

Chapter 2 Flue gases and fuel gases

2.1 Introduction

Combustion processes for heat and power generation and the incineration of household waste generate gaseous “by-products” that are virtually useless when their temperature is below, say, 200°C. By means of a stack of sufficient height these can be dispersed into the atmosphere without much effect to the environment at short range. At the same time the mere presence of a stack indicates that there must be reasons for actively transporting the gases away from the facilities that generate them. These reasons are that the temperature, and, more importantly, the composition of the gases are different from those of the ambient atmosphere at ground-level. The formation of ground-level ozone from traffic exhaust gases during sunny summer days is a good example of what happens when large amounts of flue gases are released at ground-level.

Flue gases from combustion facilities have a composition very different from air because of high concentrations of the combustion products water (H_2O) and carbon dioxide (CO_2). More concern, however, goes to what is in these gases besides these bulk species, such as oxides of sulphur and nitrogen, fine dust, trace elements such as mercury and nickel, and super-toxics such as dioxins. All these compounds are actually unwanted by-products from a power plant or a waste incinerator, since the first has the objective to convert hydrocarbon fuels (C_xH_y) into CO_2 , H_2O plus heat and power, whilst the second aims at reducing a large volume of solid or liquid waste into a small amount of solid ashes plus, again, CO_2 and H_2O from the combustion of the organic compounds. Unfortunately the “fuel” or “waste” materials that are combusted contain chemicals that are vaporised or converted chemically into gases that mix with the harmless gases H_2O , CO_2 , O_2 and N_2 as, for example SO_2 , NO , fly ash, HCl *etc. etc.* Nowadays it is well accepted that also CO_2 should be included in the list of species not be emitted into the atmosphere carelessly. CO_2 concentrations in the atmosphere are rising at ~1% per year from ~355 ppmv (parts per million by volume) in 1990 to ~380 ppmv nowadays, which many researchers connect to measurable climate change effects such as sea-water temperature rise and more frequent extreme weather situations.

The following chapters will address the control of emissions from thermal processes such as power plants, waste incinerators and cement plants. For power plants the species for which emissions are regulated at this moment are SO_2 , NO_x and particulates, although mercury and, if the Kyoto Protocol from 1997 will be enforced, carbon dioxide will be added to the list during the next years. More extensive regulations hold for cement plants and incinerators for municipal solid waste (MSW) and hazardous wastes, where, besides SO_2 , NO_x and particulates also CO and other unburned hydrocarbons, mercury (Hg) and several other trace elements, acidic compounds such as HCl and HF, and dioxins/furans must be controlled as well.

Flue gases from power plants and waste incinerators will receive most attention in this text. Besides these, gases are emitted or released by all sorts of industrial processes and small-scale activities (for example dry cleaners) where organic solvents are used. These off-gases generally contain volatile organic compounds (VOCs) that are often halogenated, such as acetone, formaldehyde and tri-chloroethene, and chemicals such as chlorofluorocarbons (CFCs) and SF_6 that contribute to the enhanced greenhouse effect and/or interfere with the tropospheric ozone layer.

The purpose of the remaining part of this chapter is to give some background information and definitions on flue gases, fuel gases and the various thermal processes that generate or consume them.

2.2 Flue gases and fuel gases: combustion, gasification, pyrolysis incineration and other processes

Combustion can be defined as the complete exothermic oxidation of a fuel with sufficient amount of oxygen or air with the objective of producing heat, steam and/or electricity. The final gaseous product of combustion is then a *flue gas*. Fuels used for this purpose are mainly hydrocarbons (natural gas, coal, fuel oil, wood *etc.*) that are thereby converted to CO_2 and H_2O , the other fuel components may form by-products such as ash, and gaseous pollutants that may need emission control equipment. Solid fuels such as coal, peat or biomass are typically fired at air factors 1.1 - 1.5, *i.e.* 110-150% of the oxygen needed for complete oxidation of the hydrocarbon fraction of the fuel to CO_2 and H_2O .

Gasification can be defined as partial combustion of a fuel, resulting in ash and a combustible gas. These *fuel gases* typically contain significant amounts of CO and H_2 that may be combusted in a separate process equipment. Gasification is an

exothermic process that is operated at air factors of the order 0.25 - 0.4, *i.e.* operating at 25 - 40% of the oxygen that would be needed to convert the hydrocarbon fraction of the fuel to CO_2 and H_2O . Basically, part of the fuel is combusted to provide the heat needed to gasify the rest.

Pyrolysis can be defined as thermal decomposition of a fuel into smaller fractions: combustible gases such as C_2H_6 , CO , CO_2 , H_2 , H_2O , oily liquids and a solid carbonaceous char residue. This process is operated under exclusion of air or other oxidising species, *i.e.* the air factor equals zero. Pyrolysis is an endothermic process. In most cases the fuel gas produced is combusted to provide the heat needed for a pyrolysis process of which the solid and liquid residues are the valuable products.

Incineration is a combustion process where the material that is combusted is not considered to be useful as a fuel - instead the goal is to reduce the volume. Solid waste incineration and natural gas flares at oil fields are the most important examples of incineration processes.

Besides gasification and pyrolysis product gases, also natural gases can be used as fuel. Natural gases contain methane and other lower alkanes as the main constituent, whilst fuel gases that are produced by the gasification or pyrolysis of non-gaseous fuels such as coal, wood or waste-derived fuels typically contain CO and H_2 (and, if any, only small amounts of methane) as the most important combustible components. Table 2.1 lists the composition of a few typical flue gases and fuel gases.

2.3 Combustion and gasification technologies for heat and power

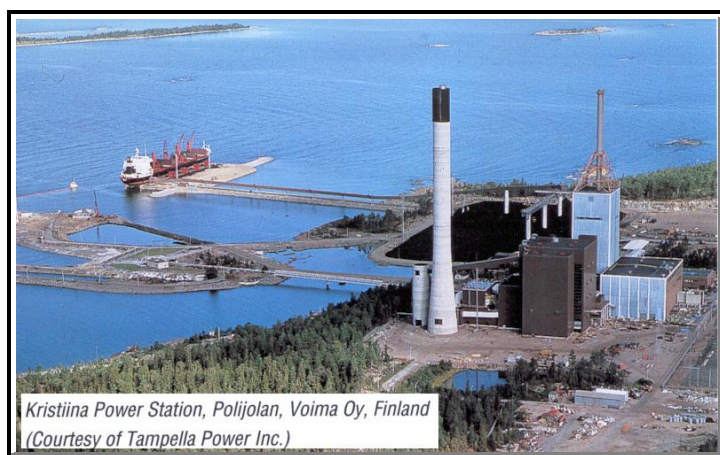


Figure 2.1 A Finnish pulverised coal combustion plant (picture from OECD/IEA & ETSU, 1993)

Flue gases from fossil fuel-fired combustion facilities are major contributors to atmospheric pollution. Figure 2.2 shows an oil-fired furnace/boiler in which, with different burners, natural gas or pulverised coal or peat may be fired as well. A birds-eye picture of a Finnish pulverised coal-fired plant is shown in Figure 2.1.

Table 2.1 *Typical compositions of some raw flue gases and fuel gases
i.e. before gas clean-up*

*(data from Alderliesten et al., 1990, Gasunie, 1988, Göttlicher, 1999,
Maskuniitty, 1995, Werther, 1999)*

	Pulv. coal combustion flue gas	Waste incinerat. flue gas	Coal gasification fuel gas §	Coal-fired IGCC flue gas	Natural gas Groningen	Gas-fired CC flue gas
O ₂ %-v	~ 6	7 - 14		~ 12		~14
N ₂ %-v	~ 76	balance	~4 / ~1	~ 66	~14	~76
CO ₂ %-v	~11	6 - 12	~4 / ~13	~ 7	~1	~ 3
H ₂ O %-v	~ 6	10 - 18	~4 / ~1	~ 14		~ 6
CO %-v		0.001-0.06	~58/~40			
H ₂ %-v			~30/~29			
Ar %-v	~ 1	~ 1	~ 1	~ 1		~1
SO ₂ ppmw		200 -1500		10 - 200		
H ₂ S ppmw			1000-4000			
NO _x ppmw	500 - 800	200 - 500		10 - 100		10 - 300
NH ₃ ppmw			300 - 800			
HCN ppmw			40 - 150			
HCl ppmw		400 - 3000	500 - 600			
HF ppmw		2 - 100	150 - 250			
dioxine ppb	<< 1	1 - 10				
CH ₄ %-v					~ 81	
C _n H _m %-v		< 0.002			~ 4	
Hg ppmw	0.1 - 1	0.1 - 1	0.01 - 0.1			
Cd ppmw	0.01 - 1	0.1 - 0.5	0.01 - 0.2			
other heavy metal ppmw	0.5 - 2	1 - 5	~ 20			
dust g/m ³	5 - 20	0.2 - 15	~17 / ~8	<< 0.02		

§ Two values : Shell / Texaco entrained bed gasifiers

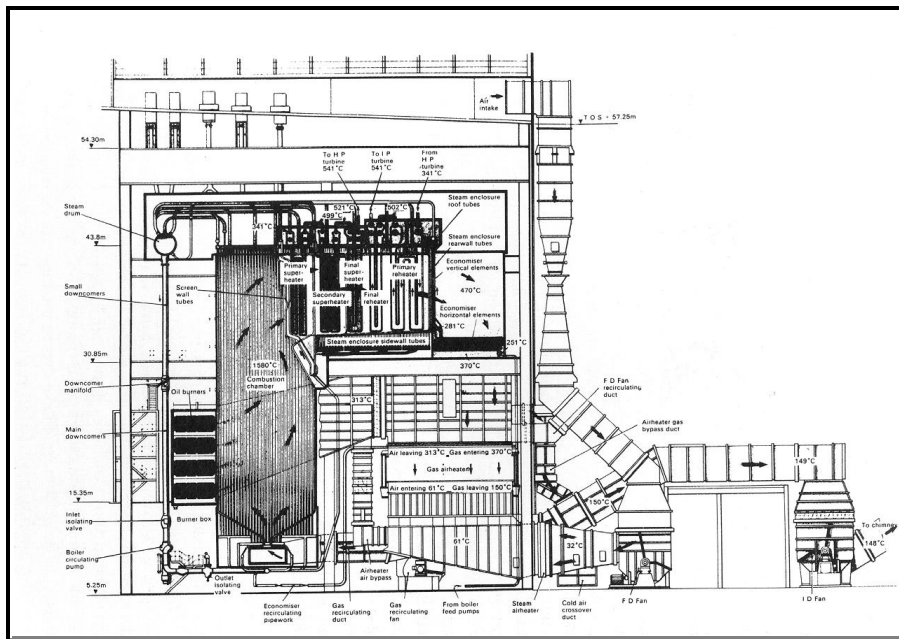


Figure 2.2 A typical oil-fired furnace (picture from Lancaster, 2000)

An impression of the flames involved in pulverised coal combustion is given in Figure 4.20. This technology is used for the majority of fossil-fuel fired electricity generation; flue gas cleaning typically involves particulate (*i.e.* fly ash) emissions

control plus, if needed, methods for reducing the emissions of oxides of sulphur and nitrogen. An example of a pulverised coal combustion unit plus gas clean-up train is shown in Figure 10.1. Thermal efficiency improvements from typically 37% up to 47% have been obtained with supercritical and ultra-supercritical steam cycles (ETSU/DTI, 1999).

An alternative type of reactor for the combustion or gasification of solid fuel are bubbling or circulating fluidised beds (BFBs and CFBs), as shown in Figure 2.3. This

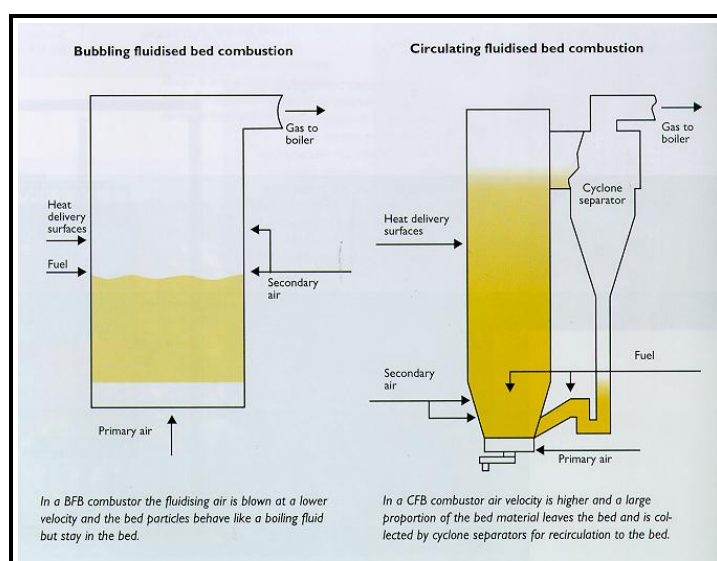


Figure 2.3 Bubbling (left) and circulating (right) fluidised bed combustors (picture from Tekes, 1996)

technology operates at lower furnace temperatures with somewhat larger fuel particles than pulverised coal furnaces. The fuel is combusted in a hot fuel / bed material (mostly sand) / ash mixture which is fluidised by the combustion air which is fed from below. Benefits of this technology are flexibility for low grade fuels such as wet sludges or waste-derived fuels, relatively low NO_x emissions due to the

relatively low combustion temperature and the possibility to trap sulphur by adding *e.g.* a limestone or lime to the bed (see section 3.11). Disadvantages are that emissions of N_2O (a greenhouse gas) may be high and the limited use of the bottom ashes that must be disposed of. BFB combustors appear less suitable than CFB combustors for low-volatile fuels such as coal (char burnout problems), and for high sulphur fuel due to gas/solid contact limitations (bypassing of gases in the bubbles).

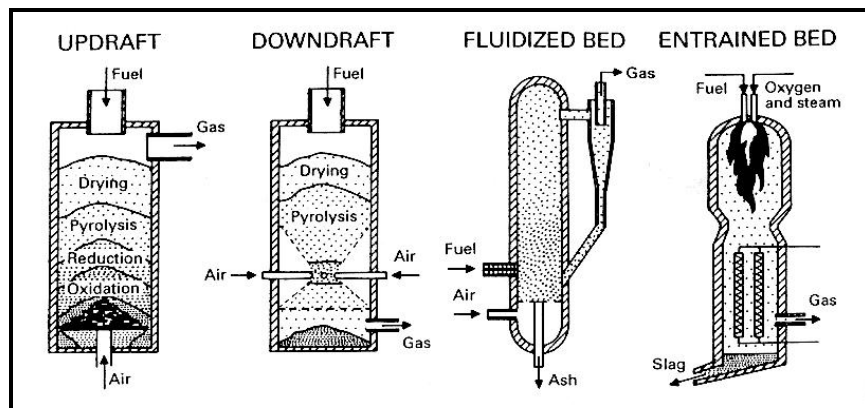


Figure 2.4 Gasification reactor types (picture from Kurkela *et al.*, 1993)

Solid fuels may also be converted by gasification, with the benefit that product gas streams are much smaller which is advantageous for gas clean-up. This holds especially for gasifiers that are operated with oxygen + steam

instead of air as the gasifying agent. Figure 2.4 shows the most important reactor types for solid fuel gasification. Entrained bed gasifiers are most suitable for coal, whilst for other solid fuels such as waste-derived fuels, circulating fluidised bed gasifiers (CFBCs) seem most suitable. For smaller scales the updraft and downdraft moving bed gasifiers are preferred.

For coal, an additional option is underground gasification, as illustrated by Figure 2.5:

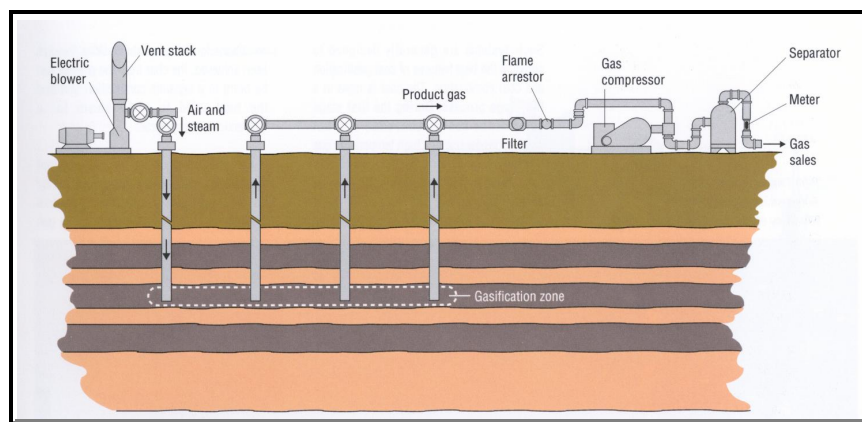


Figure 2.5 Underground gasification of coal (picture from OECD/IEA & ETSU, 1993)

the gasification agent (air or oxygen, plus steam) is pumped into the coal layer, from which fuel product gases are extracted. At the same time, most of the ashes stay underground.

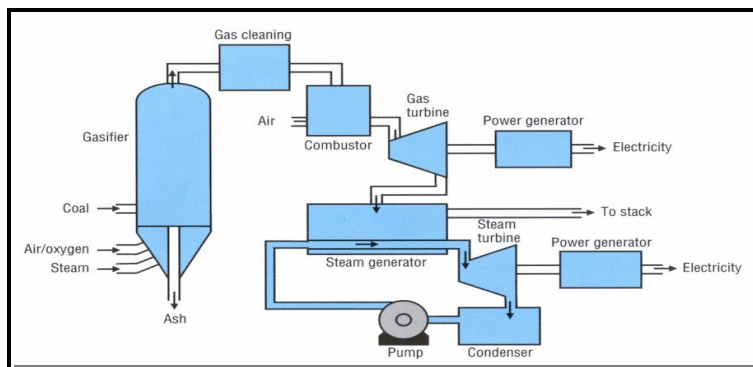


Figure 2.6 Principle of coal-fired integrated gasification combined cycle (IGCC) (picture from OECD/IEA& ETSU, 1993)

fired combined cycles (NGCC) thermal efficiencies of the order of 60% may be reached, whilst several coal-fired integrated gasification combined cycle (IGCC) processes of $\sim 250 \text{ MW}_{\text{thermal}}$ have demonstrated thermal efficiencies of the order of 46%. Figure 2.6 illustrates the principles of solid fuel-fired IGCC.

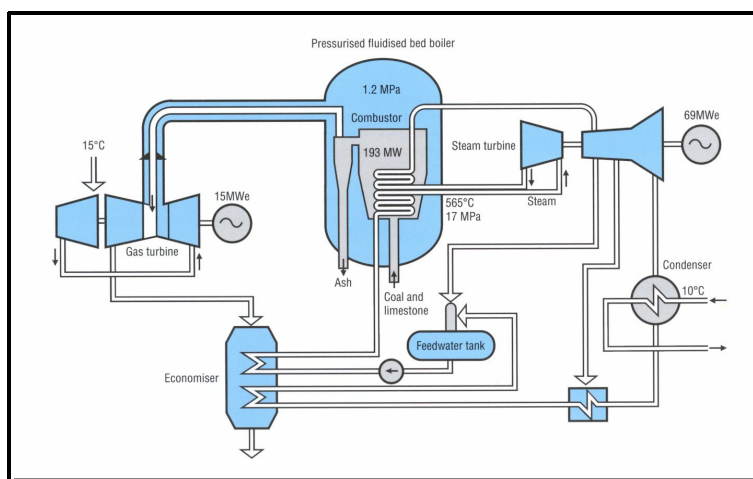


Figure 2.7 Principle of coal-fired pressurised fluidised bed combustion combined cycle (PFBC-CC) (picture from OECD/IEA&ETSU, 1993)

Since the 1970s combined cycle technologies have been developed based on gas turbine technology. After combustion of fuel gas (natural gas or a gasification product gas) in a gas turbine, increased thermal efficiency can be achieved by using the gas turbine exhaust in a steam cycle. For natural gas-

Similarly, pressurised fluidised bed combustion combined cycle (PFBC-CC) illustrated by Figure 2.7, was developed by ABB Carbon (currently Ahlstrom Power) based on BFBC until around 2000. Approx. 10 facilities of 200 or $800 \text{ MW}_{\text{thermal}}$ have been built, several in Japan. Development work on circulating bed PFBC-CC is ongoing at Foster Wheeler.

Solid fossil fuels, solid renewable fuels such as biomass and waste-derived fuels and also solid wastes that are to be incinerated generate a wide spectrum of gaseous pollutants, not to mention solid residues. From that point of view gaseous or liquid fuels or waste streams for thermal treatment tend to be “cleaner”, or they can be cleaned more easily than solids, for example oil refining. Liquid and gaseous fuels do not or hardly contain ash-forming elements which makes them suitable for application in internal combustion engines and gas turbines. As a rule, emissions per unit heat or power generated are smaller for liquid/gaseous fuels than for solid fuels.

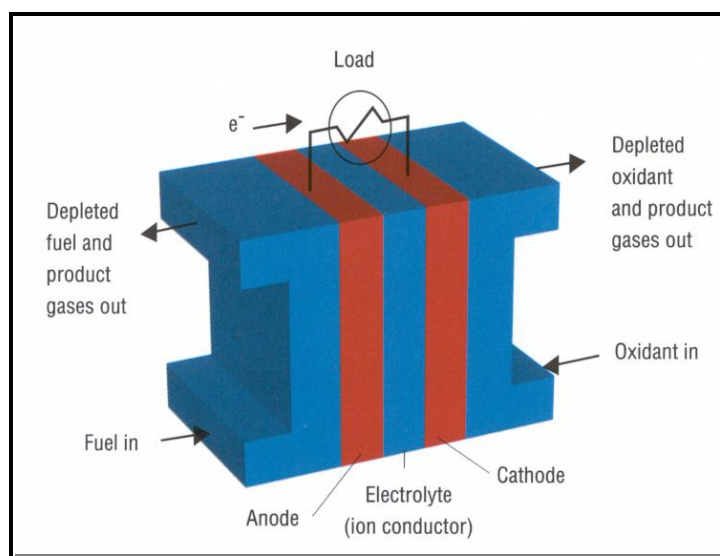


Figure 2.8 Principle of a fuel cell (picture OECD/IEA&ETSU, 1993)

Future technologies will be based increasingly on the direct oxidation of fuel gases in fuel cells, which implies direct conversion of chemical potential energy into electricity. Also for cars and other vehicles this may be a future alternative for internal combustion engines. The principle of “combustion” of fuel gas in a fuel cell is shown in Figure 2.8. The gases that are “fired” in a fuel cell may be hydrogen, obtained from natural gas reforming; product

gases from gasification reactors, after cleaning; or natural gas, depending on the electrolyte that is used and the temperature of operation.

2.4 Waste incineration and waste-to-energy processes

A schematic picture of a waste incineration process with flue gas clean-up train is shown in Figure 10.2. Similar to other low-grade fuels such as straw and other biomasses wastes and waste-derived fuels are typically combusted on grates. As a result of fuel size and composition, high fuel moisture and non-perfect fuel/air mixing, the concentrations of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) (L chapter 6), trace elements (L chapter 8), halogen compounds and dioxines and furanes (L chapter 7) are relatively high and a complex emission control system is needed. This is further complicated by cross-effects between various pollutants and pollutant control devices.

The chlorine content of waste streams generally enforces relatively low combustion temperatures (mainly as to avoid corrosion) which results in thermal efficiencies of the order of 20 %. For refuse derived fuel (RDF) or recovered fuels (REF) a classification according to chlorine content may separate waste streams into fuels for waste-to-energy processes and wastes that must be otherwise incinerated. For example, the Finnish classification distinguishes REF I (< 0.15 %-wt chlorine), REF II (< 0.5 %-wt chlorine) and REF III (< 1.5 %-wt chlorine). Plastics may add

significant heating value to a waste stream, whilst on the other hand PVC (poly vinyl chloride, chlorine content ~55%-wt) presents many problems (see *e.g.* La Mantia, 1996).

2.5 Cement plants

The production of clinker that can be mixed with ashes and other additives to form cement is a very energy intensive process that is characterised by rather high emissions of nitrogen oxides (NO_x) and carbon dioxide (CO_2). In a two-stage (so-called “dry”) process, limestone (CaCO_3) is first calcined to lime (CaO) in a preheater section (temperatures up to ~1000EC), followed by the clinker reactions in a rotary kiln which involves the formation of calcium silicates ($x\text{CaO} \cdot y\text{SiO}_2$) at temperatures up to 1500EC. This is illustrated by Figure 2.9 in which also the more energy intensive “wet” process is indicated. The high emissions of CO_2 are due to the combustion of fuel (*e.g.* coal, petcoke, or waste-derived fuels such as car tyre scrap) plus the CO_2 released during the limestone calcination; NO_x emissions are high apparently due to the high temperature in the kiln and the temperature profile along the route from the kiln through to the stack. Many other pollutants such as sulphur and trace elements are trapped in the clinker product.

Figure 2.10 shows a “dry” cement plant located in Finland.

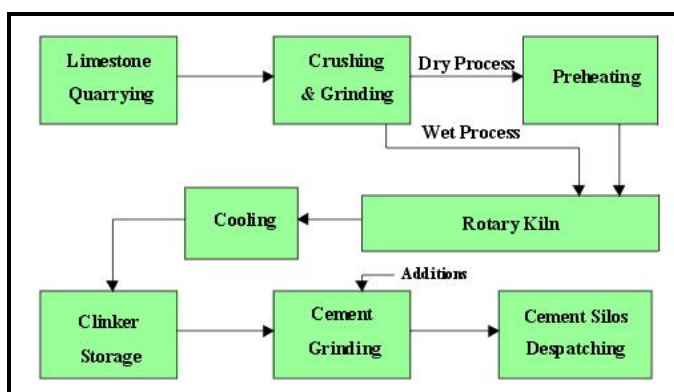


Figure 2.9 Schematic lay-out of cement plants (picture from IEA GHG, 2000)



Figure 2.10 Rotary kiln and precalciner cyclone tower of a cement plant (Finnsementti Oy, Finland, 1998)

2.6 Emission standards and exhaust gas composition

Emissions regulations and standards, as listed for the several compounds and species in the chapters that follow are based a normalisation to a certain concentration of oxygen (O_2) in the gas. This makes a comparison between processes possible and blocks the route of lowering pollutant concentrations by dilution with clean air. Typically, for power plants the standards are given for 6%-vol O_2 in dry flue gas, for waste incineration systems for 10 or 11%-vol O_2 in dry flue gas. For NO_x ($=NO + NO_2$), while NO is the major NO_x species that is emitted from a combustion process (the molar ratio $NO : NO_2$ is typically >20 in a flue gas). Emission regulations refer to NO_x calculated as NO_2 , for the simple reason that in the ambient atmosphere NO is oxidised within ~ 1 day to NO_2 .

Calculating from a given case with a certain (wet) flue gas is accomplished by considering the relations between concentration, C , volume, V and the overall air factor or stoichiometry of the combustion process, AF . For dry flue gases from carbon-containing fuel combustion the relation between the air factor and the oxygen concentration is approximately

$$AF = \frac{21}{21 - \%O_2(dry)} \quad (2-1)$$

At the same time, the volume of the flue gases increases with increasing air factor, *i.e.* $V \sim AF$, and since concentration is related to volume as $C \sim 1/V$, it is found that

$$C \sim \frac{1}{AF} \quad \text{which gives} \quad \frac{C_i @ x \% \&vol O_2(dry)}{C_i @ y \% \&vol O_2(dry)} = \frac{21 - x}{21 - y} \quad (2-2)$$

for the concentration C_i of the species i . The transformation from wet to dry flue gas is a simple re-normalisation of the concentrations after removing the water.

Example: 360 ppmv SO_2 in a (wet) flue gas containing 10 % H_2O and 13.5%-vol O_2 . Concentration at 6 %-vol O_2 (dry) ?

Answer: Re-normalisation to 90%-vol dry flue gas gives 400 ppmv SO_2 and 15 % O_2 (dry). Equation (2-2) gives then

$$C_{SO_2} @ 6 \% O_2 (dry) = (21-6)/(21-15) * C_{SO_2} @ 15 \% O_2 (dry) \\ = 1000 \text{ ppmv}$$

2.7 References

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