene	1 590	2 960	2 158
Perylene	57,4	233	47
Phenanthrene	544	650	576
Pyrene	149	298	153

(\*) results from single test.

At the beginning of 1996, seven PAHs (phenanthrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene and dibenzo(a,h)anthracene) were selected for the preparation of a possible protocol on persistent organic pollutants in the context of work undertaken by the United Nations Economic Commission for Europe (UN-ECE Convention on long-range transboundary air pollution).

#### “Dioxins [(11), (12), (13), (14), (15), (16), (17), (18), (19)]

The combustion of fossil fuels also gives rise to a potential emission of polychlorinated dibenzodioxins and dibenzofurans.

These aromatic molecules are characterised by a high liposolubility (octanol/water partition coefficient, log Pow, greater than 6) and by toxic effects revealed in laboratory experiments on a number of animal species [(11), (12)].

PCDD and PCDF molecules are not very volatile and, when adsorbed on particles produced by combustion, have a high thermal and chemical stability in the environment. They can only be destroyed above temperatures of the order of 1 000°C.

The liposolubility and persistence of PCDDs and PCDFs mean that these molecules are liable to accumulate in living organisms. For example, bioconcentration factors of the order of 26 700 have been reported for rainbow trout (*Salmo gairdneri*) during an exposure to 2,3,7,8-TCDD [(13)].

There are 75 congeners for dioxins and 135 for furans. In order to quantify dioxin and furan emissions by taking into account their toxicity, the concentration or emitted flux is weighted by a coefficient (the Toxic Equivalency Factor TEF) characteristic of each of the molecular forms of PCDD/PCDF found in the mixture in question<sup>2</sup>. 2,3,7,8-tetrachlorodibenzodioxin is reputedly the most toxic PCDD and is taken as a reference substance, being given by convention a TEF value of 1. The other congeners considered to be worrying are 2,3,7,8 substituted molecules.

The dioxinic activity of a mixture is expressed by its TEQ (Toxic Equivalent Quantity) defined by:

$$\text{TEQ} = \sum \text{isomers} \times \text{TEF}$$

The burning of coal for domestic heating has received particular attention. Studies have revealed that the presence of chlorine and of aromatic and phenolic precursors in the structure of the coal, associated with the specific temperature and redox conditions under which pyrolysis takes place in a domestic stove, is in fact of a kind to lead to the formation of PCDDs and PCDFs [(12)].

Combustion installations using wood are also mentioned as a possible source of emissions. The main process involved is the recycling of wood for power production, for example in the form of chipboard or of waste from wood that has been treated or that includes chlorinated organic compounds (PCP, lindane, PVC, NH<sub>4</sub>Cl, etc.). Moreover, the introduction of combined combustion for the disposal of waste (used tyres, sludge from the purification of waste water, etc) in certain conventional combustion installations could also lead to significant emissions of dioxins.

A number of recent reports [(12), (14), (15), (16), (17), (18)] are nevertheless in agreement in assessing that the combustion of fossil fuels would not be a major source of PCDDs and PCDFs in comparison with other activities, particularly the incineration of municipal waste:

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<sup>2</sup> The TEF values for the various PCDD/PCDF molecules differ according to the system used. However, the NATO-CCMS (NATO Committee on the Challenges of the Modern Society) system is commonly used internationally.



- according to estimates for 1991 [(14)], emissions due to the domestic or industrial combustion of coal, fuel oil and wood in the Netherlands are, for example, of the order of 16,7 g TEQ/year or about 3,5% of the total emissions in the country;
- in the United Kingdom emissions of between 99,8 and 153 g TEQ/year have been evaluated according to estimates for 1989/90 as resulting from all the domestic and industrial uses of coal and the combustion of heavy fuel oil in power stations, values to be compared with assumed total emissions of 157 to 933 g TEQ/year [(11)];
- in Germany, the total dioxin emissions over the period 1994/95 were estimated at 510 g TEQ/year, of which 220 g TEQ/year came from the production and transformation of metals. On the other hand, emissions due to waste incineration were considerably reduced at the beginning of the 1990s and amounted to no more than approximately 30 g TEQ/year over the period in question [(19)].

However, all these data result from preliminary estimates and require a cautious interpretation. In addition, being concerned with national data, they do not enable us to predict emissions in other countries, particularly because of the specific nature of the industrial infrastructure in each state.

### **3. The principal fuels and processes used in large combustion installations ( $\geq 50$ MWth)** [(5), (20), (21)]

Each of the sections in this chapter includes basic information on the main fuels and processes used in large combustion installations ( $\geq 50$  Mwth). Environmental factors are dealt with later (the next two chapters).

#### **3.1 Solid fuels**

The solid fuels in use are coal, brown coal, peat and wood. Coal is far from being the most used fuel. The combustion processes used are the following:

##### ***“Moving grate boilers***

Moving grate boilers are widespread in the power range 50 - 100 MWth. Most of the boiler slag and ash is trapped at the level of the grate, while the finest particulate fractions are entrained in the flue gases.

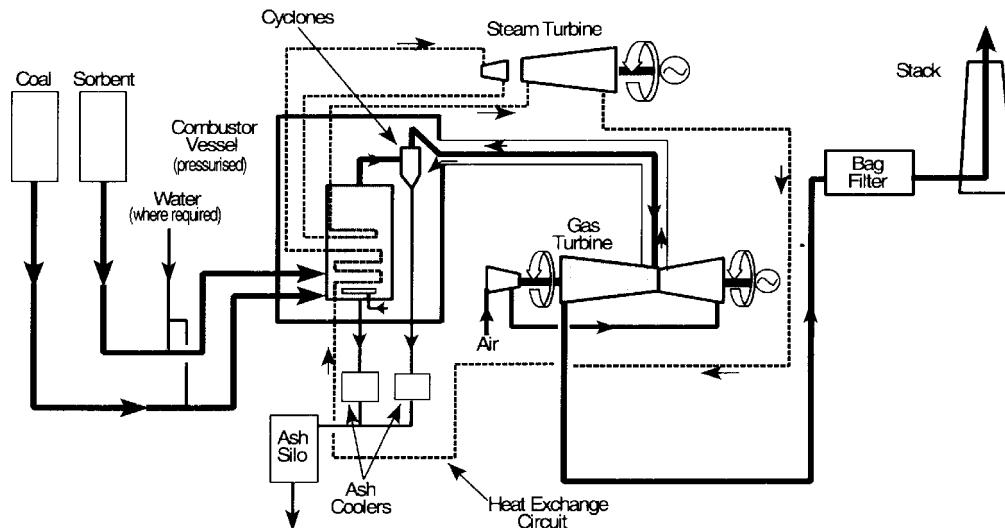
### ***"Pulverised coal boilers***

This process is at present used for all boilers of more than 50 MWth. It enables a high combustion efficiency to be achieved. Compared with moving grate boilers, a smaller proportion of carbon is found in the ash. Preparation of the coal involves fine crushing and careful mixing to give a homogeneous fuel.

### ***"Fluidised bed boilers***

Fluidised bed combustion (FBC) is currently undergoing considerable development in many countries. Fluidised bed boilers can run on very diverse fuels, including the three solid fuels mentioned above but also including liquid fuels.

**Figure 2: Pressurised fluidised bed combustion system [(21)]**



Circulating fluidised bed combustors (CFBCs) are now widely used, but the size of the units is still quite small. Installations with a capacity up to 660 MWth are currently in service throughout the world.

We are also beginning to see pressurised fluidised bed combustors (PFBCs) being developed. Installations of capacities up to 400 MWth are operational worldwide. PFBCs have higher thermal efficiencies and are smaller in size than atmospheric fluidised bed boilers or pulverised coal boilers.

### **3.2 Liquid fuels**

The vast majority of liquid fuels used originate from the refining of oil. Commercial heavy fuel oil is the fuel most commonly used, other fuels such as liquefied petroleum gas (LPG) and various bituminous emulsions being used to a lesser extent. Large combustion installations combined with refineries often use the heaviest fraction of the residues from refining (asphalt).

The burners are supplied by atomisation, which must be efficient to obtain good conditions for combustion and which requires, in particular, good control over the viscosity of the fuel.

### **3.3 Gaseous fuels**

The most widespread gaseous fuel is natural gas. Other fuels, particularly various industrial gases (from refineries, blast furnaces, etc.) can also be used.

Gaseous fuels can also be produced from an industrial process of gasifying solid or liquid fuels. These are then burnt in conventional boilers or in combined cycle gas turbines.

Along with boilers equipped with supercritical steam cycles and pressurised fluidised beds, the last-named process (known as IGCC or Integrated Gasification Combined Cycle) is among the most worthwhile combustion methods having a high energy conversion efficiency [(20)].

The particular case of gasification is dealt with in section 6.

## **4. Emissions due to large combustion installations**

Emissions generally associated with the running of large combustion installations are liable to affect all compartments of the environment.

The table below and the diagram on the following page provide an overview of the potential emission pathways and the interfaces that a typical large combustion installation has with the environment. This survey cannot claim to be exhaustive because of the large number of possible emission pathways and environments that might be involved for many pollutants.

**Table 19: Potential emission pathways by type of source and by substance [(from 21)]**

<b>A =Air W=Water L=Land</b>	Particulate matter	Oxides of sulphur	Oxides of nitrogen	Oxides of carbon	Hydrogen chloride/fluoride	Volatile organic compounds	Suspended solids	Acids/alkalis/salts etc	Metals and their salts	Chlorine (as Cl <sub>2</sub> )	Sulphates	Chlorides	Mercury and/or cadmium	Organic compounds	PAHs	Dioxins
Fuel storage and handling	A					A								W		
Water treatment								W		W		W	W	W	W	
Boiler blowdown							W	W						W		
Flue gas	A	A	A	A	A	A			A				A	A	A	A
Flue gas treatment							W		L		W	W	W	W		
Furnace bottom ash/clinker	A								L							
Fly ash	A								A							L
Site drainage including rain water							W		W					W		
Waste water treatment							W	W	W		W	W	W	W		
Cooling water blowdown							W		W	W	W	W	W	W		
Cooling tower exhaust						A										

## 4.1 Atmospheric emissions

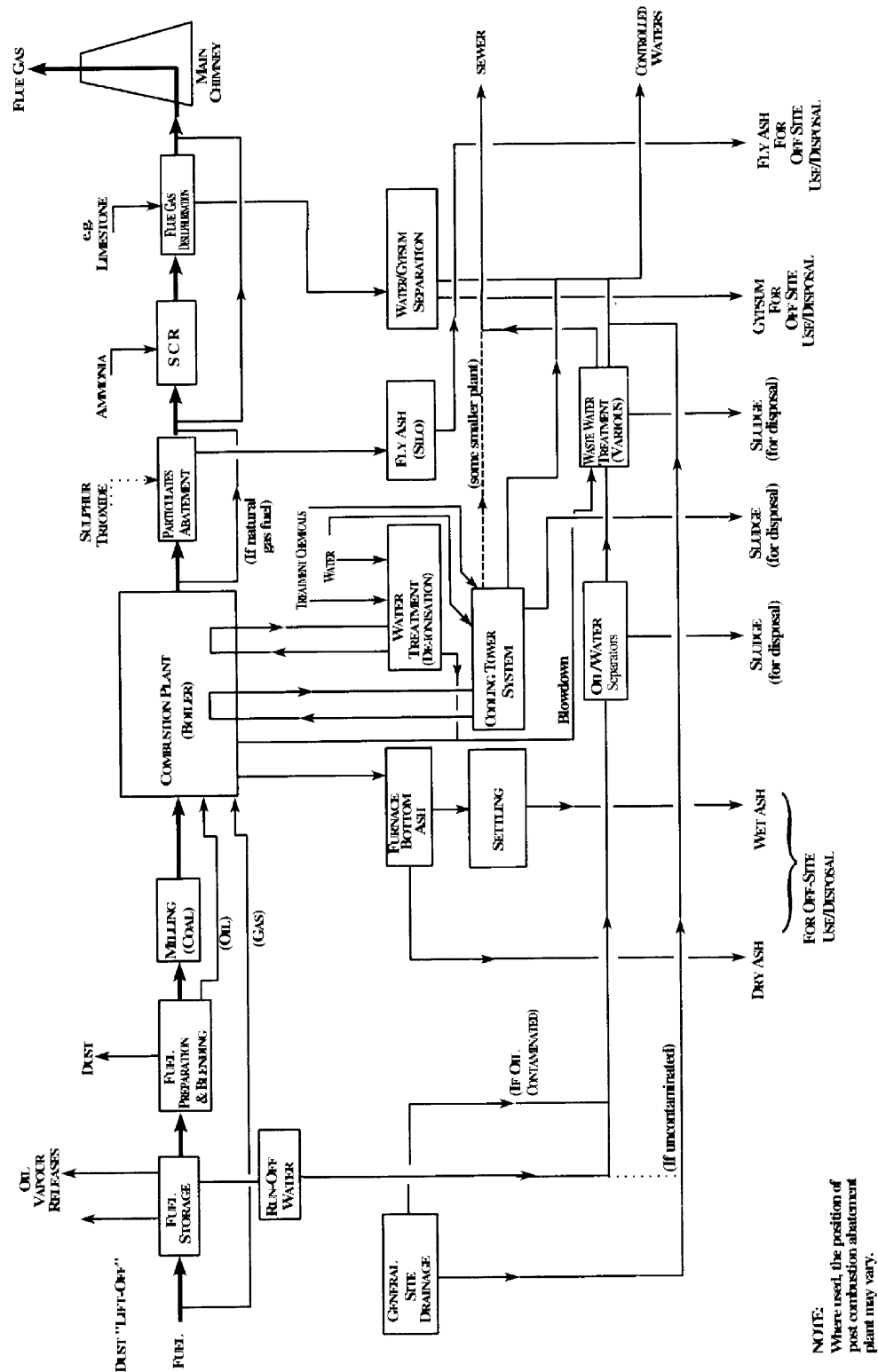
### 4.1.1 Oxides of sulphur and oxides of nitrogen [(3), (21), (22), EC]

During combustion, by far the majority of oxides of sulphur are produced in the form of sulphur dioxide (SO<sub>2</sub>).

For solid and liquid fuels, 1 to 3% of the sulphur is also oxidised to sulphur trioxide (SO<sub>3</sub>), the presence of transition metals in the fuel tending to catalyse this reaction. The sulphur trioxide is adsorbed on particulate emissions and, in the case of liquid fuels, contributes to the formation of acid soots.

Natural gas is generally considered as being free from sulphur. This clearly cannot be the case for certain industrial gases and desulphurisation of the gaseous fuel might then be necessary.

Figure 3: Diagram showing the typical flow of material in running a large combustion installation and the associated operations [(21)]



Heavy fuel oils contain sulphur in proportions varying from 0,4% to more than 4% by weight. The maximum levels of emission capable of being generated in flue gases as a function of the sulphur content of heavy fuel oil are given below [(21)].

<b>Sulphur content of heavy fuel oil (weight %)</b>	<b>SO<sub>2</sub> (mg/m<sup>3</sup> at 3% residual O<sub>2</sub> in the flue gases)</b>
0,4	685
1	1 710
2	3 420
3	5 130
4	6 840

The sulphur content of coal varies between 0,1% and more than 3,5% by weight. The maximum levels of emission capable of being generated in flue gases as a function of the sulphur content of coal are given below [(21)].

<b>Sulphur content of coal (weight %)</b>	<b>SO<sub>2</sub> (mg/m<sup>3</sup> at 6% residual O<sub>2</sub> in the flue gases)</b>
0,1	225
1	2 250
2	4 500
3	6 750

The principal oxides of nitrogen emitted during the combustion of fossil fuels are nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). The first two of these form the mixture known as NO<sub>x</sub>, which contains more than 90% of NO in the main types of large combustion installations.

The formation of NO<sub>x</sub> is governed by three essential mechanisms, characterised by the origin of the nitrogen and the environment where the reaction takes place:

- thermal NO results from the reaction between the oxygen and nitrogen from the air;
- fuel NO is formed from the nitrogen contained in the fuel;
- prompt NO is formed by the conversion of molecular nitrogen in the flame front in the presence of intermediate hydrocarbon compounds.

The quantity of NO<sub>x</sub> formed by the prompt NO mechanism is generally much smaller than that generated by the other reaction paths.

The formation of thermal NO is highly dependent on temperature. When combustion can be achieved with temperature peaks below  $1\,000^{\circ}\text{C}$ , emissions of NO<sub>x</sub> are reduced. The formation of thermal NO is the dominant path by which NO<sub>x</sub> is generated in installations using gaseous or liquid fuels.

The formation of fuel NO depends on the nitrogen content of the fuel and the oxygen concentration of the reaction medium. The quantity of fuel NO produced is greater in installations using coal, since this has larger amounts of nitrogen in its structure than other types of fuel. The mean nitrogen content generally found in different types of fuel is given below [(22)].

<b>Fuel</b>	<b>Nitrogen Content (weight %, dry, ash-free basis)</b>
Coal	0,5 - 2
Fuel Oil	< 1,0
Natural Gas	< 0,1

Not only that, but the type of combustion process used is not without its effect on the amounts of nitrogen oxides emitted. In the case of coal, for example:

- NO<sub>x</sub> emissions are low with a moving grate boiler because of the relatively low temperature of combustion and the progressive nature of the combustion as it advances over the grate;
- emissions are higher in a pulverised coal boiler, varying with the type of burner and the design of the combustion chamber;
- NO<sub>x</sub> emissions in a fluidised bed boiler are lower than those produced in conventional boilers, but N<sub>2</sub>O emissions are higher.

In applying Directive 88/609/EEC of 24 November 1988 relating to Large Combustion Installations (nominal thermal power  $\geq 50$  MWth), each Member State must, since 1990, carry out an annual census of SO<sub>2</sub> and NO<sub>x</sub> emissions from installations falling within its field of application.

The table below gives the data for 1980, 1990, 1991, 1992 and 1993 relating to existing installations within the meaning of Directive 88/609/EEC (initial authorisation for operation granted before 1 July 1987).

**Table 20: Emissions (in kt/year) of SO<sub>2</sub> and NO<sub>x</sub> from Large Combustion Installations in 11 Member States of the European Union which are also signatories to the Paris Convention [EC, DGXI]**

	1980		1990		1991		1992		1993	
	SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	NO <sub>x</sub>
Belgium	530	110	141,7	72,5	141,3	72,4	137,0	69,9	124,9	65,1
change / 1980 (%)	-	-	(-73,3)	(-34,1)	(-73,3)	(-34,2)	(-74,2)	(-36,5)	(-74,4)	(-40,8)
Denmark	323	124	119,0	83,0	175,0	124,0	130,0	82,0	100,0	86,0
change / 1980 (%)	-	-	(-63,2)	(-33,1)	(-45,8)	(0)	(-59,7)	(-33,9)	(-69,0)	(-30,6)
Germany (1)	2 225	870	320,7	327,2	319,6	317,0	2452,3	430,5	2196,5	424,6
change / 1980 (%)	-	-	(-85,6)	(-62,4)	(-85,6)	(-63,6)	(-51,0)	(-85,7)	(-56,1)	(-85,8)
Spain	2 290	366	1 612,0	250,0	1 580,0	252,0	1 564,0	264,0	1 564 (2)	264 (2)
change / 1980 (%)	-	-	(-29,6)	(-31,7)	(-31,0)	(-31,1)	(-31,7)	(-27,9)	(-31,7)	(-27,9)
Finland	-	-	52,1	39,6	49,2	40,9	34,6	32,7	31,1	33,6
change / 1980 (%)	-	-	-	-	-	-	-	-	-	-
France	1 910	400	540,2	141,4	632,6	179,8	507,2	149,4	412,8	105,0
change / 1980 (%)	-	-	(-71,7)	(-64,7)	(-66,9)	(-55,1)	(-73,4)	(-62,7)	(-78,4)	(-73,8)
Ireland	99	28	114,3	45,6	115,4	46,3	108,4	53,0	99,1	47,2
change / 1980 (%)	-	-	(15,5)	(62,9)	(16,6)	(65,4)	(9,5)	(89,3)	(0,1)	(68,6)
The Netherlands	299	122	103,9	106,1	98,1	100,4	81,5	88,2	75,9	80,5
change / 1980 (%)	-	-	(-65,3)	(-13,1)	(-67,2)	(-17,7)	(-72,7)	(-27,7)	(-74,6)	(-34,0)
Portugal	115	23	205,1	58,2	204,4	61,9	261,6	72,9	213,3	65,1
change / 1980 (%)	-	-	(78,3)	(153,0)	(77,7)	(169,1)	(127,5)	(217,0)	(85,5)	(183,0)
United Kingdom	3 883	1 016	2 953,5	802,2	2 746,6	746,1	2 674,3	697,1	2 329,2	598,2
change / 1980 (%)	-	-	(-23,9)	(-21,0)	(-29,3)	(-26,6)	(-31,1)	(-31,4)	(-40,0)	(-41,1)
Sweden (3)	-	-	-	-	-	-	12,0	16,0	11,3	14,7
change / 1980 (%)	-	-	-	-	-	-	-	-	-	-
Total (4)	11 674	3 059	6 162,5	1 925,8	6 062,2	1 940,8	7 962,9	1 955,7	7 158,2	1 784,5
change / 1980 (%)	-	-	(-47,2)	(-37,0)	(-48,1)	(-36,6)	(-31,8)	(-36,1)	(-38,7)	(-41,7)

- (1) Data for 1990 and 1991 refer to the former West Germany. Data for 1992 and 1993 refer to Germany after reunification. The reference figures for emissions from East and West Germany together in 1980 are estimated at 5 000 kt for SO<sub>2</sub> and 3 000 kt for NO<sub>x</sub>.
- (2) Emissions for 1993 not being available, the 1992 emissions have been transferred.
- (3) Data prior to 1992 are not available
- (4) Excluding Finland and Sweden.

Using 1993 as a reference year, these data can be compared with the total emissions of SO<sub>2</sub> and NO<sub>x</sub> as given in Tables 9 and 10.



**Table 21: Contribution of large combustion installations to the total SO<sub>2</sub> and NO<sub>x</sub> emissions for the 11 Member States of the European Union which are also signatories to the Paris Convention (1993)**

	Emissions of SO <sub>2</sub> (kt/year)			Emissions of NO <sub>x</sub> (kt/year)		
	LCI (EC)	Total (EMEP)	Contribution (%)	LCI (EC)	Total (EMEP)	Contribution (%)
Belgium	124,90	294,00	42,48	65,10	340,00	19,15
Denmark	100,10	157,00	63,76	86,50	267,00	32,40
Germany	2 196,50	3 153,00	69,66	424,60	2 274,00	18,67
Spain	1 564,00	2 071,00	75,52	264,00	1 227,00	21,52
Finland	31,10	123,00	25,28	33,60	280,00	12,00
France	412,80	1 121,00	36,82	105,00	1 544,00	6,80
Ireland	99,10	157,00	63,12	47,20	122,00	38,69
The Netherlands	75,90	157,00	48,34	80,50	552,00	14,58
Portugal	213,30	300,00	71,10	65,10	246,00	26,46
United Kingdom	2 329,20	3 184,00	73,15	598,20	2 339,00	25,58
Sweden	11,30	101,00	11,19	14,70	398,00	3,69
Total	7 158,2	10 818,00	66,17	1 784,50	9 589,00	18,61

#### **4.1.2 Dust [(5), (17), (21)]**

The dust emitted during the burning of coal arises almost entirely from the mineral fraction of the fuel, but a small proportion may consist of very small particles formed by condensation of compounds volatilised during the combustion.

The type of combustion used has a considerable effect on the proportion of ash entrained in flue gas emissions from boilers. For example, moving grate boilers produce a relatively small amount of fly ash (20 - 40%), whereas pulverised coal boilers produce an appreciable amount of it (80 - 90%).

The combustion of liquid fuels is also a source of particulate emissions, although to a lesser extent than coal. In particular, poor combustion conditions lead to the formation of soot, which is liable to produce acid agglomerates with corrosive properties in the presence of sulphur trioxide.

The combustion of natural gas is not a significant source of dust emissions. On the other hand some industrial gases may contain particles which should be filtered out in the production process or, failing that, before combustion.

For many installations, there are also potential diffuse emissions (open-air handling and storage of coal, the crushing of the coal used in pulverised coal boilers, the handling of ash, etc.).

Dust emission is not included in the obligations laid down for the annual census of emissions in the Directive 88/609/EEC, neither does

it occur among the pollutants to be monitored as part of the CORINAIR programme.

The data available on such emissions are mainly those previously communicated for 1989 by the signatories to the Paris Convention (INDSEC 1993, doc. 5/8/1).

For some countries, national figures showing the changes in emissions from year to year also exist. Nevertheless, these do not necessarily cover the same categories of combustion installation and it is therefore difficult to compare one country with another.

Because of this, only the following few example are given:

**Table 22: Dust emissions due to combustion installations for a few Contracting Parties to OSPAR**

Country	Installations involved	Estimated discharge of dust (t/year)		
		1980	1993	1995
Belgium	Power stations	23,730	7,929	-
France	Oil-fired and coal-fired power stations	104,000	9,000	-
Switzerland	Industrial and craft activities	27,000	-	12,100

#### **4.1.3 Heavy metals**

Heavy metal emissions are dealt with later for each fuel in turn.

However, looking first in a more general way at the heavy metal emissions from combustion installations as a whole, we should point out that some national assessments of these do exist. In the particular case of fossil fuel combustion for electricity generation, data that have been published are listed in the following table.

**Table 23: Heavy metal emissions from the network of power stations operated by some of the Contracting Parties to OSPAR**

Country	Year	Estimated heavy metals discharges (tonnes/year)								
		Cd	Cr	Cu	Hg	Pb	Ni	Sb	Se	Zn
Belgium	1993	0,022	1,155	1,129	0,708	0,599	1,814	0,029	2,267	4,135
Netherlands	1995	0,079	0,156	0,39	0,194	2,32	0,938	0,094	0,005	4,55

**“Coal [(7), (23), (24), (25), (26), (27), HMIP]**

There are more data about the problem of heavy metals emissions from coal than about any other fuel.

However, both the trace element concentrations in the fuels and their releases into the environment are liable to show large variations from one situation to another, depending on the source of the fuel and the particular conditions of its combustion and of the decontamination of gaseous effluent.

Concentrations in fuels vary enormously with both the geological rank and the geographical origin of the coal. The distribution of trace elements in a coal can vary significantly within the same mine, even within the same seam. During extraction, moreover, minerals from adjacent soil or seams may modify the initial trace element concentration.

This extreme non-uniformity of coal makes it difficult to establish orders of magnitude for trace element concentrations that are generally applicable to this type of fuel.

Not only that, but there are great difficulties in determining trace element concentrations in coals which, amongst other things, stem from the fact that the concentrations to be measured are very low and that coals are complex compounds in which trace elements occur in diverse chemical forms.

Certain trace elements, like Beryllium, are mainly associated with the organic part of the coal; others, like zinc, are almost entirely found in the mineral part; and others, like mercury, are associated with both the organic and mineral parts [(24)].

As an example, a study carried out by Laborelec [(26)] on the heavy metals emitted by coal-fired power stations in Belgium gives the concentrations listed in the tables below.

**Table 24: Concentrations of non-volatile heavy metals in 14 samples of coal [(26)]**

Sample/ Source (*)	Concentration (mg/kg dry coal)										
	Be	Co	Cr	Cu	Mn	Ni	Pb	Sb	Ti	V	Zn
n° 1 / RUS	0,62	8,62	22,40	18,60	140,00	27,20	32,50	< 0,12	3,08	10,70	27,80
n° 2 / SAF	1,30	6,40	27,90	10,50	58,00	24,90	< 3	< 0,15	< 2,2	14,00	22,60
n° 3 / SAF	1,50	11,00	37,40	22,30	45,40	40,80	3,70	< 0,15	< 2,2	22,70	29,70
n° 4 / SAF	0,68	2,10	14,30	14,70	72,00	23,70	< 2,8	< 0,14	< 2,1	14,80	16,80
n° 5 / USA	1,94	2,65	11,10	12,90	23,10	21,90	< 2,4	< 0,12	< 1,82	13,40	39,80
n° 6 / SAF	1,46	12,20	31,30	11,60	49,30	42,00	< 3	< 0,15	< 2,2	19,50	29,50
n° 7 / SAF	1,57	10,10	30,70	15,70	41,70	39,20	16,10	< 0,14	< 2,1	16,50	24,70
n° 8 / USA	1,73	8,00	21,00	28,00	41,20	27,70	16,50	< 0,11	< 1,6	22,10	44,30
n° 9 / CHI	1,14	2,90	8,90	14,70	25,60	17,80	11,30	< 0,14	< 2,1	8,80	25,40
n° 10 / SAF	1,46	6,90	25,40	9,70	54,80	28,60	< 3,1	< 0,16	< 2,4	16,20	17,10
n° 11 / SAF	1,17	6,80	23,80	8,60	58,40	28,30	< 3	< 0,15	< 2,3	15,20	15,30
n° 12 / AUS	3,77	12,20	6,10	7,30	15,90	39,90	< 2,6	< 0,13	< 2	13,90	103,00
n° 13 / SAF	1,03	6,10	24,20	7,30	57,90	28,80	3,5	< 0,15	< 2,3	12,60	20,10
n° 14 / SAF	1,24	8,70	24,40	11,20	61,60	29,50	< 3,1	< 0,16	< 2,4	17,60	15,10
Mean	1,47	7,46	22,07	13,80	53,21	30,02	7,62	0,14	2,20	15,59	30,80
Minimum	0,62	2,10	6,10	7,30	15,90	17,80	< 2,4	< 0,11	< 1,60	8,80	15,10
Maximum	3,77	12,20	37,40	28,00	140,00	42,00	32,5	< 0,16	3,08	22,70	103,00

(\*) RUS = Russia, SAF = South Africa, USA = USA, CHI = China, AUS = Australia

**Table 25: Concentrations of volatile heavy metals in 7 samples of coal [(26)]**

Sample/ source (*)	Concentration (mg/kg dry coal)			
	As	Cd	Hg	Se
n° 1 / RUS	4,20	0,028	0,05	0,70
n° 2 / SAF	4,20	0,03	0,09	1,00
n° 3 / CHI	3,70	0,063	0,12	3,40
n° 4 / AUS	3,90	0,065	0,04	1,50
n° 5 / USA	12,50	0,20	0,11	4,10
n° 6 / POL	7,00	0,23	0,11	2,60
n° 7 / B	8,00	0,26	0,16	1,70
Mean	6,21	0,13	0,10	2,14
Minimum	3,70	0,028	0,04	0,70
Maximum	12,5	0,26	0,16	4,10

(\*) RUS = Russia, SAF = South Africa, USA = USA, CHI = China, AUS = Australia, POL = Poland, B = Belgium (coal from Campine)

The great majority of trace elements are associated with the mineral constituents of the coal (illite, kaolinite, quartz, pyrites, ankerite). The heavy metal concentration in most coal can be considerably reduced by washing it before combustion (enhancing the economic value of the coal). [(24)]

During combustion, the behaviour of the trace elements present in fossil fuels depends on their volatility.

The main constituent of fly ash is a vitreous substance (aluminosilicate) which is formed during combustion from the clay minerals contained in the coal. The fly ash contains substantially the same trace elements as those present in the fuel, but with some enrichment due to the recondensation of trace elements downstream from the boiler.

Aluminium is often used as a reference element in defining the enrichment factor, EF:

$$EF = (X_S/X_C) \cdot (Al_C/Al_S)$$

- where -  $X_S$  and  $X_C$  are the concentrations of element X in the fly ash and the coal respectively, and
- $Al_S$  and  $Al_C$  are the concentrations of aluminium in the fly ash and coal respectively.

The amount of enrichment can vary considerably from one installation to another, depending on particular factors.

Moreover, very fine particles (< 1 µm) with their very large specific area (surface area per unit mass) are the seat of maximum enrichment. This is because, depending on the element and the form in which it occurs, the dewpoint is reached during the cooling of the gaseous effluent in the various items of equipment downstream from the combustion and the smallest particles then form privileged sites for adsorption.

The largest granulometric fraction (10 µm) can also be considerably enriched: Bouchereau [(27)], for example, gives enrichment factors of 8 to 10 for zinc, 6 to 8 for lead, 5 to 7 for copper and 3 to 4 for nickel. In practice, it is observed that the enrichment is increased when the gases pass through an electrostatic dust precipitator.

R. Meij [(23)] suggests the following classification for the behaviour of various trace elements.

**Table 26: Classification of trace elements according to their enrichment factor and their behaviour during combustion [(23)]**

Class		Elements	Fly ash EF (*)	Behaviour in installation
I		Al, Ca, Ce, Cr, Cs, Eu, Fe, K, La, Mg, Na, Rb, Sc, Sm, Sr, Si, Th, Ti	# 1	Not volatile
II	Ila	As, Cd, Pb, Tl, Zn	> 4	Volatile, but condensation within the installation on ash particles
	Ilb	Be, Co, Cu, Ge, Mo, Ni, P, U, V, W	2 < ≤ 4	
	Ilc	Ba, Mn, Rb, Sr	1,3 < ≤ 2	
III		B, Br, C, Cl, F, Hg, I, N, S, Se	-	Very volatile, hardly condensation

(\*) Fly ash = emitted fly ash and ash collected in the electrostatic precipitators.  
(EF factors estimated with an ash content of the coal of 11%).

Several sets of parameters affect the destiny of the trace elements.

As mentioned previously, the type of combustion affects the relative proportions of fly ash and boiler ash. We should also stress the great influence of the operating conditions on the behaviour of the trace elements, conditions such as the differences in temperature at different points in the combustion chamber, the surplus air flow, the temperature field in the flame, etc.

The third set of parameters to be considered relates to the treatment of the gaseous effluents. Comparatively few precise data exist on the proportion of trace elements retained in different types of separator. As regards elements of class III, which are totally or partially released into the air in a vapour phase, the devices controlling particulate emissions are relatively inoperative. On the other hand, emissions of class I and class II elements can be reduced by these devices.

A series of measurement campaigns undertaken in the Netherlands and reported by Meij [(23)] gives the following collection efficiencies during dust removal by high efficiency cold-side electrostatic precipitators (ESPs).

**Table 27: Collection efficiencies for fly ash and trace elements [(23)]**

Campaign number	Particulate loadings downstream of the ESP in mg/Nm <sup>3</sup>	Mass median aerodynamic diameter of D(m)50 in µm	Collection efficiency in % of the ESP (η)		
			Fly ash	Mean elements	Elements with η < 99%
I	15	5	99,99	99,80	none
II	50	5	99,69	99,17	none
III	25		99,80	99,30	Sb (94,56)
IVa,b	20	2	99,8	99,00	Cd (98,3), Sb (98,3), Se (97,1)
IVc	100	4	99,2	98,00	not studied
V	10	2	99,92	99,70	Se (97,79)
VIa	30	2	99,9		not studied
VIb	20	6	99,8		not studied
VIIa	4	3	99,95	99,79	Se (98,45)
VIIb	8	3	99,90	99,58	Cd (98,48)
VIII	20		99,81	99,46	Cd (98,35), Se (97,49)
IX	17		99,90		
X	30	9			
XI	5	10			
XII	11	12	99,91	99,81	none
XIII	2	3			
XIV	10	9			

When dust removal is achieved using "hot" electrostatic precipitators (hot-side ESPs) operating at a temperature of about 350°C, the collection efficiency observed for trace elements of class IIa is significantly lower.

When bag filters are used, small quantities of a few trace elements in the vapour phase (mercury, for example) may be retained by adsorption on the fly ash already captured. The operating temperature of the filter is in any case a decisive factor in the collection efficiency for this type of trace element.

Measurements made by Laborelec [(26)] at the Rodenhuijze power station in Belgium, also fitted with an electrostatic dust precipitator, give detailed results for the percentage emissions by trace element, together with those for the change in concentration as the point at which the measurement is made varies. These data also provide an interesting illustration of the enrichment effect during electrostatic dust removal.

These data were obtained from analyses of samples of combustion gases taken from the combustion chamber and the flue, followed by an assessment of the various materials based on a theoretical distribution of the deposited ash and the fly ash. Samples were taken from:

- the deposited ash;
- the fly ash at the ESP intake;
- the fly ash received at field 1 of the ESP;
- the fly ash received at field 2 of the ESP;
- the fly ash received at field 3 of the ESP;
- the fly ash at the ESP outlet (fly ash emitted by the stack).

**Table 28: Heavy metal concentrations adsorbed by or included in the fly ash [(26)]**

Element	Concentration (mg/kg of ash)						Emission (%)
	Deposited ash	Fly ash					
		ESP intake	Field 1	Field 2	Field 3	ESP outlet	
Be	9,3	12,5	11,5	14,5	15,3	19,7	0,85
Co	73,8	38,6	39,4	52,1	57,5	94,1	1,08
Cr	203,0	254,0	197,0	255,0	262,0	337,0	0,84
Cu	75,0	131,0	128,0	165,0	183,0	258,0	1,03
Mn	162,0	189,0	171,0	236,0	253,0	363,0	1,04
Ni	97,0	101,0	91,0	114,0	125,0	204,0	1,10
Pb	12,0	55,0	57,0	93,0	105,0	175,0	1,54
Sb	< 2,90	5,1	4,8	8,2	10,1	21,6	2,09
Tl	< 17,0	< 17,0	< 17,0	< 17,0	< 17,0	< 17,0	2,00
V	233,0	260,0	255,0	319,0	337,0	456,0	0,97
Zn	26,0	107,0	93,0	148,0	172,0	365,0	1,96

The same study also determined, by directly analysing the flue gases, the proportions of heavy metal emissions assumed to be emitted partially in gaseous form. The mean results obtained give percentage emissions of 2,36% for arsenic, 20,2% for selenium and 2,56% for cadmium. These results differ from those obtained in the Netherlands and reported by Meij [(23)], particularly for selenium, but this can be explained both by the specific nature of each installation and the different methodologies.

The following table suggests emission factors for trace elements during the use of coal in a large combustion installation (ash level of 10%, installation equipped with an electrostatic precipitator).

**Table 29: Emission factors of trace elements (mg/MJ) when using ESP [HMIP, UK]**

Element	Bituminous coal			Subbituminous coal			lignite		
	cyclone	stoker	pulverized	cyclone	stoker	pulverized	cyclone	stoker	pulverized
As	23,6	28,1	15,9	28,6	34	19,2	39,8	47,3	26,7
Be	2,5	3,7	1,6	3	4,5	2,0	4,1	6,2	2,7
Cd	7,3	8,7	5,1	8,8	10,5	6,1	12,3	14,7	8,5
Co	44,4	51,3	25,3	53,9	62,2	30,6	74,9	86,4	42,6
Cr	119,6	199,8	84,7	145	242,2	102,7	201,5	336,7	142,7
Cu	94	163,8	62,9	114	198,5	76,2	158,4	275,9	105,9
Hg	10	20	8	12	26	8	18	36	12
Mn	101,9	186,2	70	123,5	225,7	84,9	171,6	313,7	118,0
Mo	30,7	42,5	19,1	37,2	51,5	23,2	51,7	71,5	32,2
Ni	150,4	242,9	96,5	182,3	294,4	117,0	253,4	409,3	162,6
Pb	85,2	128,5	54,8	103,3	155,8	66,4	143,6	216,6	92,3
Sb	15,0	23,0	9,3	17	27,8	11,3	23,6	38,7	15,7
Se	27,5	46,8	18,3	33,3	56,8	22,3	46,3	78,8	31
V	83,7	162,5	58,4	101,4	196,9	70,8	141	273,7	98,4
Zn	118,7	190,8	78,9	143,9	231,3	95,7	200	321,5	133,0
Zr	82,2	178,7	60,1	99,7	216,6	72,9	138,6	301,0	99,3

**“Heavy fuel oil [ (27), (28), (29), (30)< (31), HMIP]**

The type and abundance of trace elements in crude oil depend on its origin, its migration and its maturation process. The elements that have received the most attention, since they are present in the largest amounts, are vanadium and nickel, although other metallic compounds are also present (Fe, Mn, Zn, Mo, Co, Pb, Cu, Hg, Cd, ...).

The concentrations reported in the literature vary greatly with the author. Examples of concentrations found in crude oils are given in the following two tables.

**Table 30: Trace metal contents of crude oil [HMIP, UK]**

Element	Concentration range (ppm)	Average concentration (ppm)
As	0,046 - 1,11	0,263
Cd	-	0,03
Co	0,032 - 12,751	1,71
Cr	0,0016 - 0,017	0,008
Fe	3,365 - 120,84	40,67
Hg	0,023 - 30	3,240
Mn	0,630 - 2,54	1,17
Mo	0,008 - 0,053	0,031
Ni	<2 - 344,5	165,8
Pb	0,17 - 0,31	0,24
Se	0,026 - 1,396	0,53
V	<2 - 298,5	88,5
Zn	3,571 - 85,8	29,8

**Table 31: Average concentrations (ppm) of nickel and vanadium in crude oils from different source areas [HMIP, UK]**

Element	North Africa	North Sea	Middle East	North America	South America
Ni	<2	4	13	13	177



V	<2	8	50	25	14 - 15
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The variability in the recorded heavy metal content of the oils studied above is due not only to their differing source areas, but also to uncertainties in the sampling and analytical methods used. As an example, a recent study carried out in the Netherlands showed that data in the literature normally used as a basis for estimating the cadmium content of the crude oil in use (mainly Arabian Light and Iranian Heavy) in fact exceeded the actual mean content (generally less than 0,005 ppm) by a factor of about 100 [(28)].

In general, the operations involved in refining crude oils lead to a concentration of metallic compounds in the residual heavy fractions (asphalt, heavy fuel oil). In contrast to that, the refined fraction contains relatively small concentrations. The Union Française des Industries Pétrolières (UFIP) estimates that the heavy metal content of domestic fuel oil is approximately 1 000 times less than that in heavy fuel oil. Table 32 gives an example of the mean trace elements concentrations observed in the heavy fuel oils used in the UK.

The type of metallic compound formed during combustion generally depends on the temperature:

- vanadium is emitted in the form of vanadium pentoxide ( $V_2O_5$ ) in roughly constant proportions over the temperature range 230 - 1 500°C;
- nickel occurs as sulphates (water soluble) and complex oxides. Although a reaction between nickel and carbon monoxide is theoretically possible, the presence of  $Ni(CO)_4$  has not so far been found in gaseous discharges;
- lastly, other metals form sulphates.

**Table 32: Metal content in residual oils [HMIP, UK]**

Element	Concentration range (ppm)	Average concentration (ppm)
As	0,17 - 1,28	0,8
Cd	1,59 - 2,27	1,93
Co	0,26 - 12,68	2,11
Cr	0,26 - 2,76	1,33
Cu	0,28 - 13,42	2,82
Mo	0,23 - 1,55	0,95
Ni	12,5 - 86,13	42,2
Pb	2,49 - 4,55	3,52
Se	0,4 - 1,98	0,75
V	7,23 - 540	160

The proportion of metals in the form of sulphates varies inversely with temperature. Vanadium and nickel do not exist as sulphates above 500°C.

Metallic oxides formed during combustion are responsible for the formation of ash known as fatal ash, i.e. those from which escape is

impossible whatever the practical conditions governing the operation of the burner in the combustion chamber.

From the analytical properties of the fuel and the oxygen content of the flue gases, the concentration of fatal ash can be expressed using the following formula [(29)]:

$$\text{Fatal ash (mg/Nm}^3\text{)} = \frac{\sum m_M \cdot (M_xO_y / x \cdot M)}{V\alpha\%}$$

where  $m_M$  is the mass of metal M in the fuel (mg/kg);  
 $M$  is the atomic mass of the metal M;  
 $x$  is the number of atoms of M in the oxide;  
 $y$  is the number of oxygen atoms in the oxide  $M_xO_y$ ;  
 $V\alpha\%$  is the volume of dry smoke at  $\alpha\%$  oxygen (Nm<sup>3</sup>/kg).

The inclusion of the oxides of vanadium and nickel, together with the oxides of iron and sodium which are generally present in small amounts, is most often sufficient to obtain a good approximation to the quantity of fatal ash.

As an example, Table 33 below gives the fatal ash concentrations capable of being emitted in the absence of a retention device for 20 heavy fuel oils studied by the French Oil Institute.

The effect of boiler design on trace element emissions during the combustion of heavy fuel oil is not as well known as it is for the combustion of coal.

In comparable conditions, the emission rates are roughly the same with the two main types of boiler, i.e. tangential boilers and horizontal boilers (Pacyna, 1982).

On the other hand, the type of atomisation seems to affect the levels of dust emission and hence those of trace elements: high pressure atomisation would make it possible to obtain lower levels of particulate emission. Moreover, it has been shown that particulate emission increases linearly with the sulphur content of the heavy fuel oil used (US Environmental Protection Agency, 1977).

Pacyna [(30)] has specified the emission factors for 12 metallic trace elements for a fuel with a sulphur content of 1%. These factors are listed in Table 34.

**Table 33: Characteristics of 20 heavy fuels and fatal ash content capable of being emitted in the absence of retention devices [(29)]**

Fuel reference		<u>1</u> RSV	<u>2</u> Heavy fuel oil No 2 1984	<u>3</u> BTS	<u>4</u> Boscan crude	<u>5</u> Laguna crude	<u>6</u> Sarago crude	<u>7</u> Khafji crude	<u>8</u> RSV Iran	<u>9</u> Ref 78 1986	<u>10</u> Ref 93 1988
Simple ash (ppm)		280	410	50	2 300	700	900	150	460	300	500
Metal content in oxide form (ppm)	Na <sub>2</sub> O	13	38	11	45	40	40	10	30	47	60,6
	Fe <sub>2</sub> O <sub>3</sub>	30	35	10	40	40	40	10	35	42,9	42,9
	NiO	23	41	19	123	38	112	19	71	50,8	76,2
	V <sub>2</sub> O <sub>5</sub>	125	187	12	2 136	516	635	62	326	178,5	294,5
Sulphur (weight %)			3,7	1,7	5,2	2,8	8,3			2,9	2,3
Σ metal oxides (ppm)		191	301	52	2 344	634	827	101	462	319	474,2
Fatal ash (mg/Nm <sup>3</sup> ) (3% O <sub>2</sub> - zero retention)		16,7	26,4	4,6	205	55,6	72,5	8,8	41	28	41,6

Fuel reference		<u>11</u> S2575 bituminous emulsion ARAMCO	<u>12</u> S2927 bituminous emulsion SAFANIYA	<u>13</u> S3006 bituminous emulsion BOSCAN	<u>14, 15, 16</u> Commercial heavy fuel oils 1988			<u>17</u> US fuel no 6 1988	<u>18, 19</u> Commercial heavy fuel oils 1989		<u>20</u> Commercial heavy fuel oil 1990
Simple ash (ppm)		1 400	700	2 500	530	400		660	530		
Metal content in oxide form (ppm)	Na <sub>2</sub> O	114,5	26,9	10,8	37,7	20,2	26,9	206	40,4	40	40
	Fe <sub>2</sub> O <sub>3</sub>	64,3	21,4	21,4	42,9	42,9	42,9	42,9	21,4	40	40
	NiO	71,1	74,9	143,5	40,6	69,8	63,5	63,5	70	80	63,5
	V <sub>2</sub> O <sub>5</sub>	833,7	185,6	2 142,2	187,4	276,7	267	430	267	304,4	240,3
Sulphur (weight %)		4,45	4,42	4,54	2,95	3,1	3,15	1,35	2,8	2,36	3,18
Σ metal oxides (ppm)		1 083,6	308,8	2 318	308,6	409,6	400,3	742,4	400	464,4	383,8
Fatal ash (mg/Nm <sup>3</sup> ) (3% O <sub>2</sub> - zero retention)		95	27	203	27	35,9	35,1	65,1	35	40,2	33,2

\*  
( ) For fuels no 5, 6, 19 and 20, the iron and sodium contents have been estimated

**Table 34: Emission factors for 12 trace elements in the case of thermal power stations burning heavy fuel oil [(30)]**

Element	Emission factor (µg/MJ )	Element	Emission factor (µg/MJ )
As	24,4	Mo	28,1
Cd	11,6	Ni	1 020,6
Co	129,4	Pb	125,7
Cr	43,3	Se	18,5
Cu	173,8	V	3 697,7
Mn	40,7	Zn	88,7

Based on Pacyna's work, heavy metal emissions in France due to the combustion of heavy fuel oil in large industrial combustion installations (apart from thermal power stations) have been estimated for five heavy metals [(27)]

**Table 35: Emissions of five heavy metals by combustion of heavy fuel oil in French industrial combustion installations in 1989 [(27)]**

Element	Emissions (tonnes)
Cr	22
Cu	88
Ni	520
Pb	64
Zn	45

According to Bouchereau [(27)]. emissions due to the liquid fuels used for energy production in French thermal power stations would for its part be at most of the order of some ten kg because of the small consumption of this type of fuel (2 400 tonnes in 1989).

In the United Kingdom, similar assessments were made for 1990 and these are given in the table below.

**Table 36: Emissions of heavy metals through combustion of heavy fuel oil in thermal power plants and industrial combustion units in the United Kingdom in 1990 [HMIP]**

Element	Power plants (tonnes)	Industrial units (tonnes)
As	1,47	10,37
Cd	0,70	5,19
Co	7,81	57,04
Cr	2,61	19,01
Cu	10,51	76,06
Mn	2,46	18,15
Mo	1,69	12,10
Ni	61,14	449,44
Pb	7,59	55,32
Se	1,12	7,78
V	223,55	1 616,25
Zn	5,35	38,89

In order to achieve a global approach to the emissions resulting from the whole cycle of oil usage, we should add to the above emissions those due to refining.

Catalytic crackers in particular are a potential source of pollution by dust. The particles released have sizes lying between 0,5 and 100  $\mu\text{m}$ . Aluminium silicate is their main constituent, but an examination of their composition also shows the presence of iron (1%), sodium (0,2%) and the heavy metals mentioned above (vanadium, nickel, chromium) [(31)].

For the particular case of combustion to produce electrical power, we set out below as an example that of the French thermal power stations at Loire-sur-Rhône, Aramon and Martigues-Ponteau [(31)].

The station at Loire-sur-Rhône consists of four 250 MWe units, two of them heavy fuel oil-fired. The fuel burnt had the following properties in 1982 (heavy fuel oil type 2):

-density:	1 - 1,02	
-PCS:	9 900 - 10 100 $\text{th.t}^{-1}$	
-ash:	0,02 - 0,07%	
-S:	2,5 - 4%	-Co: < 2 $\mu\text{g.g}^{-1}$
-Na:	20 - 90 $\mu\text{g.g}^{-1}$	-Cu: < 2 $\mu\text{g.g}^{-1}$
-V:	105 $\mu\text{g.g}^{-1}$	-Cd: < 1 $\mu\text{g.g}^{-1}$
-Ni:	33 $\mu\text{g.g}^{-1}$	-Mn: < 1 $\mu\text{g.g}^{-1}$
-Cr:	< 3 $\mu\text{g.g}^{-1}$	-Be: < 1 $\mu\text{g.g}^{-1}$
-Pb:	< 2 $\mu\text{g.g}^{-1}$	

The Aramon power station has two 700 MWe units, and its output in 1987 was 46 GWh for a consumption of 20 ktonnes of heavy fuel oil type 2. The Martigues-Ponteau station has four 250 MWe units. In 1987, it produced 414 GWh for a consumption of 110 ktonnes of heavy fuel oil type 2.

Using the emission factors resulting from the measurement campaigns undertaken in 1982, the emissions of heavy metals were calculated in 1987 for the latter two power stations. The corresponding data are given in the following table.

**Table 37: Releases of dust and trace elements into the atmosphere estimated for the Aramon and Martigues-Ponteau power stations in 1987 [(31)]**

		Aramon	Martigues-Ponteau
Dust (kg)		9 000	158 000
Heavy metals (kg)	As	0,055	1,6
	Be	0,133	0,124
	Cd	0,055	1,1
	Co	1,3	-
	Cr	0,12	0,5
	Ni	101	827
	Pb	1,9	17
	Se	0,4	3,6
	V	276	4 400

Fly ash is emitted directly into the atmosphere at the Martigues-Ponteau station and is filtered through a cyclone dust separator at the Aramon station.

It should be pointed out that, during the combustion of heavy fuel oil, boiler ash forms deposits on the floor of the steam generators. These deposits are then removed during regular cleaning operations (after running for about 10 000 hours) without the resultant emissions being subjected to any kind of assessment.

## “Gases

The only heavy metals that might be found in gaseous fuels are either metals that are capable of occurring in a gaseous phase or metals that might be associated with any particles included in the fuels. In fact, the composition of natural gas means that we can rule out any significant emission of heavy metals during combustion. The situation may be different for industrial gases, but the emissions can be limited by efficient dust removal before combustion.

As an example, the mean concentrations of heavy metals in the natural gas used by large Swedish combustion installations are given below.

**Table 38: Concentrations of heavy metals in the natural gas used by large Swedish combustion installations (Swedish environmental protection agency)**

Trace-element	Concentration (µg/MJ)	Trace-element	Concentration (µg/MJ)
As	0,00003	Mn	0,001
Cd	0,04	Ni	0,001
Co	0,0001	Pb	0,006
Cr	0,003	Se	0,0005
Cu	0,0003	V	0,0003
Hg	0,004	Zn	0,003

### “Other fossil fuels [(32), Swedish EPA]

Peat, wood (bark, wood chips, sawdust), and sometimes other plant-derived fuels such as straw, are used more marginally in a few large combustion installations. They then form either the only fuel in a given installation or one of the fuels on which the installation can call, along with, for example, coal or heavy fuel oil.

Among member countries of the European Union, peat is used in several large combustion installations of at least 50 MWth in Finland, Ireland and Sweden. Particular use is made of wood in Sweden [(32)].

Some information about the heavy metal concentrations in fuels and about the emission factors estimated for the use of peat and wood in Sweden are given in the table below.

**Table 39: Heavy metal concentrations in peat and wood and the emission factors relating to their use in large Swedish combustion installations (Swedish environmental protection agency)**

Trace-element	Concentrations in fuels (µg/MJ)		Emission factors after filtration (µg/MJ)	
	Peat	Wood	Peat	Wood
As	100	5	2	0,1
Be	5	5	0,25	0,25
Cd	10	10	0,5	0,5
Co	100	7	1	0,07
Cr	250	50	2,5	0,5
Cu	500	100	10	2
Hg	5	1	2,5	0,5
Mn	4 500	5 000	90	100
Ni	300	30	6	0,6
Pb	250	200	12,5	10
Se	50	10	2,5	0,5
V	450	100	9	2
Zn	900	1 200	9	12

#### 4.1.4 Persistent organic compounds

There is little precise information about emissions of persistent organic compounds due to the operation of large combustion installations.

Data that are available are most often incomplete and not easily comparable because of the variety of sampling and analytical methods used.

Generally speaking, because the combustion conditions are better, it is observed that emissions of persistent organic compounds into the air per unit of energy produced are potentially lower for large combustion installations than they are for other uses of fossil fuels (domestic heating, motor vehicles, etc).

#### “PAHs [(21), (33)]

According to measurements made in the United Kingdom [(21)], the total emissions of PAHs in the flue gases of large coal-fired or oil-fired combustion installations would be of the order of 10 to 100 µg/m<sup>3</sup>.

Measurements on emissions carried out recently in the UK also indicate releases of benzo(a)pyrene of between 10 and 100 ng/m<sup>3</sup> for large coal-fired combustion installations.

In France, measurements have been made on six coal-fired and oil-fired power stations of more than 50 MWe [(33)]. Samples were taken in the smokestack and analyses were made on the total emissions of PAHs (gaseous phase and particulate phase).

The results of these measurements are given in the following table.

**Table 40: PAH concentrations (ng/m<sup>3</sup>) in emissions of six French power plants [(33)]**

Plant	A	B	C	C'	D1	D4	E	F
Fuel	Polish coal	French coal	South African coal		Australian coal		Oil	Oil (gas turbine)
Rated power (MW)	250	250	600	600	600	600	600	80
Effective power (MW)	250	250	400	600	400	600	300	80
Sampling height (m)	10	10	120	120	60	40	80	5
Sampling time (min)	45	45	120	60	45	45	120	120
Sampling temperature (°C)	140	115	115	130	140	120	130	500
Excess O <sub>2</sub> (%)	6	9	-	6	7	5	-	16
NO <sub>x</sub> (ppm)	730	290	nm	420	610	370	nm	175
Particles (ng/m <sup>3</sup> )	50	140	nm	10	20	10	nm	70
1-Methylnaphthalene	nm	nm	500	1 100	600	2 730	600	900
2-Methylnaphthalene	nm	nm	60	140	60	450	200	200
Fluorene	nm	nm	160	300	50	390	600	450
Phenanthrene	nm	nm	350	900	830	4 430	2 500	2 000
Fluoranthene	130	375	20	70	380	2 470	960	315
Pyrene	20	85	80	210	570	6 370	530	420
Benzo(a)anthracene	20	25	130	290	140	390	90	275
Chrysene	15	70	180	320	200	500	450	100
Benzo(b)fluoranthene	t	15	t	10	0	t	t	t
Benzo(b)fluoranthene	t	8	t	5	0	t	t	t
Benzo(e)pyrene	t	35	t	10	5	20	15	5
Benzo(a)pyrene	0	25	t	t	0	t	20	20
Σ PAH (µg/m <sup>3</sup> )	0,185	0,638	1,480	3,355	2,835	17,750	5,965	4,685

nm = not measured; t = trace



**Table 41: PAH emission factors for six French power plants [(33)]**

Plant	µg/kg of fuel				ng/KWh							
	A	B	C'	D4	F	A	B	C	C'	D1	D4	F
1-Methylnaphthalene	nm	nm	11,48	25,38	39,60	nm	nm	2 000	4 400	2 080	8 420	12 380
2-Methylnaphthalene	nm	nm	1,46	4,18	8,80	nm	nm	240	560	210	1 390	2 750
Fluorene	nm	nm	3,13	3,63	19,00	nm	nm	640	1 200	170	1 200	6 190
Phenanthrene	nm	nm	9,39	41,18	88,00	nm	nm	1 400	3 600	2 870	13 660	27 500
Fluoranthene	1,66	4,65	0,73	22,96	13,86	500	1 900	80	280	1 320	7 620	4 330
Pyrene	0,26	1,65	2,19	59,22	18,48	80	430	320	846	1 970	19 640	5 780
Benzo(a)anthracene	0,26	0,31	3,03	3,63	12,10	80	130	520	1 160	480	1 200	3 780
Chrysene	0,19	0,87	3,34	4,65	4,40	60	350	740	1 280	690	1 540	1 380
Benzo(b)fluoranthene	t	0,19	0,10	t	t	t	80	t	40	0	t	t
Benzo(b)fluoranthene	t	0,09	0,05	t	t	t	46	t	20	0	t	t
Benzo(e)pyrene	t	0,43	0,10	0,19	0,22	t	180	t	40	20	60	70
Benzo(a)pyrene	0	0,31	t	t	0,88	0	130	t	t	0	t	80

Σ PAH (µg/MJ)	0,20	0,90	1,65	3,73	2,73	15,20	17,84
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The results of these measurements clearly show the variability of the emissions with the type of fuel and the type of plant.

Moreover, for a given plant, it appears from the measurements made on stations C and D that emission factors are higher when the station operates at full power and that the PAH emissions vary inversely to the NO<sub>x</sub> emissions.

### “Dioxins [(11), (18), (19)]

Preliminary estimates for the cumulative emissions of PCDDs and PCDFs due to coal-fired and oil-fired power stations were made for the period 1989/1990.

These estimates give the following releases [(11), (19)]:

- 1 g TEQ/year for Sweden;
- 5 g TEQ/year for Germany;
- 9.8 to 30 g TEQ/year for the United Kingdom.

In addition, measurements of releases have recently been made in Germany at several potential dioxin sources, including large combustion installations [(18)].

These measurements show that the emission levels from large combustion installations running on coal, oil or untreated wood are less than 0,1 ng TEQ/m<sup>3</sup>.

Table 42 below gives the results of a few of these measurements, made on installations of more than 50 MWth.

**Table 42: Dioxin Emissions from Power Stations, Heating Power Plants and Wood-Firing Installations in Germany [(18)]**

Installation	Fuel	Output a) long distance thermal/ electrical output b) measured	Operating/ reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow (Nm <sup>3</sup> /h)	Waste Gas Treatment  Remarks
					Crude Gas (ng TE/m <sup>3</sup> )	Clean Gas (ng TE/m <sup>3</sup> )	Filter Deposits (ng TE/kg)		
Power Plant	hard coal	a) 523 MWth	6.3/5 5.7/5 6.7/5 5.5/5	4		<0,002 <0,002 <0,002 <0,002		1 270 000 1 270 000 1 240 000 1 250 000	normal without FGD/with Denox with FGD/without Denox without FGD/without Denox
Power Plant	hard coal	b) 63 MWth	6.1/7 4.6/7 8.7/7	3		0,014 0,009 0,011	15	39 400 68 100 46 700	H <sub>2</sub> O conditioned, Ca(OH) <sub>2</sub> additive, fabric filters
Power Station	brown coal	a) 760 MWth	8.6/6	8		0,0001-0,0054		1 000 000	E-filter
Heating Plant	heating oil EL	a) 397 MWth	3.7/3	3		<0,005		252 000	Denox, FGD, E-Filter
Vertical cyclone furnace	chipboard rests (Cl: 0,05-0,08%) solid wood chippings	a) 800 MWth	4-8/11	6	0,039 0,075 0,024	0,006-0,021 0,003-0,006 0,007-0,003		full load 1 350 partial load 1 030 low load 890	waste gas return E-filter addition of lime to fuel

## 4.2 Liquid effluent

Liquid effluent accompanying the operation of large combustion installations may originate from various sources depending on the type of fuel, the nature of the combustion processes and the methods of decontamination used.

### 4.2.1 *Boiler water* [(21), (34), (35), (36)]

All boilers need to be supplied with relatively pure water, and high pressure boilers require demineralised water.

The process adopted involves treatment of untreated water with ion exchange resins, possibly with pretreatment (flocculation, decarbonation, filtration). The water required for the production of demineralised water may either be taken from the surface, from boreholes or from the mains supply.

Regeneration of ion exchange resins produces alkaline and acid waste water which is discharged after neutralisation. The effluents contain salts, e.g. sulphates when sulphuric acid is used during the regeneration.

The operation of systems for the pretreatment and the neutralisation of effluent from the regeneration of ion exchange resins leads to the production of sludge.

Boiler water is also given treatment for preventing corrosion and the formation of crystalline deposits reducing heat exchange:

- the chemicals used to prevent corrosion are corrosion inhibitors (chromates, nitrites, molybdates, borates, ...) or reducing agents (sulphites, hydrazines, tannates, ...);
- the formation of deposits on the boiler walls is slowed down by the use of dispersants based on phosphates or organic polymers possibly with specific inhibitors added (zinc, chromates, ...).

In a continuous operational mode, the concentration of boiler water is held constant by purging (blowdown) and supplying make-up water.

Finally, the boilers are given periodic chemical cleaning to get rid of the scale that continually accumulates while running. The frequency of these operations depends on the way the installations are run and the rate at which fouling occurs.

Various chemical formulations are or have been used, involving as constituents formic acid, citric acid, hydrofluoric acid, ammonium fluoride, hydrazine, ethylene-diamine-tetra-acetic acid (EDTA), etc. However, the most environmentally harmful of these products, such as EDTA, have gradually been abandoned and replaced by substances with fewer disadvantages.

In France, the cleaning of power station boilers includes a reduction phase (injection of acid and a corrosion inhibitor into the boiler filled with demineralised water at 80°C), followed by a passivation and copper-removal phase (injection of ammonia to make the medium more alkaline, sodium nitrite for the passivation and potassium bromate to dissolve the copper) [(36)].

Passivation is essential to protect the surfaces of the pipes exposed during the cleaning, since they would otherwise be in danger of degrading in contact with the atmosphere.

The nature and quantity of effluent produced depends on the chemicals used and the power of the boiler: for example, cleaning a 250 MWe boiler with citric acid and formic acid produces of the order of 120 m<sup>3</sup> of effluent (apart from rinsing water).

#### **4.2.2 Cooling water** [(21), (35), (36), (37), (38), (39)]

Large combustion installations operating with large combustion equipment generally use condensers cooled by water from a river or the sea.

As with boilers, various problems relating to water quality may arise in the cooling circuits. These are:

- scaling, mainly through precipitation of carbonates, sulphates and phosphates of calcium;
- corrosion;
- fouling, through the deposition of suspended matter, the formation of a bacterial layer (microfouling) and the growth of molluscs and colonies of bryozoa (macrofouling) in the condenser pipes and water intake ducts.

If poorly controlled, these problems may cause the operating conditions of the plant to deteriorate, posing safety risks and reducing the efficiency of energy conversion.

The cooling water is therefore subjected to treatment appropriate to the nature of each installation, including in particular the use of chemical reagents (corrosion inhibitors, descaling agents, dispersants, biocides).

The environmental implications of discharging cooling water are closely related to the nature, the concentration, the toxicity and the persistence of the chemicals used for the prevention of scaling, corrosion and fouling. Nevertheless, other factors ought clearly to be taken into consideration, especially the heating effects of the discharge.

It should be pointed out that, in some cases, wear on the condensers can also be the source of significant discharges of metals. For example, when the condenser pipes are made of brass, estimates made by EdF [(36)] at a power station quote a discharge rate of the order of 20 to 60 kg/day for copper and of 10 to 30 kg/day for zinc per 1 300 MWe unit.

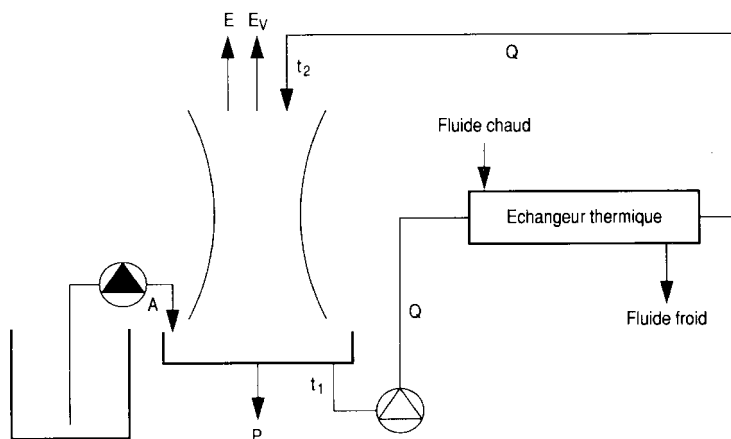
### **“Types of Cooling Water Systems**

The most frequently-used types of cooling water systems (CWS) are open systems (once-through CWS) and semi-open ones with atmospheric cooling (semi-open recirculating CWS).

Open circuits assume that large amounts of water are available of the order of 30 to 45 m<sup>3</sup>/s for a 1000 MWe unit [(39)] and, because of this, are installed in large combustion installations located on the coast or near water courses with large flow rates. Since the water taken up is then most often returned directly into the aquatic environment, a large amount of heat is discharged: of the order of twice the electrical power produced per unit for a power station [(36)].

In the case of semi-open circuits with atmospheric cooling, the water from the heat exchanger is directed to a cooling tower, where the heat is then dissipated by evaporation and convection. The principal of the semi-open circuit is explained by the figure below.

**Figure 4: Semi-open circuit with atmospheric cooling [(38)]**



A = make-up water (m<sup>3</sup>/h)  
 Q = recycled flow (m<sup>3</sup>/h)  
 E = evaporation (m<sup>3</sup>/h)  
 Ev = convection (m<sup>3</sup>/h)  
 P = dilution purge (m<sup>3</sup>/h)

t<sub>1</sub> = cooling output temperature (°C)  
 t<sub>2</sub> = coolant input temperature (°C)  
 D = total purging rate (m<sup>3</sup>/h)  
 C = level of concentration

Liquid discharges from semi-open cooling circuits are limited to those from dilution purges.

The nature of the treatment given to the cooling water depends on the type of circuit used. We examine in turn below the prevention of fouling, scaling and lastly corrosion.

#### ❑ FOULING

In the case of open circuits, the potential for fouling is related directly to the elements contained in the aquatic environment used (suspended matter, micro-organisms, macro-organisms, etc.). The water treatment programme is mainly limited to macrofiltration and the use of single biocide, very often sodium hypochlorite.

For semi-open circuits, fouling can be prevented by action taken at the level of the make-up water (filtration, coagulation, precipitation) and at the circuit level. Among the latter, organic dispersants (sulphonated compounds, acrylic polymers, ...), surfactants, as well as various oxidising or non-oxidising biocides can be used.

Oxidising biocides have a non-specific biocidal action. Whatever the type of cooling circuit, sodium hypochlorite has been and remains the most commonly used biocide because of its effectiveness and relatively low cost. Other chlorinated reagents and various bromine derivatives are also used.

Oxidising biocides react not only with the organisms to be eliminated, but also with other organic compounds and with the suspended matter present in the cooling water. Various organohalogen compounds are then formed, some of which are well known (haloforms, haloamines, haloacetonitriles, bromate and chlorate etc), but many are still unidentified.

In order to avoid the risks inherent in the transport and storage of chlorine, units for the production of sodium hypochlorite by electrolysis of seawater are frequently used for large coastal combustion installations.

Non-oxidising biocides have a specific biocidal action on the metabolism of organisms by acting either on the cell wall or inside the cell. Many compounds can be used here. For example, a recent Dutch study mentions the use of more than ten non-oxidising biocides in the Netherlands (isothiazolines,  $\beta$ -bromo- $\beta$ -nitrostyrene, methylenebisthiocyanate, 2,2-dibromo-3-nitrilopropionamide, ...) [(39)].

#### ☐ SCALING

In the case of semi-open circuits, evaporation of part of the cooling water leads to an increase in the concentration of dissolved salts and a change in the free  $\text{CO}_2$  content. These conditions cause the pH to rise and encourage the conversion of calcium bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ ) into calcium carbonate ( $\text{CaCO}_3$ ), the precipitation of which causes scaling of the condenser pipes and the packings of the atmospheric coolants.

To restrict the scaling, whose extent depends on the mineralisation of the water being used, an extra supply of untreated water is constantly provided and continuous purging is used to dilute the cooling water. When the dilution by continuous purging is not enough because of the high level of mineralisation in the water supply, additional treatment is necessary. This involves a vaccination (controlled addition of acid) of the circuits by injecting an acid, usually sulphuric acid, into the water supply. In addition, organic anti-scaling agents (polyphosphates, phosphonates, polyacrylates,...) may be used.

Expressed as a flow rate, the dilution purges of semi-open circuits represent of the order of 2 to 4% of the discharges associated with a comparable installation equipped with an open circuit configuration. They can then be subjected to an appropriate treatment before discharge.

#### ☐ CORROSION

Corrosion is prevented by the use of corrosion inhibitors. A distinction is generally drawn between anodic inhibitors (orthophosphates, chromate, nitrite, silicate, molybdate) and cathodic inhibitors (polyphosphates, hydroxyphosphonic acids, zinc salts).

The choice of a corrosion inhibitor depends on the materials forming the circuit and on its operating conditions, particularly the pH. Apart from the use of corrosion inhibitors, anodic protection is sometimes employed.

#### **4.2.3 Scrubbing of gases by the wet method**

[(21), (23), (40), (41), (42), (43)]

Wet scrubbing is used for dust removal and/or desulphurisation of flue gases.

Pollutants other than these whose removal is particularly desirable are then liable to be transferred to the liquid effluent (hydrochloric acid, heavy metals, persistent organic compounds, ...).

The methods used for desulphurisation are seawater scrubbing and wet lime or limestone scrubbing.

##### **☐ Seawater scrubbing**

Seawater scrubbing is used for some large combustion installations located on the coast. The water used for the scrubbing is not purified before discharge: this process is thus accompanied by a direct transfer of pollutants to the marine environment.

##### **☐ Desulphurisation by the wet method**

During desulphurisation by the wet method using calcium carbonate, the absorbing agent is mixed with the water to make a slurry which circulates in a closed circuit. Although sulphur dioxide is trapped in this way, as calcium sulphite ( $\text{CaSO}_3$ ) and calcium sulphate ( $\text{CaSO}_4$ ), other pollutants in the flue gases are also transferred into the liquid phase, particularly hydrogen chloride (which reacts to produce calcium chloride) and many metallic compounds [(43)].

In order to control the progressive increase in the calcium chloride concentration in the flue gas desulphurisation unit, which is necessary to maintain a satisfactory efficiency of desulphurisation and to prevent the risk of corroding equipment, a fraction of the circulating slurry is drawn off from the circuit. The quantity of slurry drained off in this way depends both on the amount of hydrochloric acid present in the flue gases and on the maximum desirable calcium chloride concentration in the system, in practice a maximum of 20 to 30 g/l for the above technical reasons, of the order of 0,11 to 0,17 m<sup>3</sup>/MWh of slurry is extracted, amounting to about 30% by weight of fly ash, 20 to 30% of water and 40 to 50% of gypsum.



After the gypsum has been removed, the waste water from the wet desulphurisation processes contain:

- dissolved salts (chlorides, sulphates, magnesium, calcium, ...);
- suspended matter (particles of gypsum, aluminium hydroxide, calcium fluoride, ...);
- trace elements originating both from the flue gases and the calcium carbonate used for the desulphurisation.

The desulphurisation reagents introduce significant quantities of trace elements into the FGD unit. For some of these, the amounts can even prove to be greater than those from the dust-free flue gases [(23), (40)].

The table below gives the typical composition of an effluent from desulphurisation by calcium carbonate before treatment [(43)].

**Table 43: Mean concentrations of an effluent from desulphurisation using calcium carbonate before treatment [(43)].**

Parameter	Range (mg/l)	Parameter	Range (mg/l)
Chloride (Cl)	10 000 - 40 000	Cadmium (Cd)	0,04 - 0,05
Sulfate (SO <sub>4</sub> )	1 500 - 18 000	Cobalt (Co)	0,05 - 0,4
Nitrate (NO <sub>3</sub> )	300 - 1 400	Chromium total (Cr tot)	0,3 - 5
Fluoride (F)	30 - 200	Copper (Cu)	0,1 - 0,85
Calcium (Ca)	4 000 - 20 000	Mercury (Hg)	0,05 - 0,8
Magnesium (Mg)	200 - 5 600	Nickel (Ni)	0,2 - 6
Sodium (Na)	75 - 1 200	Lead (Pb)	0,1 - 3
Iron (Fe)	30 - 400	Antimony (Sb)	< 0,5
Aluminium (Al)	50 - 800	Selenium (Se)	0,2 - 1
Arsenic (As)	0,05 - 3	Vanadium (V)	< 2
Beryllium (Be)	0,05 - 0,1	Zinc (Zn)	0,4 - 8

Recent measurements made in Germany on effluents from wet desulphurisation at three power stations running on lignite or coal did not detect any traces of PCDDs or PCDFs [(42)].

The methods used for the treatment of waste water from desulphurisation by the wet method are described in the section 5.2.

#### **4.2.4 Ash-contaminated water [(36)]**

Large combustion installations produce ash-contaminated water when the boiler ash is handled hydraulically or when washing operations are carried out in the smoke circuits (air heaters, dust collectors, combustion chambers).

Ash-contaminated water has various physico-chemical properties depending on its origin. It is then subjected to selective collection, followed by various treatments after storage in sedimentation pits.

For example, at the French Cordemais power station, which consists of three coal-fired units and two oil-fired units:

- the water loaded with lower levels of metal (handling of boiler ash, scouring of steam generators) is subjected to physico-chemical precipitation and is recycled;
- the water loaded with higher levels of metal (scrubbing of flue gas circuits) is directed to the treatment system for the water from flue gas desulphurisation.

The table below gives the results from analyses of the effluents from the washing of air heaters carried out in 1991 at the Cordemais power station (the coal-fired units are nos 1, 4 and 5).

**Table 44: Analysis of waste water from the washing of air heaters  
- Cordemais power station [(36)]**

	T1	T1	T1	T2	T3	T4	T5
pH (20°C)	3,3	6,1		2,7	1,8	3,4	2,8
MES (mg/l)	20	91		137,2	93	1 026	216,2
Cu (mg/l)		0,001	0,058	5,78	20	3,87	3,91
Cr total (mg/l)			11,4				
Cr VI (mg/l)		0,01		0,01	0,01	0,01	0,01
Fe (mg/l)	639	74,1	9 645	1 800	3 200	448	1 400
Hg (mg/l)		0,0001	0,0001	0,0001	0,001	0,0002	0,0008
Mn (mg/l)		12,6	5,5	33,5	77	9,5	13,7
Ni (mg/l)	2,12	0,925	12,4	37	130	4,57	4,15
Pb (mg/l)		0,003	19,7	0,003	0,9	0,008	0,036
V (mg/l)	0,4	0,031	26,4	63	410	3,87	5,3
Zn (mg/l)	3,05	0,49	52	4,6	9	5,6	4,5

#### **4.2.5 Other liquid effluent [(21)]**

Rainwater contaminated during run-off from the site of the plant, leachates due to open-air storage of coal or waste: these form other potential sources of pollution of the aquatic environment.

What should be particularly stressed is the many possible sources of pollution by hydrocarbons: leaks occurring from oil storage tanks, dripping from burners, leaks and drips from flanges and from the lubrication circuits of machinery, ...)

### **4.3 Waste**

Residues arising directly from combustion are boiler slag, ash and fly ash. The properties of such waste can vary enormously from one site to another, depending on the type of fuel used and its source, the combustion process employed, even the method of waste management used (wet or dry method).

Many other classes of waste can arise:

- waste from treatment of fuel (coal washing, etc);
- sludge, solid waste, boiler slag, fly ash from periodic maintenance and cleaning operations (storage tanks for liquid fuels, boilers, cooling plant, smokestacks, dust collectors, ...);
- spent ion-exchange resins from the treatment of boiler water;
- by-products from flue gas desulphurisation (gypsum, sulphur, ...);
- spent catalysts from SCR processes;
- sludge from purification of waste waters (wet desulphurisation, chemical cleaning, ...);
- (...).

The fact that each category of waste has its own special properties makes it impossible to give a detailed description of the environmental problems that its management raises. We simply note that, among such problems:

- some of the waste products (gypsum, sulphur, certain types of ash, ...) may be exploited particularly in the building industry or in civil engineering work when it is technically possible, environmentally acceptable and economically viable;
- other types may be returned to the manufacturer (spent catalysts, ...);
- others should be disposed of in dumps for special industrial waste.

Among the waste generally disposed of by dumping, fly ash seems most particularly to require special precautions.

Table 45 on the following page gives illustrative examples of the quantities of waste resulting from the treatment and combustion of the fuels used for electricity and steam generation in some of the Contracting Parties to the Paris Convention [(44)].

#### **4.3.1 *Ash from the combustion of heavy fuel oil*** [(31), (44), (45), (46)]

Because of the concentration of heavy metals in heavy fuel oils during refining, the combustion of this type of fuel creates residues which in their turn are rich in metallic derivatives, particularly nickel and vanadium.

**Table 45: Waste from the treatment and combustion of the fuels used for electricity and and steam generation in some Contracting Parties [from (45)]**

Country	By-Products from Solid Fuel Treatment			Bottom and Fly Ash			By-products from FGD Systems			By-products from Fluidized Bed Combustion Systems		
	Amount (t)	Year	Remarks	Amount (t)	Year	Remarks	Amount (t)	Year	Remarks	Amount (t)	Year	Remarks
Federal Republic of Germany	58 786 000	1988	Hard coal cleaning	5 000 000 5 600 000	1989 1989	hard coal lignite	3 000 000 500 000 30 000 40 000 60 000 4 000	1989 1989 1989 1989 1989	gypsum FGD-mixture sulphuric acid SO2 sulphur ammonium sulphate	500 000	1989	ash and slag
Finland	none	-	-	740 000 100 000	1988 1987	coal peat	30 000  10 000	1988  1988	FGD-mixture from wet-dry process FGD-mixture from LIFAC-process	11 500	1988	ash
Netherlands	none	-	-	780 000	1988	-	190 000	1989	gypsum	3 800	1984	ash
Sweden	none	-	-	350 000 4 000 140 000	1988 1988 1988	coal (1) oil biomass and peat	80 000	1988	FGD-products	80 000	1988	ash
United Kingdom	data not available	-	-	13 000 000	1988		none	1988	-	50 000	1986	ash

(1) Including FGD-products

The table below gives the characteristics of residues from the combustion of heavy fuel oils.

**Table 46: Characteristics of residues from the combustion of heavy fuel oils [(45)]**

Residue	Characteristics
Boilers slag	high temperature deposits: ⇒ vanadium (7-20%), carbon (1-10%)
Fouling ash	ash deposited in circuits between the boiler and dust collector: ⇒ vanadium (10%), carbon (30%), sulphates (40%)
Soot or fly ash	Sticky black particles trapped in the dust collector: ⇒ vanadium (0,5-5%), carbon (40-90%), sulphates (10-30%)

Three samples of residues from the combustion of heavy fuel oil were taken and analysed in 1982 at the French power station at Aramon. Two of the samples related to ash deposits at the bottom of the steam generator. They were taken after a maintenance operation following a continuous period of running amounting to about 10 000 hours. The third sample was taken from the fly ash at the power station cyclone.

The results of the analyses are listed in Tables 47 and 48 below [(31)].

**Table 47: Analysis of two samples taken from the deposit at the bottom of the steam generator at the Aramon power station in 1982 (approximately 10 000 hours running time) [(31)]**

	Sample no 1	Sample no 2
Al (expressed as Al) (%)	16,65	17,30
V (expressed as V <sub>2</sub> O <sub>5</sub> ) (%)	6,60	6,40
Ni (expressed as NiO) (%)	2,85	3,95
Zn (expressed as ZnO) (%)	0,15	0,15
Fe (expressed as Fe <sub>2</sub> O <sub>3</sub> ) (%)	4,45	6,20
Ti (expressed as TiO <sub>2</sub> ) (%)	0,85	0,85

**Table 48: Concentrations of trace elements measured in the fly ash from the combustion of heavy fuel oil type 2 at the Aramon power station in 1982 [(31)]**

		Concentration in the heavy fuel oil	Concentration in sample no 3
Heavy metals (in $\mu\text{g.g}^{-1}$ )	As	-	< 6
	Be	< 1	2
	Cd	< 1	2
	Co	< 2	160
	Cr	< 3	220
	Cu	< 2	-
	Mn	< 1	-
	Ni	33	16 800
	Pb	< 2	230
	Se	-	46
	V	105	56 000

The recovery of vanadium from this type of waste product has been studied by many research workers. Giorgini *et al.* (1978), Giavarini and Tombolini (1981) and Corigliano *et al.* (1983) mention vanadium extraction efficiencies of between 80 and 90%. In spite of that, the industrial use of such exploitation has so far remained marginal; one Austrian plant is mentioned as recovering vanadium from the ash produced by the combustion of heavy fuel oil [(44)].

Dumping these types of waste or storing them under poor conditions are liable to lead to a migration of trace elements into the natural environment by leaching under the action of rainwater or run-off.

Tests on leaching have been carried out on soots from the French power station at Martigues-Ponteau [(46)].

The properties of the soots used and the extraction efficiencies obtained are given in Tables 49 and 50 below. The tests that gave these results were column tests carried out in accordance with the French standard NF-X-31.210. Leaching was performed with distilled water both on the untreated soots and on the soots calcined at 550°C.

The calcination produces a structural change in the waste (formation of haematite) which has a favourable effect on its behaviour under leaching by making the metallic elements less easily extractable. It is, however, accompanied by emission of oxides of carbon and of sulphur.

**Table 49: Characteristics of the soots examined [(46)]**

	untreated soots	calcined soots
Density (kg/m <sup>3</sup> )	2 650	3 450
Permeability (x 0,00001 m/s)	2 - 4	2,5 - 3,5
Carbon (%)	9,6	0,07
Sulphur (%)	17	4,3
Iron (%)	34	61
Vanadium (%)	2	3,4
Nickel (%)	0,6	1,1
Manganese (%)	0,12	0,22

**Table 50: Extraction efficiencies obtained in column tests [(46)]**

	untreated soots	calcined soots
Iron (%)	10,5 - 11,5	3,3
Vanadium (%)	40 - 44	3
Nickel (%)	50	29,5

Roussy [(45)] mentions comparable results during the leaching of soots by solutions of reconstituted rainwater.

Having said that, dumped industrial waste is not necessarily subjected to the action of water with properties comparable to those of rainwater, but it may be put into contact with acid or basic leachates.

Tests have also been carried out under these conditions, including those with high concentrations unlikely to be encountered in dumps but useful in highlighting certain aspects connected with the possible commercial exploitation of the soots.

The results show that batch leaching in the presence of 5N hydrochloric acid and with a contact time of one hour gives an extraction efficiency of 95% for vanadium. Iron and nickel are also dissolved.

In a basic medium (a 5N aqueous solution of sodium carbonate), a contact time of one hour enables 80% of the vanadium to be extracted without any significant effect on the iron and nickel. Extraction in a basic medium is thus a favoured method for the selective extraction of vanadium.

#### **4.3.2 Ash from the combustion of coal**

The ash from the combustion of coal has different characteristics according to the type of fuel and the combustion process.

We examine in turn the ash from pulverised coal and fluidised bed processes.

##### **□ Pulverised coal processes [(47), (48)]**

As an example, Table 51 below gives the analytical composition of fly ash taken from a Danish pulverised coal power station (Studstrupvaerket) using coal from the USA [(47)].

**Table 51: Analytical composition of fly ash from the Danish power station at Studstrupvaerket [(47)]**

<u>Major elements (g/kg)</u>		<u>Minor elements (mg/kg)</u>	
Si	221	Ag	0,41
Al	123	As	130
Fe	75	Cd	1,5
Ca	20	Cr	230
Mg	8	Cu	170
K	16	Hg	0,4
Na	2,5	Mo	18
Ti	7,3	Ni	210
S	2,9	Pb	170
P	1,1	Se	22
Mn	2,9	Sr	400
		V	230
		Zn	450

Table 52 gives the results of a leaching test in a lysimeter (percolation of rainwater falling on ash stored in the open).

Since the ash has a low permeability (coefficient K between  $10^{-6}$  and  $10^{-8}$  m/s), the leachates were collected and analysed over a period of just over five years.

With the coal in a pulverised coal power station burning at a high temperature (between 1 300 and 1 600°C), it is observed that a number of volatile compounds capable of yielding acids in an aqueous medium ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ , ...) do not occur in fly ash.

As a result, leached ash generally produces alkaline reactions and the trace elements that are liable to be entrained in significant quantities are those which occur in the form of anions in an alkaline medium (e.g.  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{VO}_4^{3-}$ , ...).

**Table 52: Composition of leachates in the lysimetric test (recording chamber 3 x 3 m, height 1.41 m) [(47)]**

Parameter	Unit	L/S (*) 0,06-0,08	L/S 0,16-0,19	L/S 0,26-0,32	L/S 0,43-0,51	L/S 0,81-0,86	L/S 1,41-1,44	L/S 1,89-1,93
pH	-	9,4	9,6	9,1	8,8	9,5	8,5	9,0
Conductivity	mS/m	510	420	280	250	230	220	210
Sulphate	mg/l	2 920	2 430	1 730	1 480	1 400	1 370	1 330
Fluoride	mg/l	0,16	0,12	0,47	0,06	-	-	-
Chloride	mg/l	72	33	16	13	3,7	5,7	2,4
Na	mg/l	500	250	115	45	17	6	4,3
K	mg/l	800	500	270	140	59	34	25
Ca	mg/l	380	510	500	570	550	560	530
Mg	mg/l	2,7	3,7	6,2	4,5	12	19	19
As	mg/l	0,077	0,67	0,05	0,062	0,10	0,077	0,047
Cd	mg/l	0,00022	0,0002	0,00004	0,00013	<0,0001	<0,0001	<0,0001
Co	mg/l	<0,0005	-	-	<0,0005	<0,001	-	-
Cr	mg/l	14	8,8	4,6	2,3	0,52	0,40	0,25
Cu	mg/l	0,0011	-	-	<0,001	<0,001	<0,001	<0,001
Hg	mg/l	<0,0005	<0,0005	<0,0005	<0,0005	<0,001	-	-
Mo	mg/l	43	23	7,4	2,9	0,53	0,41	0,30
Ni	mg/l	0,002	-	-	<0,001	<0,001	-	-
Pb	mg/l	<0,0005	-	-	<0,0005	<0,001	-	-
Se	mg/l	3,8	1,5	0,56	0,28	0,20	0,15	0,12
V	mg/l	0,79	0,59	0,43	0,31	0,23	0,18	0,18
Zn	mg/l	0,023	-	-	<0,01	<0,01	-	-
Sampling date		28/04/83	29/11/83	02/02/84	24/11/84	10/12/85	11/09/87	28/11/88

(\*) L/S= liquid/solid ratio, with L= total volume of leachate produced at time t and S= total amount of ash deposited (dry bulk weight)

## ❑ Fluidised bed processes [(49)]

With fluidised bed stations being currently developed in considerable numbers, it seems important to determine in detail the properties of the ash produced and, independently of any methods of exploiting it commercially that might be developed in the future, its behaviour when it is leached.

Unlike the ash produced in pulverised coal processes, which is rich in silica and aluminium, the ash produced in fluidised bed combustion is characterised by an abundance of lime and sulphates.



Table 53 below gives the concentrations of eight trace elements measured in 1993 on samples of fly ash from the circulating fluidised bed at Carling (France) and the Lurgi pilot circulating fluidised bed at Frankfurt (Germany). The first of these plants was supplied with ash slurry resulting from coal-washing operations, while the second was tested with coal and petroleum pitch.

The table also recalls the usual concentrations observed for fly ash from pulverised coal.

The sulpho-calcic ash from fluidised bed stations has a tendency to agglomerate under the effect of water (formation of ettringite) and to cause clogging and hence a low permeability (coefficient K of the order of  $10^{-9}$  m/s).

Leaching tests were carried out on these ashes in accordance with the French standard NF-X-31.210.

The pH of the leachates obtained is of the same order of magnitude as that of leachates from pulverised coal ash, or even higher (up to 12.5).

**Table 53: Trace element concentrations in samples of fly ash from fluidised beds [(49)]**

	Fly ash from Carling (mg/kg)	Fly ash from Frankfurt (mg/kg)	Fly ash from pulverised coal (mg/kg)
As	73-74	42-52	11-118
Cd	<0,2-1,8	<1	0,5-3
Cr	147-194	49-118	50-307
Cu	106-151	43-48	59-258
Hg	0,6-1,6	0,1-0,7	0,1-2,8
Ni	101-126	63-153	42-449
Pb	95-128	14-27	27-669
Zn	176-299	62-100	64-771

Table 54 below gives the measured concentrations in the leachates of the eight trace elements studied and compares them with values measured on leachates of aluminosilicate ash (values expressed in  $\mu\text{g}$  per kg of leached ash).

With the exception of arsenic, the orders of magnitude of the measured trace elements are more or less the same for the fluidised bed ash leachates as for the pulverised coal ash leachates.

However, it would seem that complex effects involving adsorption of the metals on the ash particles or coprecipitation with major elements can occur with the specific composition and structure of this type of ash.

These effects would explain, in particular, the small proportion of arsenic leached.

**Table 54: Leaching tests on fluidised bed fly ash [(49)]**

	Leachates of fly ash from Carling (µg/kg)	Leachates of fly ash from Frankfurt (µg/kg)	Leachates of fly ash from pulverised coal (µg/kg)
As	350-740	<30	50-7 320
Cd	<1	<30	<1
Cr	2 960-6 010	1 700-2 800	210-6 370
Cu	70-160	50-100	1-29
Hg	30-40	30-40	-
Ni	<19	50-80	<25
Pb	<7	<30	<10
Zn	30-180	70-260	25-200

#### **4.3.3 Ash from combustion of peat and wood [(44, (50))]**

Several studies give orders of magnitude for the trace-element concentrations that may occur in the ash produced during the combustion of peat and wood.

Table 55 gives the analytical composition of peat ashes in comparison with that of coal ashes. Table 56 records the concentrations recently measured on wood ashes (Oberberger, 1995).

Some ashes from installations using bark, chips or sawdust from wood have also been analysed to ascertain their concentration of persistent organic compounds (PCCD, PCCF, PAH, PCB, HCH, HCB) (Oberberger, 1995). This work shows that using wood generally leads to low concentrations when the wood used is untreated and when the installation provides good combustion conditions (proportion of unburnt coal in the ash  $\leq$  5% by weight [(50)]).

**Table 55: Chemical composition of peat ashes from different burner systems in comparison with coal ashes [(44)]**

Element (mg/kg)	Fluidized Bed		Grate		Pulverized Bed		Coal Combustion	
	fly ash	bed ash	fly ash	bed ash	fly ash	bed ash	fly ash	bed ash
As	37-116	2	47-436	4-5	45-97	3	2-1 700	1-250
Be	2-3	6	1-12	<1-17	-	-	1-1 000	0,4-11
Cd	4	<0,05	0,4-7	<0,05-0,6	0,5-5	0,1	0,01-250	0,01-<250
Co	20-50	<10	10-50	<10-40	10-25	2-10	5-1 500	3-380
Cr	80-122	50-80	70-113	120-200	43-200	26-200	3-7 400	3-270
Cu	60-106	30	90-190	50-180	68-160	15-25	30-3 000	0,01-720
Hg	0,5-2	-	0,7-2	0,5	0,3-0,4	0,001	<0,01-80	<0,01-2
Mo	20-40	<10	<10-50	<10-30	14-19	<1-4	3-500	1-45
Ni	30-80	20	40-95	5-110	110-700	13-20	1-800	10-700
Pb	170-370	<10-70	80-430	30-80	160-970	5-20	3-1 800	1-250
Se	<10-21	<10	<10-26	<10	-	<3	0,7-<500	0,08-10
V	60-70	10-30	40-100	40-80	18-590	28-50	20-1 200	<24-300
Zn	220-469	60-160	230-2 600	60-370	48-540	20-22	14-13 000	<8-1 800

**Table 56: Average concentrations of heavy metals in various wood ash fractions [(50)]**

Element (mg/kg)	Bottom ash		Cyclone Fly Ash		Filter Fly Ash	
	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation
Cu	164,6	85,6	143,1	46,7	389,2	246,4
Zn	432,5	305,2	1 870,4	598,5	12 980,7	12 195,9
Co	21,0	6,5	19,0	7,3	17,5	5,2
Mo	2,8	0,7	4,2	1,4	13,2	9,8
As	4,1	3,1	6,7	4,3	37,4	41,4
Ni	66,0	13,6	59,6	19,0	63,4	35,4
Cr	325,5	383,0	158,4	61,0	231,3	263,7
Pb	13,6	10,4	57,6	20,5	1 053,3	1 533,0
Cd	1,2	0,7	21,6	8,1	80,7	59,2
V	43,0	10,0	40,5	16,6	23,6	9,1
Hg	0,01	0,03	0,04	0,05	1,47	2,05

#### **4.3.4 Waste products from desulphurisation** [(40), (42), (51), (52), (53), (54)]

Non-regenerative scrubbing methods pose a considerable problem for waste management.

For the most widespread method (wet scrubbing with lime or calcium carbonate), the amounts of gypsum produced by desulphurisation are of the order of 2,7 to 2,8 tonnes per tonne of sulphur dioxide removed.

The gypsum from desulphurisation consists approximately of 85 to 96% pure gypsum (hydrated calcium sulphate), 5% of calcium and magnesium carbonate, 1 to 2% inert substances, and 6 to 12% of water. It also includes many trace elements from the flue gases or from the desulphurising reagents.

The heavy metal concentrations in the gypsum are generally below 10 ppm. Table 57 gives the concentrations reported by several authors.

**Table 57: Trace element concentrations in gypsum from desulphurisation**

Element	Concentration (mg/kg) [(51)]	Concentration (mg/kg) [(52)]	Concentration (mg/kg) [(53)]	Concentration (mg/kg) [(54)]
As	$1,9 \pm 0,2$	1,2	2,0 - 2,5	1
Br	$< 0,19$	-	-	-
Cd	$< 0,05$	-	0,03	$< 0,1$
Co	$< 0,5$	-	-	-
Cr	$< 3$	3 - 5,8	1,3 - 1,6	-
Cu	$0,6 \pm 0,07$	3,5 - 5,2	1,2	5
Hg	$< 0,5$	1,6 - 1,7	0,6	$< 0,2$
Mn	$< 2$	-	-	-
Ni	$< 0,5$	3,8 - 4,8	1,0 - 1,4	-
Pb	$5,7 \pm 0,5$	0,7	6 - 10	11
Sb	$0,12 \pm 0,005$	-	-	$< 1$
Se	$< 2$	1,8 - 2,7	$< 3$	$< 1$
V	$< 10$	3,4	-	-
Zn	$< 10$	6,7	$< 5$	-

In Germany, Rotard *et al.* [(42)] took 17 samples of gypsum from desulphurisation in various power stations powered by lignite or coal and then analysed them for PCDDs and PCDFs.

In the majority of cases, no PCDD or PCDF was found. For only a few of the samples studied, traces of HpCDD and OCDD were measured at maximum concentrations of 0,17 ng TEQ/kg.

Sludge from purification of effluents from desulphurisation (about 5 to 7.5 kg/t SO<sub>2</sub>) forms another class of waste product from wet desulphurisation.

The composition of the sludge depends mainly on the conditions under which the effluent is treated.

The sludge consists essentially of calcium sulphate (60 to 90% of dry matter) and the fly ash stopped by the FGD (8 to 18%). It also contains trace elements in concentrations quite consistent with this distribution between gypsum and fly ash, except for volatile elements (Hg, Se, ...) which occur in relatively high concentrations [(40)].

#### **4.3.5 Poned storage of ash or waste products from desulphurisation**

Many power stations rely on waste storage within the site of the plant. Of these methods, the most common is storage in settling ponds making it possible to receive sludge resulting from wet methods of removing boiler ash or slurry from non-regenerative methods of flue gas desulphurisation.

Historically, this type of storage was not always undertaken in adequate conditions because not enough account was taken of the environmental risk associated with the waste involved and, in some countries like the USA or Japan, because of the urgency with which specific measures had to be implemented to control atmospheric pollution.

Many studies [ (55), (56), (57), (58), (59)] describe the harmful effects on underground and surface water quality from infiltration or run-off of pollutants (heavy metals, sulphites, ...) since areas for storage of ash or waste products from desulphurisation were established.

Washing the boiler ash with water, pumping it to the ash ponds and the ponded storage of slurry from wet desulphurisation are thus high risk activities as far as the aquatic environment is concerned when the technical recommendations are not complied with (imperviousness of the storage ponds or areas, collection and treatment of drainage water and leachates, adequate dimensioning of the settlement pits, etc.).

### **5. Best available techniques for large combustion installations ( $\geq 50$ MWth)**

The best available techniques for the combustion of fossil fuels in Large Combustion Installations ( $\geq 50$  MWth) can be assessed from the work reported in various publications, particularly from work carried out by the European Commission (DG XI) for the revision of the Directive 88/609/EEC.

This project is motivated by the wish to lay down new emission limit values taking into account the progress made in methods since 1988. A preliminary document describing the Best Available Techniques (BATs) has been drawn up [(22)].

Moreover, Directive 96/61/CE of 24 September 1996 on the integrated prevention and reduction of pollution defines the new framework for future actions relating to the industrial environment at the European level. The best available techniques to be established in

this new context will take into consideration the criteria detailed in Annex IV of the Directive and, in particular, must:

- prove to be particularly effective in preventing or reducing the emission of pollutants;
- produce little waste and encourage the choice of methods that increase recovery and recycling;
- optimise the use of raw materials used and maximise energy efficiency;
- to have well established references from users in industry.

It should be stressed that, for economic reasons, it might often be difficult to replace existing equipment with new equipment corresponding to the BAT. In general, this should lead to a distinction being made between new and existing installations, the latter being given sufficient time to introduce the best available techniques.

The data given below are based on several recent publications dealing with the BATs for large combustion installations of at least 50 MWth, and more particularly on:

- the descriptive document drawn up as part of the work of the European Community;
- the Guidance Note S2 1.01 from the UK HMIP [(21)].

## **5.1 Atmospheric emissions**

### **5.1.1 Sulphur dioxide [(5), (21), (22), (60)]**

Emissions of sulphur dioxide into the environment can be reduced by taking action on the fuel, the combustion environment or the flue gases (flue gas desulphurisation or FGD).

Although it is not dealt with specifically here, it should be pointed out that techniques for reducing sulphur dioxide emission also contribute towards a reduction in sulphur trioxide emission.

#### **“Choice of fuel**

The sulphur contained in fuels is the source of the sulphur dioxide emissions produced during combustion. Particularly for large installations, it is therefore essential to try to choose fuels with the lowest possible sulphur content.

## **“Fuel desulphurisation**

Fuels may also be subjected to desulphurisation before combustion.

For coals, only physical methods are at present operational on an industrial scale. Coals are treated by mechanically crushing them into fine particles, followed by a partial removal of the inorganic sulphur present as pyrites and of the ash content of the fuel. Between 20 and 80% of the pyrites can be removed in this way. However, the method has the drawback that it produces waste water and a significant volume of waste (of the order of 30% of the fuel produced). [(50)]

For gaseous fuels, several processes are available for reducing the sulphur content. These processes are at least 99% efficient.

As regards liquid fuels, the treatment of heavy fuel oils to produce fuel oil with a low sulphur content is carried out at the refining stage. Since it occurs before being marketed, this type of treatment is distinct from the desulphurisation before combustion that may be used in the case of solid or gaseous fuels.

## **“Control at the combustion stage**

Sulphur dioxide emissions can be significantly reduced by the injection of adsorbents (e.g. limestone) into the combustion chamber. Fluidised bed combustion methods are particularly well suited to this process, with efficiencies capable of reaching 90%.

Control at the combustion stage can also be used in pulverised coal boilers, but with lower efficiencies (50 - 70%) than those obtained with desulphurisation of flue gases.

The limestone injected into the combustion chamber is converted into calcium sulphate. Depending on the level of desulphurisation sought, using this method has variable quantitative and qualitative effects on the ash produced.

## **“Flue gas desulphurisation (FGD)<sup>3</sup>**

There are two large groups of FGD processes:

- regenerative processes, in which the reagent is regenerated and an economically valuable substance is produced (elemental sulphur, etc.);

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<sup>3</sup> Germany considers the qualification of “sea water scrubbing” as BAT for flue gas desulphurisation inappropriate and incompatible with the spirit of the Convention for the Prevention of Marine Pollution from Land-Based Sources since this method transfers pollutants directly to the marine environment.

- non-regenerative processes, which may or may not lead to economically valuable products.

The large combustion installations sited in various European countries belonging to the OECD and equipped with a desulphurisation unit had an aggregate capacity of about 130 000 MWth in 1991, 96% of which was of the non-regenerative type [(60)].

Methods which could be adopted from among the BATs in the context of the work by the European Commission will have an efficiency of at least 90%, even 95% and more for some of them. For fuels with low sulphur content or those used only for limited periods during the year, less efficient and cheaper processes are acceptable, particularly semi-dry desulphurisation processes (70% efficient) or even a simple dry injection into the combustion chamber. A dozen processes are mentioned, the principal one being wet lime (CaO) or limestone (CaCO<sub>3</sub>) scrubbing. This process has been very successful in Germany and the Netherlands because of its efficiency (purification ≥ 90% for SO<sub>2</sub>) and because it produces gypsum, which in the very great majority of cases is capable of being exploited commercially.

In order to obtain a marketable by-product, wet lime or limestone scrubbing should be designed in such a way that as high as possible a ratio of calcium sulphate to calcium sulphite is achieved. This assumes efficient removal of dust before the gases pass through the FGD unit, together with a stage of forced oxidation of sulphites (formation of pure gypsum CaSO<sub>4</sub>·2H<sub>2</sub>O) complementing the reactions occurring between the sulphur dioxide and the adsorbent during desulphurisation.

Gas desulphurisation by the wet process requires treatment of the liquid effluent produced.

Sea water scrubbing, which is particularly practised in Norway and Spain, is also mentioned and has an efficiency that may be as much as 99%. However, this process is accompanied by a direct transfer of pollutants to the marine environment, on whose protection the Paris Commission has precisely the job of concentrating its efforts.

### **5.1.2 Oxides of nitrogen [(5), (21), (22), (60)]**

The control of emissions may involve altering the design of the combustion chamber or modifying the combustion process (primary methods), or treating the gases (secondary methods).

The basic principle of primary methods is to adjust one or more of the combustion parameters in order to reduce NO<sub>x</sub> formation. This adjustment is made either in the burners (low-NO<sub>x</sub> burners) or in the design of the combustion chamber.

Using primary methods always requires a search for the optimum solution between a reduction in NO<sub>x</sub> and the disadvantages which can



also result from the changes (increase in carbon monoxide and particle emission, increase in the amount of unburnt residue in the ash, problems of deposits and corrosion in the combustion chamber, etc.).

Modifications to combustion are the subject of a special study in the descriptive document of the European Commission. The efficiencies expected for each of them are summarised in Table 58.

**Table 58: Efficiency of NO<sub>x</sub> removal of various techniques for modifying combustion [(22)]**

Technique	NO <sub>x</sub> Removal Levels
Low excess air	17-44 %
Reduced air preheat	20-30 %
Flue gas recirculation	15-75 %
Air staging (in the furnace)	40-65 %
Low-NO <sub>x</sub> burners	40 %
Fuel separation	60%
Fuel staging (reburning)	50-70 %

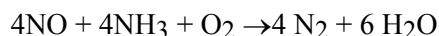
The primary methods for reduction prove to be cheaper than the secondary methods. In particular, we can say that the use of low-NO<sub>x</sub> burners is now the minimum acceptable method for any new installation.

For additional NO<sub>x</sub> removal, we have to call on secondary methods: selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).

### **“Selective catalytic reduction (SCR)**

NO<sub>x</sub> are reduced to nitrogen and water by injection of ammonia (1,1 to 1,5 kg/MWh) into the flue gases in the presence of a catalyst.

The principal reaction is:



The catalysts can be of various kinds and forms: titanium dioxide, vanadium pentoxide, zeolite, etc., as granules, platelets or honeycombs. They may be either attached to the surface or included in the supporting mass. The optimum reaction temperature, generally between 300 and 400°C, depends on the specific nature of the installations and the type of catalyst used.

SCR technology is used in large combustion installations with capacities varying between less than 50 MWth and more than 1 000 MWth. Efficiencies lie between 80 and 95%.

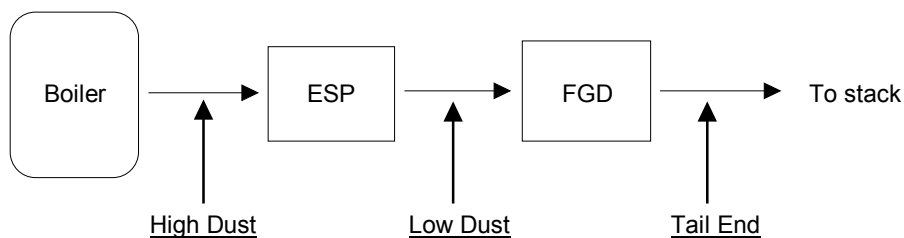
This method has the advantage of not producing liquid effluent or solid waste. Among its disadvantages should be mentioned the surplus ammonia liable to be entrained with the gases from the SCR unit (ammonia slip) which can also evolve into other ammonium

compounds such as ammonium chloride (gaseous) and ammonium bisulphate (solid).

The efficiency of the methods does not generally enable the amount of unreacted ammonia to be reduced to below 1 to 5 ppm. The deposition of ammonium bisulphate on the catalyst is one of the possible causes of the loss of activity of the SCR unit, with the poisoning of the active sites by metallic ions, with clogging up by dust and with mechanical and thermal stresses.

The denitrification unit may be located either just after the combustion chamber (high dust SCR), after dust removal (low dust SCR) or after desulphurisation (tail end SCR).

**Figure 5: Possible locations for an SCR unit [(22)]**



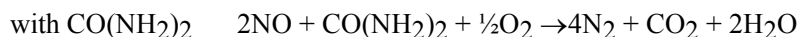
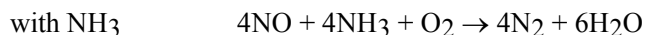
Several factors determine the choice of location, for example:

- in “high dust” position, there is a risk of fouling of the reactor by dust and contamination of the fly ash by surplus ammonia, thus preventing it from being commercially exploited in the cement industry;
- in “tail-end” position, the gases must be heated to the optimum temperature for reducing the emissions of nitrogen oxides.

SCR technology is very widespread. In Germany for example, 95% of stations with denitrification (representing 30 000 MWe) were of the SCR type in 1992.

### **“Non-selective catalytic reduction (NSCR)**

The NO<sub>x</sub> are reduced to nitrogen and water by injecting ammonia or urea into the flue gases. The main reactions are:



The required temperature ranges are quite small: the reaction occurs between 850 and 1000<sup>0</sup>C for ammonia and between 950 and 1100<sup>0</sup>C for urea.

Because of the demands on the temperature, this technology may not be applicable to all large combustion installations. In particular, many injection points and careful design of the mixing zones are necessary in large boilers. Selective non-catalytic reduction could nevertheless be used successfully in lower temperatures ranges with circulating fluidised bed or pressurised fluidised bed processes.

As in the case of SCR technologies, atmospheric emission of ammonia and ammonium chloride as well as deposits of ammonium bisulphate can occur. When urea is used, N<sub>2</sub>O emission can also occur in certain cases.

The maximum efficiency in the reduction of NO<sub>x</sub> with the SNCR technology is about 70%. However, the need to limit the entrainment of ammonia in the treated gases may lead to a reduction of this to 50 - 60% or even lower. The importance of the SNCR technology in comparison with SCR is therefore mainly due to its cheapness.

In 1992, the SNCR technology was used in Germany and Austria at eight installations, representing an aggregate power of 1000 MWe.

#### **5.1.3 Combined SO<sub>2</sub>-NO<sub>x</sub> technologies [(60)]**

The simultaneous reduction of SO<sub>2</sub> and NO<sub>x</sub> emissions is mainly achieved by using activated carbon fluidised beds (BF/UHDE process).

The method using activated carbon is a dry method of the regenerative type: after adsorption of the pollutants, the activated carbon is regenerated in a desorption unit and leads at this stage to a sulphur-rich gas capable of being commercially exploited. In the particular context of this study, we should also point out its importance in reducing emissions of any heavy metals and persistent organic compounds that may occur among the adsorbed pollutants (arsenic, mercury, selenium).

This technology has been installed in four German power stations representing a total power of 950 MWe (or 2,3% of the net electric power installed in the area corresponding to the former West Germany). The efficiency of the purification processes are more than

70% for the NO<sub>x</sub> and more than 95% for SO<sub>2</sub>. Downstream from the desorption unit, the gas is subjected to wet scrubbing and the waste water produced by this is treated by vacuum filtration. The captured trace elements thus occur in the residual sludge produced after filtration, which is disposed of in storage centres for special industrial waste.

Other processes (DESONO<sub>x</sub> process, SNO<sub>x</sub> process), based on a simultaneous catalytic reduction of the nitrogen oxides to nitrogen and water and the oxidation of sulphur dioxide to sulphur trioxide have been developed but have not been much used so far (one plant at Münster in Germany and one at Vendsyssel in Denmark). The efficiency of the purification is above 95% both for NO<sub>x</sub> and SO<sub>2</sub>.

#### **5.1.4 Dust [(5), (7), (19), (21), (22), (61)]**

Dust emission may be diffuse or channelled.

Various arrangements can be combined to prevent diffuse emission. For example:

- introduce the requirement to prevent this type of emission at the design stage, and then ensure regular maintenance of the coal crushing plant used in pulverised coal boilers;
- use compressed air devices to allow the boiler ash to be handled in a dry state and in a confined space, and then store it in closed silos before removal.

For channelled emission, which covers the majority of dust emission, five type of dust collector are currently used: cyclones, wet scrubbers, electrostatic filters or precipitators, bag filters and ceramic filters.

The efficiency of cyclones approaches that of other dust collectors only for particles of diameter greater than 20  $\mu\text{m}$ .

Wet scrubbers produce liquid effluent requiring later purification.

For these reasons, cyclones and wet scrubbers are not generally considered to be among the Best Available Techniques for controlling dust emission.

Electrostatic filters, bag filters and ceramic filters may have dust removal efficiencies up to 99,75% when they have a design well adapted to the specific characteristics of the installation and when their operation is accompanied by regular monitoring and careful maintenance. In particular, the exact properties of the fly ash (particle sizes, resistivity, etc.) and of the gases to be filtered (flow rate, dust concentration, etc.) must be taken into consideration at the design stage.

Electrostatic precipitators and bag filters are the ones used most frequently. They make it possible to capture, with an efficiency  $\eta > 99\%$ , particles of diameters up to about 1 mm.

The importance of dust collectors in the specific area of trace element emissions reduction is dealt with in sections 5.1.5 and 5.1.6.

### **“Electrostatic filters**

Modern electrostatic filters provided with systems for continuous monitoring and for optimising their functioning make it possible to achieve permanent concentrations below  $25 \text{ mg/m}^3$ .

They operate optimally in the temperature range  $200 - 300^\circ\text{C}$ .

Fuels with a low sulphur content require either higher efficiencies in the electrostatic filter or treatment of the flue gases by means of a controlled injection of sulphur trioxide to raise the filtration efficiency.

Electrostatic filters may be used in both small and large installations, and with the combustion of both liquid and solid fuels.

However, although they are still competitive as regards dust removal down to  $50 \text{ mg/m}^3$ , their cost increases rapidly beyond this value and then becomes more expensive than the bag filter (additional cost of 30% for dust collection down to  $30 \text{ mg/m}^3$ ).

### **“Bag filters**

Bag filters (baghouses) are designed to obtain permanent dust concentrations down to at least  $25 \text{ mg/m}^3$ , but they may, during most of their running time, enable lower concentrations ( $10 \text{ mg/m}^3$ ) to be reached.

They are made from synthetic fibres (polyamide, polytetrafluoroethylene, glass fibre, etc.), which have a good thermal and chemical resistance.

Using these materials enables bag filters to operate at temperatures which are nevertheless quite low ( $270 - 280^\circ\text{C}$ ).

A low temperature limit should also be complied with so that the dust collector operates above the dewpoint of the gases (sulphuric acid, ...), and so that the filtering medium is not prematurely degraded.

Adequate monitoring of the operating temperature is therefore required in order to prevent the thermal or chemical degradation of the filtering medium. The bag filter should be well insulated and heated after any technical stoppage.

The deposited dust gradually obstructs the pores of the filter. It thus increases the efficiency but also the head loss. The filter should therefore be cleaned regularly (by blowing through it with a counter-current of compressed air, etc.).

With electrostatic filters, bag filters are normally used in plant running on solid fuel.

Their use in installations running on liquid fuels is more tricky because of the danger of clogging the filter coupled with the possibility that sticky soots may be formed and small globules of fuel may be entrained from the combustion chamber. When combined with good combustion conditions, however, they have been successfully incorporated in several installations using filters precoated with lime or ash [(21)].

### **“Ceramic filters**

Ceramic filters are currently available for small installations, but are only at the development stage for medium-sized or large installations.

Unlike other filters, they can operate at high temperatures (800 - 900°C). They can trap particles with diameters up to about 0,2 µm and can achieve concentrations in the emissions of less than 10 mg/m<sup>3</sup> very reliably.

#### **5.1.5 Heavy metals [(7), (22), (23), (40), (51), (62)]**

To various extents depending on the fuel and combustion process used, the majority of metals and metalloids capable of being emitted into the air are found in fly ash. For this reason, an efficient control of the emissions of dust, and more particularly of fine particles, is fundamental in limiting atmospheric emission of heavy metals.

Since trace elements have a tendency to accumulate preferentially on the finer dust particles, the limited efficiency of cyclones ( $\eta \leq 27\%$  for 1 µm particles [(22)]) make it impossible to consider this type of equipment as adequate for the reduction of heavy metal emissions. Electrostatic filters, bag filters or ceramic filters are required.

In this connection, considerable efforts still need to be made in developing filters for the combustion of liquid fuels, in which the dust often remains unfiltered, or only partially so, in cyclones.

Table 59 gives the minimum reductions possible by using electrostatic filters or bag filters with a 99% efficiency for dust removal.

**Table 59: Reduction in heavy metal emissions by using electrostatic filters or bag filters with a 99% efficiency for dust removal [(7)]**

Trace element	Reduction degree (%)	Trace element	Reduction degree (%)
As	98	Mn	98
Be	95	Ni	98
Cd	95	Pb	95
Co	99	Se	95
Cr	99	V	98
Cu	98	Zn	99

The use of efficient dust collectors does not mean that the emissions of the volatile forms of some metals and metalloids (mercury, selenium, arsenic, etc.) can be controlled effectively enough, although it is possible to increase their efficiency in reducing this type of emission as well.

In particular, cooling the gases (120 - 140°C) before discharge into the atmosphere may be attempted in order to facilitate the retention of volatile heavy metals by condensation and agglomeration on the dust then stopped by the filter. Over this temperature range, for example, reductions of 35 - 40% in mercury have been measured [(7)].

Other methods of reducing heavy metals should also be examined.

Some of these are specifically directed towards the retention of gaseous mercury and are summarised in the following table.

**Table 60: Performance of some of the methods for retaining gaseous mercury [(7)]**

Method	Mercury concentration after purification
Selenium filter	< 0,01 mg/Nm <sup>3</sup>
Selenium purifier-scrubber	0,2 mg/Nm <sup>3</sup>
Carbon filter	0,01 mg/Nm <sup>3</sup>
Sodium chloride process	0,05-0,1 mg/Nm <sup>3</sup>
Lead sulphide process	0,01-0,05 mg/Nm <sup>3</sup>

Desulphurisation can also contribute to a reduction in trace element emission in particulate or gaseous form. Smith [(62)] reports the following efficiencies for five trace elements from the work of Gutberlet.

**Table 61: Vapour phase concentrations before and after an FGD unit ( $\mu\text{g}/\text{m}^3$ ) [(62)]**

Element	Before FGD	After FGD	% Efficiency
As	< 0,2	< 0,2	-
Cl	178 000- 208 000	12 000-22 000	>90 - >99
F	5 500-8 100	<200	> 96
Hg	14,7-15,1	9,4-10,0	36-33
Se	60,0-104	27,6-32,3	54-69

Meij [(23)] gives some figures from measurements made at thermal power stations in the Netherlands which use wet scrubbing with calcium carbonate.

For emissions in particulate form, he estimates that desulphurisation makes it possible to achieve a significant reduction in the particle load of gaseous effluents: a measurement campaign carried out in 1986 at the Gelderland power station recorded a collection efficiency of 90% due to the desulphurisation unit, i.e. an overall efficiency due to electrostatic filters and the desulphurisation of the order of 99,99%. Concentrations after an FGD unit are generally below  $10 \text{ mg}/\text{m}^3$  and the median particle diameter change from 4  $\mu\text{m}$  before it to 0,2  $\mu\text{m}$  after it [(51)].

For emissions in gaseous form, the same author gives a mean purification efficiency of 52% for mercury and 60% for selenium during desulphurisation. More than 90% of gases such as HBr, HCl, HI are also retained [(40)].

The trace element pollution is transferred in an FGD unit to the gypsum and the effluent from scrubbing, and these should therefore receive adequate treatment at a later stage.

Finally, when an installation is equipped with an SCR type NO<sub>x</sub> reduction unit, part of the mercury is oxidised to HgCl<sub>2</sub> and the overall efficiency with which this trace element is eliminated is of the order of 80% after wet desulphurisation.

#### **5.1.6 Persistent organic compounds** [(9), (11), (12), (21), (33), (18)]

The search for preventive and curative measures to deal with dioxins relies mainly on the experience acquired in the incineration of municipal waste, although one should bear in mind that the large combustion installations and their incineration unit constitute two different types of installations in their destination, their design and the way they function.

As far as preventive measures are concerned, it will be recalled that PCDDs and PCDFs can only be formed if chlorine is present during combustion. As a result, attempts are made to use fossil fuels with small concentrations of chlorinated dioxin precursors. A sulphur/chlorine ratio greater than 10 is mentioned as a potential



factor leading to dioxin emission in some large coal-fired combustion installations [(11)].

Another way to be explored for the control of dioxins is that of reducing the risk of their “de novo synthesis” by rapidly cooling the flue gases, limiting their residence time in the temperature range between 250<sup>0</sup>C and 450<sup>0</sup>C.

Included in the primary measures mentioned conventionally for the incineration of municipal waste is also the adjustment of the combustion conditions. Dioxin formation is in fact avoided by simultaneously keeping to the requirements as regards temperature (above 850<sup>0</sup>C), the residence time (at least 2 seconds) and the stoichiometry of the reaction (excess oxygen in proportions from 5 to 25%).

Nevertheless, it should be pointed out (and this shows the complexity of environmentally optimising the operation of large combustion installations) that the latter types of measure may in some cases not prove to be very compatible with the use of technologies or the implementation of measures which are important for reducing emission of other pollutants.

Particularly for NO<sub>x</sub>, fluidised bed combustion has a low potential for emission but takes place at a low temperature (750 - 950<sup>0</sup>C instead of 1 300 - 1 600<sup>0</sup>C for the pulverised coal process), while in a conventional boiler one of the primary methods for reducing emissions consists in seeking combustion conditions close to stoichiometric conditions rather than some distance from them.

This remark also applies to PAHs, whose emissions are liable to be greater if fluidised bed combustion is used or if combustion occurs in the presence of a small excess of oxygen [(9), (33)].

As in the case of heavy metals, secondary measures for reducing emissions of persistent organic compounds mainly involve the use of efficient dust collectors.

This is because some PAHs occur in solid form, while others may be adsorbed on dust particles. Similarly, the very low vapour pressure of dioxins rules out their molecular dispersion, except by adsorption on particles.

Work done on the incineration of municipal waste indicates that the combined use of several methods would enable reductions in PCDD and PCDF emissions of between 75 and 99% to be achieved [(21)].

For example, it would be possible to use the injection of dry adsorbents (activated carbon, lignite coke, etc.) or inhibitors (triethanol, triethylamine, etc.) before dust removal using a bag filter or an electrostatic filter. Some manufacturers have also developed catalytic processes specially designed to trap dioxins.

Recent measurements made in Germany [(18)] confirm that it is possible to achieve dioxin emissions considerably below  $0,1 \text{ ng/m}^3$  TEQ for large combustion installations.

For PAHs, according to note S2 1.01 of the HMIP [(21)], emissions that could be achieved for coal-fired or oil-fired plants would be of the order of 10 to  $100 \text{ } \mu\text{g/m}^3$ .

According to the Swedish Environmental Protection Agency, a PAH emission factor of less than  $0,1 \text{ } \mu\text{g/MJ}$  can be obtained for the combustion of coal, peat, wood or heavy fuel oil in a large combustion installation of more than 50 MWth.

For existing large combustion installations, which do not necessarily use the best available technology, and within the limit of the scarce data which could be collected over a restricted range of 12 PAHs (section 4.1.4), the above values for concentrations are consistent with the results of the measurements carried out. The proposed emission factor, on the other hand, is significantly lower.

#### **5.1.7 Other pollutants**

##### **"HCl, HF [(5), (21), (23)]**

Hydrogen chloride and hydrogen fluoride are emitted during the combustion of coal and heavy fuel oil. Their emissions can be reduced by adequate desulphurisation.

##### **"VOCs [(21)]**

VOCs are present at low concentrations in flue gases.

This type of emission is the result of incomplete combustion. Better control of the combustion should therefore be a priority objective to reduce its occurrence.

The use of activated carbon for the specific adsorption of certain organic substances has been subjected to pilot tests in some large coal-fired combustion installations but has not so far been developed on an industrial scale.

##### **"CO<sub>2</sub> [(22)]**

The extraction of CO<sub>2</sub>, a greenhouse gas, from the flue gases is technically possible but only at a very high cost.

It is estimated that the extra cost of electricity would be between 42% for reinjection of the flue gases into land deposits and 117% for reinjection into the bottom of the sea.

## **5.2 Liquid effluent**

As indicated on section 4.2, liquid effluent liable to be associated with the running of large combustion installations may come from many sources (purging or cleaning of boilers, cooling water, wet scrubbing of gases, etc.).

The flow rates involved in the largest of these installations may be considerable and, because of this, appreciable amounts of pollutants may be discharged into the environment even when the concentrations are low.

It is therefore essential to encourage actions to prevent pollution at source. In particular, the technical feasibility of the options available for recycling water should be systematically examined so that the volumes discharged can be strictly limited.

Non-recycled waste water and the drainage water from recycling should be given suitable treatment and monitoring before being discharged. According to note S2 1.01 of the HMIP [(21)], the releases or the reductions achievable by using the best available techniques are given in Table 62.

**Table 62: Achievable values of releases into water [(21)]**

Substance	Releases achievable with the best of the techniques described in Section 4 [of the Note S2 1.01] (note 1)
Suspended solids	1-10 mg/l (note 2)
Ammoniacal nitrogen	5 mg/l
Cadmium	10 µg/l (note 3)
Mercury	5 µg/l (note 3)
Other heavy metals	95% removal
Dioxins and furans, PAHs and other organics	(note 4)

*Notes:*

- 1) *The above levels represent a flow weighted monthly average concentration. Peak values would not be expected to exceed twice these values.*
- 2) *Some processes release only very low levels of suspended solids, other releases may be reduced to 10 mg/m<sup>3</sup> or less using settling, flocculation and filtration techniques as appropriate.*
- 3) *By precipitation and filtration which can be expected to achieve 70% reduction. Subsequent treatment in the biological treatment plant of the sewage treatment works will reduce this below the limit detection (<0,01 µg/l)*
- 4) *These substances would be removed to a large degree, either by adhering to the sludge or by genuine degradation, in a sewage treatment works.*

**In the United Kingdom, the attainable values for emission are among the technical factors taken into consideration when drawing up the specifications contained in the authorisation to operate on a given site. These are guide values and are adjusted by the competent authority by applying to each individual site the concepts of BATNEEC (Best Available Techniques Not Entailing Excessive Costs) and of BPEO (Best Practicable Environmental Option).**

**In general, most countries have either guide values taken into consideration when drawing up permits to operate or limiting values for the minimum emissions which are imposed nationally by regulation and which if necessary are made more restrictive in individual cases, particularly when the sensitivity of the local environment is involved.**

**As examples, Tables 63 and 64 give the limiting values applicable to the effluents from gas scrubbing for large combustion installations in Germany.**

**Table 63: Waste water from scrubbing of flue gases of combustion plants in Germany - Requirements according to the "Allgemein Anerkannten Regeln der Technik" [Umweltbundesamt]**

	Qualified sample or 2-hour mixed sample concentration (mg/l)	
Suspended solids	30	
Chemical oxygen demand as COD or TOC, when using:	COD	TOC
-burnt lime	80 (1)(2)	27 (2)
-limestone	150 (1)(2)	50 (2)
Sulfate	2 000	
Sulfite	20	
Fluoride	30	

- (1) Compliance with the requirement for chemical oxygen demand (COD) shall be verified by determining total organic carbon (TOC). The COD corresponds to three times the value of the TOC, determined in milligramme per litre.
- (2) After deduction of the pollution introduced with the water used (initial pollution load).

**Table 64: Waste water from scrubbing of flue gases of combustion plants in Germany - Requirements according to the "Stand der Technik" [Umweltbundesamt]**

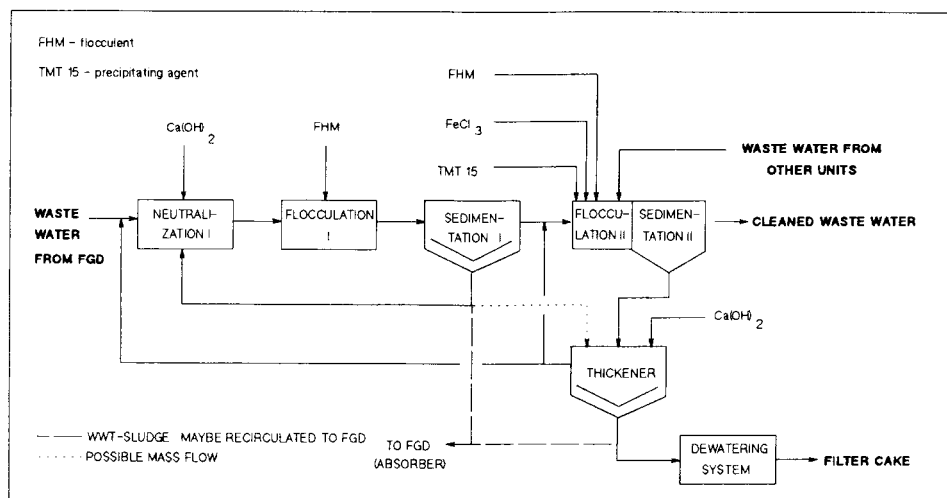
	Concentration values:  (qualified sample or 2-hour mixed sample concentration in mg/l)	Load values for hard-coal and brown-coal-fired plants: (2)	
		Chloride content in the fuel fired ≤ 0,02 wt.% Cl (in mg/t fired fuel)(3)	Chloride content in the fuel fired > 0,02 wt.% Cl (in mg/kg chloride in fired fuel)(3)
Cadmium (Cd)	0,05	0,36	1,8
Mercury (Hg)	0,05	0,36	1,8
Chromium (Cr)	0,5	3,6	18
Nickel (Ni)	0,5	3,6	18
Copper (Cu)	0,5	3,6	18
Lead (Pb)	0,1	0,72	3,6
Zinc (Zn)	1,0	7,2	36
Vanadium (V)	4,0 (1)		
Sulfide (S2-)	0,2	1,44	7,2

- (1) Only applies to oil-fired power plants.
- (2) For oil-fired combustion plants, if the wastes arising in the operation of waste water treatment systems as a result of the requirement set out above cannot be used or disposed of properly and harmlessly, the following requirements shall apply: the permissible load values shall be calculated from the concentration values stipulated as general requirements and a volume of generated waste water of 0,2 m<sup>3</sup>/t fired oil.
- (3) The load reference parameter is calculated from the coal fired at full load (t/h) and the chloride content of the coal used, as specified in the discharge license. If the chloride concentration in the waste water which is caused by the water used exceeds 2 g/t, the exceeding amount of chloride shall be added as load.

### **5.2.1 Purification of waste water from wet limestone scrubbing desulphurisation processes [(21), (22), (40< (41), (43), (51), (63), (64))]**

The coagulation/flocculation of metals followed by precipitation as hydroxides is the most widespread method of purification. This physico-chemical treatment is carried out with the use of an appropriate reagent (lime, soda, sodium carbonate).

**Figure 6: Block diagram showing the physico-chemical treatment of waste water from a wet desulphurisation unit [(63)]**



A number of metallic pollutants (Cu, Zn, Ni, Al, Hg, Cr<sub>III</sub>, Pb, Cd,...) and some ionic compounds (SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, ...) can be precipitated in this way.

However, this method requires the metals to be in the form of free ions and not of complexes. The possible presence of chelating agents in the effluent is therefore liable to be detrimental to the efficiency of physico-chemical purification. For example:

- ethylene-diamine-tetra-acetate (EDTA) may have been used as an inhibitor of oxidation in the FGD unit;
- when an SCR unit precedes wet desulphurisation, it is estimated, for example, that entrainment of ammonia or ammonium sulphate (generally below 5 ppm) leads to NH<sub>4</sub><sup>+</sup> concentrations of between 1 and 100 mg/l in the waste water from desulphurisation [(41)].

Buffers that may be used to control the pH of the slurry in the FGD unit can also make the later purification of the effluent more difficult [(21)].

Each metallic ion is precipitated within a specific range of pH values, which is moreover variable according to the reagent used. The ranges within which the main metals are precipitated are given in Table 65.

**Table 65: pH values for the precipitation of metals with various reagents [(64)]**

Ion	pH at start of precipitation	optimum pH	pH at redissolution	Reagent ( <sup>*</sup> )
Fe 3+	2,8	3,5	-	N-K-S
Sn 2+	3,9	colloïdal	10,6	N
Al 3+	4,3	4,8	8,5	N-K-S
Cr 3+	5,5	6,3 à 6,5	9,2	N-S
	5,5	6,3 à 6,5	-	K
Cu 2+	5,8	7,5	-	N-K
	5,8	8,5	-	S
Zn 2+	7,6	8,3	> 11	N
	7,6	8,3	-	K
	7,4	7,9	> 11	S
Ni 2+	7,8	9,3	-	N-K-S
Pb 2+	5,5	6,5	9 - colloïdal	S
	7	9,5	-	N-K
Cd 2+	9,1	9,5 à 9,8	-	N-K
	7	7,2	-	S

( <sup>\*</sup> ) N = soda lye (NaOH), K = lime (CaO), S = sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)

When precipitation of hydroxides seems to be inadequate in terms of its efficiency, particularly for metals with amphoteric properties or for complex metallic compounds, it is possible to call on:

- coagulating additives (iron or aluminium salts) or flocculating additives (starch, synthetic organic polymers);
- solubility-reducing or decomplexifying reagents (sulphides, hydrobromides);
- coprecipitation with ferric hydroxide;
- specific tertiary treatments appropriate to the residual pollutant being treated (ion exchange, filtration, adsorption on activated carbon, etc.).

Table 66 gives the maximum expected efficiencies in the treatment of heavy metals and metalloids according to the method employed (precipitation, activated carbon, ion exchange).

As regards the specific case of waste water from wet desulphurisation, Meij [(51)] indicates that physico-chemical precipitation with lime using a polyelectrolyte would enable the efficiencies for elimination given in Table 67 to be achieved.

The frequent use of a pre-scrubber for the humidification and cooling of flue gases before the FGD unit has effects on the distribution of trace elements in the effluents. The selenium concentrations observed in effluent from the pre-scrubber are generally of the order of 10 times as great as those from the FGD unit itself, while mercury is

distributed in almost the same way in effluent from the pre-scrubber and the scrubber [(40)].

In practice, however, effluents from the pre-scrubber and the scrubber are generally mixed before purification.

**Table 66: Maximum expected efficiencies for the treatment of metals and metalloids in waste water (US Environmental Protection Agency)**

Element	Possible concentration limit (mg/l)	Method
Arsenic	0,05	Precipitation of sulphide with filtration
	0,06	Adsorption on activated carbon
	0,005	Coprecipitation with ferric hydroxide
Cadmium	0,05	Precipitation of hydroxide at pH 10-11
	0,05	Coprecipitation with ferric hydroxide
	0,008	Precipitation of sulphide
Copper	0,02 - 0,07	Precipitation of hydroxide
	0,01 - 0,02	Precipitation of sulphide
Mercury	0,01 - 0,02	Precipitation of sulphide
	0,001 - 0,01	Coprecipitation with aluminium sulphate
	0,0005 - 0,005	Coprecipitation with ferric hydroxide
	0,001 - 0,005	Ion exchange
Nickel	0,12	Precipitation of hydroxide at pH 10
Selenium	0,05	Precipitation of sulphide
Zinc	0,1	Precipitation of hydroxide at pH 11

**Table 67: Efficiency of elimination by physico-chemical precipitation [(51)]**

Elements	Efficiency
Al, Fe, Mg, Ti, As, Be, Cd, Hg, Mn, Ni, Pb, Zn	> 90%
Cr, Cu, Sb	> 70%
Se	> 50%

J.B. LEFERS *et al.* [(41)] have carried out various laboratory tests (jar tests) aimed at determining the most suitable reagents and their amounts for the physico-chemical precipitation of the effluents from desulphurisation.

They deduce from these tests that the coprecipitation of the hydroxides and sulphides of heavy metals can give excellent results by using lime or soda in the presence of sodium sulphide and an anionic polyelectrolyte.

Table 68 gives the composition of the untreated waste water (mixture of effluents from pre-scrubber and scrubber) and the results from the tests with lime.

The last two tests were carried out in the presence of ammoniacal nitrogen so as to assess the consequences of a selective reduction of



the NO<sub>x</sub> before desulphurisation. It seems that, in the context of the tests carried out, the NH<sub>4</sub><sup>+</sup> ions have no effect on the precipitation conditions.

**Table 68: Experimental physico-chemical precipitation with lime of effluents from wet desulphurisation [(41)]**

		Raw waste water	Treated waste water			
			Exp. 1	Exp. 2	Exp. 3	Exp. 4
Dosages (g/m <sup>3</sup> waste water)	Ca(OH) <sub>2</sub>	-	8 000	8 000	8 000	8 000
	Na <sub>2</sub> S <sub>9</sub> H <sub>2</sub> O	-	0	7,8	0	7,8
	Polyelectrolyte	-	18	18	18	18
	NH <sub>4</sub> <sup>+</sup>	-	0	0	100	100
Waste water concentrations (mg/m <sup>3</sup> )	As	175	<5	<5	<3	<3
	Cd	140 (*)	1,4	1,4	1,1	1,2
	Cr	770	8,8	8,7	8,3	6,3
	Cu	410	<5	<5	5,8	4,1
	Hg	360 (*)	110	<1	30	<1
	Ni	700	<1	<1	<3	6
	Pb	425	6	<5	<4	<4
	Zn	1 400	15	<10	<10	<10
	Sb	69	-	<25	<25	-
	Se	130	9	43	-	-

(\*) Original values for Cd and Hg were 14 and 36 mg/m<sup>3</sup> respectively. In the context of the experiment, Cd and Hg content was increased to 140 and 360 mg/m<sup>3</sup>.

### 5.2.2 Cooling water [(21), (35), (38), (39))]

Open cooling circuits are the origin of direct discharges into the aquatic environment of chemicals that may have been used as anti-fouling, anti-corrosion or anti-scaling agents.

Semi-open circuits with atmospheric cooling have significantly smaller and better controlled emissions since the discharges are then limited to the purging needed to stabilise the concentration of the circulating water. The purges can thus be subjected to suitable treatment before discharge (the concentrations of some heavy metals that may be present can be reduced significantly by physico-chemical precipitation).

In general, it is important to point out that non-chemical solutions to problems liable to be experienced in the cooling circuits can often be found. Some of these solutions are related to the design of the cooling circuits (preventive), while others deal with the cleaning method (curative).

#### ☐ Preventive measures

Water sampling devices can be designed in such a way that the entrainment of organic or inorganic macro-constituents in the circuits is as low as possible. Thus, macrofiltration can prevent the largest constituents (> 5mm) from being admitted. For semi-open cooling circuits, an additional reduction in the organic load and in suspended matter can be achieved by a more thorough pretreatment (flocculation, precipitation, filtration).

Other preventive measures are mainly of four types:

a. Flow rate of the water in the circuits:

There should be a strict limitation on the regions where the flow rate might be very low or zero, since each of them become positions favourable to the attachment and growth of organisms.

In the case of macrofouling (open circuits), the circuits may be designed so as to increase the flow rate of water beyond what is generally tolerated by the larvae of macro-organisms ( $> 2$  m/s).

b. Choice of materials:

Protection against corrosion and abrasion can be sought by a suitable choice of materials, such as titanium, alloys of nickel, stainless steel (heat exchanger pipes), or enamelled cast iron (pump bodies). Non-toxic anti-fouling coatings can also be used (silicone-based coatings).

c. Level of concentration in the circulating water (semi-open circuits):

The level of concentration in the cooling circuit water is expressed as the ratio between the concentration of salts dissolved in the circuit water and the make-up water. In order to economise on water and the conditioning materials, it is worth trying to use as high a level of concentration as possible.

In practice, the required levels of concentration are of the order of 3 to 6, but it happens with some types of conditioning, that the levels of concentration may go up to 10, which accordingly reduces the problems of discharges since the purges are then significantly reduced.

A more thorough purification of the make-up water (decarbonisation, demineralisation) also allows high levels of concentration to be achieved. Demineralised water thus makes it possible to envisage levels of concentration greater than 9 with a dispersant conditioning of the phosphate type.

Example:

Let

E be the evaporation in the cooling tower ( $\text{m}^3/\text{h}$ )  
D be the purging rate ( $\text{m}^3/\text{h}$ )  
C be the level of concentration  
A be the flow rate of make-up water ( $\text{m}^3/\text{h}$ )

These parameters are related by the following equations:  
 $A = E + D$                        $D = E/(C-1)$

With evaporation of  $100 \text{ m}^3/\text{h}$ ,

we have for             $C = 3$ :  $D = 50 \text{ m}^3/\text{h}$  and  $A = 150 \text{ m}^3/\text{h}$   
and for                  $C = 8$ :  $D = 14 \text{ m}^3/\text{h}$  and  $A = 114 \text{ m}^3/\text{h}$

d. side-stream filtration:

one method that can be used is that of purifying a fraction (2 to 3%) of the total amount in circulation using a diversion system within the cooling circuit. The methods most frequently in use rely on the use of sand filters.

Experience acquired in the chemical industry shows that the use of side-stream filtration can significantly reduce the need for biocides (by something of the order of 90%) [(39)]. These methods also make it possible to achieve high levels of concentration and thus to achieve a considerable reduction in the amount of purging.

## □ Cleaning of circuits

There are many methods available for reducing the potential effects of fouling in cooling circuits. Amongst these, we look particularly at mechanical cleaning and heat treatment.

a. Mechanical cleaning:

The most widespread non-chemical types of treatment are those involving mechanical cleaning using zircon-tipped balls for descaling or rubber balls with a diameter slightly greater than that of the condenser pipes for antifouling.

However, this method is of little or no use for macrofouling.

Methods using brushes (brush and cage system) also exist, but very little experience has been acquired about these.

b. Heat treatment:

Heat treatment mainly removes the organisms responsible for macrofouling (mussels, barnacles) in open circuits by heating the cooling water to a temperature of 38-40°C for half an hour. This method requires installations to be adapted at the design stage, since subsequent adaptation of existing systems is in general technically and financially difficult to contemplate. Particular use is made of the method in the power stations at Hoogovens, IJmuiden and Eems in the Netherlands [(39)].

☐ **Other measures**

Other measures for limiting discharges of chemicals may be adopted. In particular, these involve:

- avoiding the most toxic conditioning reagents (chromates, etc);
- continuously monitoring fouling by suitable devices (plate count technique, ATP measurement, small tubing connections, etc.);
- taking into account the life cycle of the organisms that are the source of the fouling, so that the periods of the year most appropriate for treatment can be identified;
- putting in place periodic or continuous procedures for analysing biocides so as to adjust the dosages used as closely as possible to the amounts actually necessary;
- placing a strict limitation on the purging carried out during treatment when biocides are used.

### **5.2.3 Effluents from chemical cleaning**

A variety of methods can be used to dispose of effluent from chemical cleaning. The most conventional methods of disposal are discharge after on-site physico-chemical purification and treatment in a special collection centre for the treatment of industrial waste.

Disposal by controlled injection into the boiler is used in several large combustion installations. French power stations carry out an on-site incineration of cleaning effluent containing citric acid and formic acid. On the other hand, cleaning effluent containing hydrofluoric acid, whose incineration would produce atmospheric emission of fluorides, are treated by physico-chemical methods.

Disposal by incineration in the boiler has been subjected to measurements which make it possible to quantify its effect on atmospheric emission and on the composition of fly ash. According to

various tests carried out by Electricité de France (EDF) between 1983 and 1988, it appears that:

- organic compounds are decomposed into neutral gases (flame at  $1200^{\circ}\text{C}$ );
- emissions of metal (mainly iron, copper and zinc) are increased, but are retained with 95 - 99% efficiency using efficient dust collection;
- of the order of 10% to 20% of bromine is emitted in gaseous form, the rest being trapped in the form of potassium bromide during dust collection;
- there is no increase in releases of nitrogen oxides;
- leaching tests (iron, copper, zinc, potassium, bromide) carried out on fly ash sampled during incineration do not give results significantly different from those obtained under normal operation.

#### **5.2.4 Other types of effluent**

##### **“Water loaded with hydrocarbons [(36)]**

Steps should be taken at the design stage of installations to guard against any risks of polluting the aquatic environment. Among such steps should be mentioned the separation of the circuits so as to ensure that water loaded with hydrocarbons is directed to oil traps, and the introduction of fluid-tight retainers to contain any accidental spillage.

The hydrocarbons collected should then be disposed of in specially adapted treatment units (producing commercially useful energy, undergoing bacteriological treatment, etc.)

##### **“Water from coal stockyards [(36)]**

Coal stockyards, being exposed directly to rain etc. because of their location in the open, should be made fluid-tight. Run-off water containing products from seepage should be collected by a drainage system directing it to a sedimentation pit.

Generally speaking, the many potential sources of pollution demand that monitoring instruments should be installed in proportion to the risks run by the environment due to the coal.

For example, when the stocks of coal are located near a water table, checking the quality of the underground water by piezometers could prove to be a valuable monitoring tool.

### 5.3 Waste [(21), (43), (45), (47), (65)]

The combustion of solid and liquid fuels in large combustion installations is the source of a significant production of waste whose nature and quantity vary according to the type of fuel and the combustion process. The removal of pollutants from the combustion gases, particularly desulphurisation, produces additional waste.

In Europe, the list of waste products drawn up by the Directive 94/3/EEC of 20 December 1993 divides the waste from power stations and other combustion installations into thirteen categories. Amongst these, fly ash from fuel oil and sulphuric acid are considered as dangerous within the meaning of the Directive 94/904/EEC of 20 December 1994.

Faced with the quantities of waste resulting from the operation of large combustion installations, it is essential to adopt a coherent approach to this specific aspect of the integrated approach to pollution. The following order of priorities should be put into effect:

- a. limit to as low a level as possible the production of waste and its degree of contamination, especially by metallic pollutants or persistent organic pollutants;
- b. carry out a systematic study of the feasibility of options for the technical, environmental and economic exploitation of the waste;
- c. use disposal in dumps, under environmentally satisfactory conditions (stability of the waste, imperviousness of the storage site, collection and recycling/purification of leachates) for any waste when the conditions required for its commercial exploitation cannot be met (ultimate waste).

We examine below the particular cases of waste from coal cleaning, boiler ash, by-products and waste from the wet desulphurisation process and waste from the reduction of nitrogen oxide emissions.

#### ***“Waste from coal washing***

Any equipment for washing coal produces, apart from the washed coal, ashy mixtures and slurries which must then be assured of being managed under environmentally acceptable conditions.

The waste produced is generally stored on site. Economic exploitation of the waste may be considered in suitable cases.

In the present state of the method, the washing of coal for the purpose of removing fractions containing ash and/or inorganic sulphur does not allow controlled and selective disposal of impurities to be achieved. It is therefore impossible to remove some elements of the inorganic material by modifying the conditions under which the coal

is washed without at the same time losing an appreciable amount of the combustible organic matter.

At the Carling mine in France, for example, a circulating fluidised bed boiler of 125 MWe has been installed for the precise purpose of consuming old deposits of very ashy slurry which could not possibly be burnt in conventional pulverised coal boilers. However, since the slurry is a residue very rich in heavy metals, the environmental aspects of such an operation justify a very careful examination.

The combustion of ashy slurry in a limited number of pulverised coal power stations, provided that they are equipped with highly efficient devices for controlling atmospheric emissions, would seem preferable to the use of unwashed coal in the many large combustion installations which are only moderately efficient from the environmental point of view.

### ***“Boiler ash***

The handling of ash by dry methods followed by their commercial exploitation or, if this is impossible, their disposal in dumps for special industrial waste are the best available techniques.

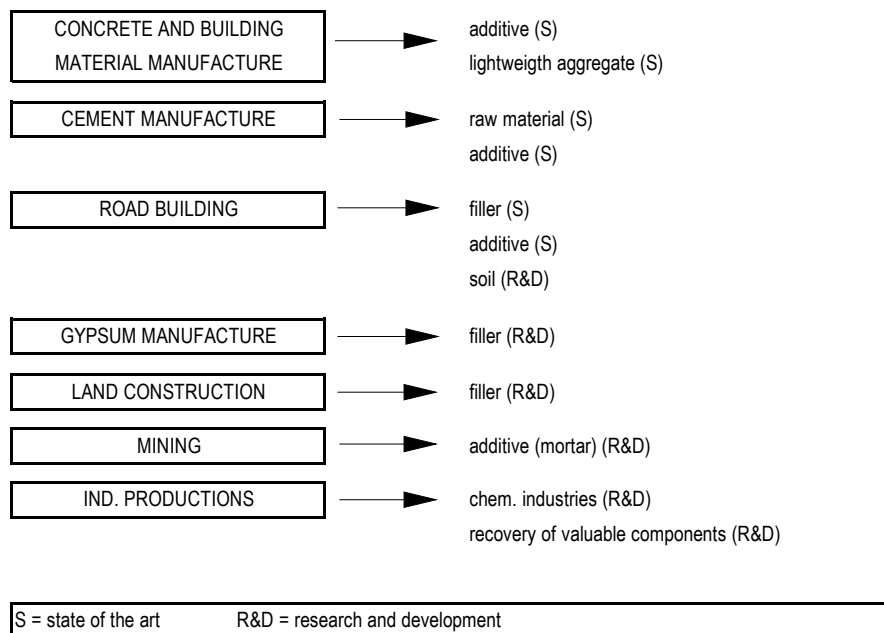
However, storage in the open can be justified in certain special cases, particularly when a large storage capacity is necessary because the periods when it is produced (centred on the winter) and the periods when it can be used (centred on the summer in the case of public works) do not coincide.

Figure 7 details the options available for putting the waste to use in the special case of coal, together with those which are in the research and development stage. [(44)]

When boiler ash is disposed of in dumps, the data given in the section show that specific precautions should be taken to avoid the salting out of metallic ions into the natural environment, particularly in the case of ash from the combustion of heavy fuel oil. For this, a leaching of the soot combined with a recovery of metallic forms is one of the possible methods of waste treatment before storage.

As regards the ash from pulverised coal power (section 4.3.2), Hjelmar [(47)] estimates that 250 years would be required from the appearance of the first leachate for a 10 metre thick deposit of fly ash subjected to a mean infiltration rate of 200 mm/year to be leached to a depth with an L/S ratio of 5.

**Figure 7: Possible uses of fly ash arising from the combustion of hard-coal applied or investigated in the FRG (Arbeitsgruppe Kraftwerksreststoffe, 1988) [(44)]**



It follows from this that the most appropriate strategy for disposal would consist in storing the ash in dumps with good compacting and a gently sloping coverage of the storage cells with a substrate of low permeability (clay substrate topped by a drainage layer of sand and then a layer of cultivated land).

Under the weather conditions investigated (Denmark), such provisions would then allow the expected rate of infiltration to be limited to 50 mm/year and would spread the leaching theoretically over a period of 1 000 years with relatively low levels of environmental contamination.

### ***“Waste from wet desulphurisation***

In comparison with the dry or semi-wet processes, wet desulphurisation methods have the advantage of producing less waste and moreover, in the current state of the methods available on an industrial scale, waste that offers a wider range of options for commercial exploitation.

The gypsum from desulphurisation is potentially a by-product which can be commercially exploited in the building industry, particularly in the cement industry and for the manufacture of plaster board.

As for boiler ash, the commercial exploitation of gypsum from desulphurisation is only possible where the technical and economic conditions permit it. These conditions mainly cover the degree of control over variations in quality of the by-product, whether there are any local deposits of natural gypsum and transport costs.



Technically, a by-product containing too high a proportion of calcium sulphite could not be exploited since sulphites are reducing agents and, in spite of their low solubility, present risks to both surface and underground waters.

Unlike the gypsum extracted from wet lime(stone) desulphurisation plants, the sludge from purification of effluent from desulphurisation contain most of the pollutants initially present in the fuel and must be disposed of in dumps for special industrial waste.

As an alternative, however, tests on disposal by mixing it with the coal followed by combustion have been successfully conducted in some thermal power stations [(43)].

### **❑ Waste from reducing emissions of nitrogen oxides**

Reducing the emissions of nitrogen oxides does not have significant effects on the volume of waste produced. It may, on the other hand, alter the characteristics of the waste and possibly make it more difficult to exploit.

Controlling emission by primary methods can, for example, affect the quality of the boiler ash by increasing the unburnt content. Similarly, the use of an SCR unit in the high dust position can lead to ash contaminated with ammonia whose use in the cement industry poses problems (cf. section 5.1.2).

Spent catalysts from SCR units may be returned to the manufacturer or used in other industrial sectors. For example, zeolite-based catalysts can be recycled in the ceramic industry or in the iron and steel industry.

## **6. Methods for increasing the efficiency of power generation**

Increasing the efficiency of power generation is a basic aim inasmuch as it is accompanied by a reduction in the quantity of pollutants emitted per unit of useful energy. Such a reduction clearly includes trace elements, which are of more particular interest to us in the context of the Paris Commission.

Among the methods capable of improving the efficiency of power generation, we might mention pressurised fluidised bed combustors (PFBCs), supercritical steam cycles, integrated gasification combined cycles (IGCC) and combined heat and power generation. The last three of these are described in detail below.

## **6.1 Supercritical steam cycles [EdF]**

Power generation using solid or liquid fossil fuels mainly involves the use of steam turbines, whose efficiency has a theoretical limit defined by that of the Carnot cycle.

The efficiency of the Carnot cycle is determined by the respective temperatures of the hot and cold heat sources according to the formula:

$$\eta_{\text{Carnot}} = 1 - (T_f/T_c)$$

where  $T_f$  is the temperature of the cold source and  $T_h$  is that of the hot source.

The temperature of the cold source, related directly to that of the condenser cooling water, is a constraint imposed on the designer by the characteristics of the natural environment at the intended site.

The temperature of the hot source (steam output from the boiler) and the pressure at the boiler outlet are defined by the designer on the basis of technico-economic considerations and previous industrial experience.

In the event, many other factors have a direct influence on the nominal expected efficiency of the installation, such as the nature of the fuel, the design of the condenser, the number of reheatings and their temperatures, the temperature of the smoke in the stack, etc.

The real water-steam cycle of a boiler is somewhat different from the ideal Carnot cycle and the efficiency thus differs quite significantly from the theoretical efficiency: for example, for a steam cycle at 540°C and a cold source temperature of 20°C, the theoretical efficiency is of the order of 64%, whereas the real efficiency is about 45%.

There are two possible ways of increasing the efficiency of the real cycle:

- a. attempting to get closer to the ideal Carnot efficiency by increasing the pressure and opting for a reheating and possibly a double reheating;
- b. modifying the theoretical limits of the Carnot cycle by seeking to lower the temperature of the cold source or raising the temperature of the hot source.

It is difficult to change the temperature of the cold source, but that of the hot source can be raised:

- either by using another means than steam to generate power. Increased efficiency can thus be obtained by using gas turbines, in which the hot source is at the temperature of combustion;

- or by raising the steam temperature in the water-steam cycle. This involves using supercritical cycles and attempting to design ultra-supercritical cycles (up to 700°C).

The table below gives an overview of the values of net efficiency on LCV corresponding to various types of cycle for power stations using conventional technologies (pulverised coal, circulating fluidised bed) and the condenser under a reduced pressure of 45 mbar.

**Table 69: Net efficiency on LCV corresponding to the type of cycle [EDF].**

type of cycle	pressure (bar)	temperature (°C)	net efficiency on LCV (%) (*)	experience gained
subcritical	180	540 single reheating	38,5	several thousand units
moderated supercritical	240-250	540-565 single reheating	40-43	several thousand units
advanced supercritical	275-300	580-600 double reheating	45-46	a few units under construction
ultra supercritical	350-375	700 double reheating	52	at the design stage

(\*) We should emphasise that a distinction should be made between the expected efficiency taking into account the guidelines adopted during the design of the installations and the efficiency observed in current operation.

The mean efficiency observed over a long period of operation can differ from the expected efficiency because of:

- climatic changes: variations in the temperature of the cold source and in the temperature of the combustion air;
- variability in the fuel used: humidity, ash content, suitability for crushing;
- the operational mode: continuous or interrupted operation during the year;
- wear and possible clogging up of installations: turbines, condensers, boiler heat exchanges, etc.

Today, there are many units with moderated supercritical cycles operating in the world with experience acquired from operation over a period of the order of 10 years. Some experimental installations incorporating advanced supercritical cycles are being constructed in Denmark (Skarbek and Nordjylland).

The technical difficulties to be overcome in implementing advanced supercritical cycles and ultra-supercritical cycles stem mainly from the nature of the materials (stresses related to the temperature and pressure of the superheated steam).

## **6.2 Gasification (IGCC: Integrated Gasification Combined Cycle) [ (20), (21), (22), (66)]**

In traditional coal combustion processes, the fuel is burnt in a boiler and the gases from the combustion are then purified.

Gasification involves converting the coal (or other solid fuels or oil residues, including oil coke) into gas, purifying this gas, and then carrying out the combustion in a turbine with the highest possible efficiency.

Occurring in the form of hydrogen sulphide ( $H_2S$ ) in the gasification reactor, the sulphur in the raw gas is removed by purification prior to combustion. It can then be extracted at an efficiency of more than 99% by various process that are well established on an industrial scale and that are also currently used in the oil industry. According to Buskies and Meisl [(66)], the sulphide content in the gas before combustion can be reduced in this way to below 25 ppm.

Certain nitrogenous compounds can also be removed. In addition, since the gas combustion takes place in a turbine, the amount of thermal NO produced is less than that resulting from combustion in a conventional boiler [(21)]. Similarly, the concentration of particles can be reduced before combustion, so that the releases of dust into the environment will be very low ( $\gg 1 \text{ mg/MJ}$  [(21)]).

Gasification takes place in a reactor in the presence of steam and oxygen. There are three known gasification processes:

- entrained flow;
- fixed bed;
- fluidised bed.

The first process is the most familiar one and is being installed in two units under construction in Europe: the Demkolec unit (250 MWe) at Buggenum (Netherlands) and the Krupp Koppers Prenflo unit (325 MWe) at Puertollano (Spain).

In the Demkolec unit, gasification takes place at a temperature of  $2\,000^{\circ}\text{C}$  and a pressure of 22 bars. It is estimated that about 85% of the ash is molten and is restored in the form of slag at the reactor outlet. This is clearly an advantage as far as waste is concerned in comparison with leachable ash which requires appropriate conditions for its disposal. The remaining 15% is removed with the exhaust gases which then have to be subjected to dust removal [(66)].

The second process is older and uses temperatures of the order of  $800 - 1\,000^{\circ}\text{C}$  and pressures of between 10 and 100 bars. It has been in service for a number of years at Sasol in South Africa and at Lunen in Germany (1972).

Lastly, the fluidised bed process is particularly suitable for lignites. It forms part of the Kobra project at Lunen in Germany.

The IGCC method potentially offers significant improvements in environmental efficiency compared with conventional technologies. According to Schmidt and Rath [(20)], emissions of sulphur dioxide and oxides of nitrogen would be about ten times less than the environmental standards generally applicable in the USA for traditional thermal power stations.

According to Buskies and Meisl [(66)], achievable concentrations in emissions would be of the order of  $10 \text{ mgSO}_2/\text{Nm}^3$  and  $25 \text{ mgNO}_x/\text{Nm}^3$  measured on dry gases with an oxygen content of 15%.

The increase in the efficiency of energy conversion for this type of installation (cf. section 3.3) would lead to a significant reduction in carbon dioxide emissions (of the order of 35%) in view of the lower consumption of fossil fuels.

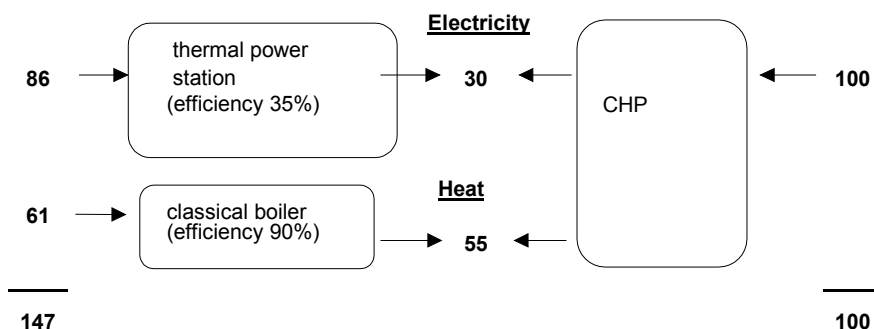
IGCC technology is at present still at the design stage. It needs further development and must demonstrate its reliability if it is to become a commercially viable technology for the combustion of coal on a par with traditional methods.

### **6.3 Combined heat and power generation (CHP)**

CHP refers to the set of techniques making it possible to combine the production of heat and mechanical energy. The mechanical energy produced by a heat engine or a turbine is most frequently used to drive alternators producing electricity.

The overall efficiency of the simultaneous production of electrical energy and heat energy is of the order of 80 - 85%, i.e. significantly higher than that obtained with separate production. As shown in the diagram below, of the order of 40 to 50% more energy must be consumed in producing a given amount of heat and electricity separately than is consumed by the use of CHP.

**Figure 8: Energy consumption for CHP and separate production of heat and electricity**



The implementation of CHP implies the existence of installations in a position to absorb, on a long-term basis, the large volumes of steam associated with the production of electricity. The method may cater, completely or partially, for the needs of industrial sites or of residential or service sectors (urban heating, hospitals, ...) with internal consumption of the electricity produced or its resale to the operator responsible for distribution.

In Western Europe, CHP accounted for about 6,2% of the total production of electricity in 1992. It has been developed more particularly in Luxembourg, the Netherlands, Denmark, Germany and Finland, which benefit from considerable experience in this field with a great variety of installations.

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