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# Environmental Toxicology & Biotechnology

**Soumitro Ghose**

**S. K. Dubey**



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# **Environmental Toxicology & Biotechnology**

## Preface

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Environmental toxicology is the study of the adverse effects of toxins within the environment upon human health. The scope of environmental toxicology is inclusive of naturally occurring agents such as metals, mycotoxins and bacterial elements as well as anthropogenic toxins like pesticides, food additives, industrial waste, and other chemicals. Environmental toxicology majors study how to quantify these agents in environmental media, identify risks, characterize exposure, model chemical movement in the environment and examine modern theory of regulations of hazardous materials.

Environmental biotechnology is when biotechnology is applied to and used to study the natural environment. Environmental biotechnology could also imply that one try to harness biological process for commercial uses and exploitation. Biotechnology offers a "natural" way of addressing environmental problems, ranging from identification of biohazards to bioremediation techniques for industrial, agricultural and municipal effluents and residues.

This book gives a deeper insight into the complex processes involved in this field of Environmental Toxicology and Biotechnology, covering the basis of toxicology, herbicide resistance, chemical control and fundamentals needed to further develop effective methodologies. The book devotes detailed chapters to the main areas of environmental toxicology. It addresses the needs of researchers in academic and commercial environments, and serves as a guide for graduate students designing, implementing, and evaluating experimental projects.

Suggestions for the improvement of the book and pointing out of errors and mistakes will be thankfully accepted.

—*Soumitro Ghose*

—*S. K. Dubey*

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## INTRODUCTION

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*Waste* is any movable material that is perceived to be of no further use and that is permanently discarded. Once in the environment, wastes frequently cause damage to ecosystems and/or human health and therefore act as pollutants.

Successful waste management can largely avoid such pollution. This chapter introduces the more widely available strategies and technologies that can be effective in this area. The first three sections deal with the approaches used in the management of the relatively low-hazard wastes that are generated in bulk by industrial, commercial and domestic activity. Consideration of the options available for the safe treatment and disposal of high-hazard wastes is given in the fourth section. The chapter closes with a brief introduction to the concepts of waste minimisation, cleaner production and integrated waste management. If more widely adopted, these ideas have the potential to greatly improve current waste management practices.

### Wastes from Fossil Fuel Combustion

The main wastes generated during the combustion of fossil fuels are sulfur dioxide,  $\text{NO}_x$ , carbon monoxide, unburnt hydrocarbons, particulates, residual solids (including ash) and carbon dioxide. The technologies that are available for the management of these wastes are briefly reviewed in this section.

#### Sulfur dioxide

Fossil fuels contain both organic sulfur (e.g. in thiophene rings) and inorganic sulfides (principally  $\text{H}_2\text{S}$  in natural gas and  $\text{FeS}_2$  in coal). During combustion these react with atmospheric oxygen ( $\text{O}_2$ ) to produce sulfur dioxide ( $\text{SO}_2$ ).

The sulfur content of fossil fuels varies considerably. For example, coals and fuel oils generally contain 1-4%, and 3-4% S respectively. However, there are naturally occurring low-sulfur fuels (e.g., coals < 1 % S and fuel oils <0.5% S). Clearly, burning these preferentially is one of the options available for diminishing the emissions of sulfur dioxide. Unfortunately, this is of only limited applicability as supplies of these low-sulfur fuels are comparatively small.

Another alternative is the dilution and dispersion of the sulfur dioxide produced, principally by building taller chimneys. This has found favour in the past and has had noticeable success in the reduction of local levels of pollution. Unfortunately, it has had no impact on overall contamination; in effect, 'what goes up must come down'.

Fuel cleaning processes that remove sulfur are routinely applied to natural gas, oil and coal. These are now considered in turn.

Natural gas contains variable amounts of hydrogen sulfide ( $H_2S$ ). This may be effectively removed by a number of processes including adsorption onto zeolites (a type of aluminosilicate mineral). The hydrogen sulfide may then be oxidised *in situ* with hot sulfur dioxide to yield sulfur vapour and regenerated zeolite adsorbent. The sulfur is then condensed and sold, while the zeolite is reused.

The desulfurisation of oils is desirable for a number of reasons that are unrelated to the lowering of sulfur dioxide emissions. These include avoiding the deactivation (poisoning) of platinum catalysts used during oil processing. Consequently, oil desulfurisation was practised before the environmental need to reduce sulfur dioxide emissions was recognised. The main process involved is hydrodesulfurisation. During this the oil is reacted with hydrogen ( $H_2$ ) at elevated temperatures, under pressure and in the presence of a catalyst. This converts the sulfur to hydrogen sulfide which can then be separated as a gas.

An important consequence of oil desulfurisation is that motor spirit (petrol, gasoline) has a very low sulfur content (between 0.026% in US Premium grade and 0.040% in the UK). As a result, transport makes very little contribution to the total anthropogenic emissions of sulfur dioxide.

Coal is cleaned by the separation of the organic fuel from the inorganic ash-forming mineral impurities that it contains. This

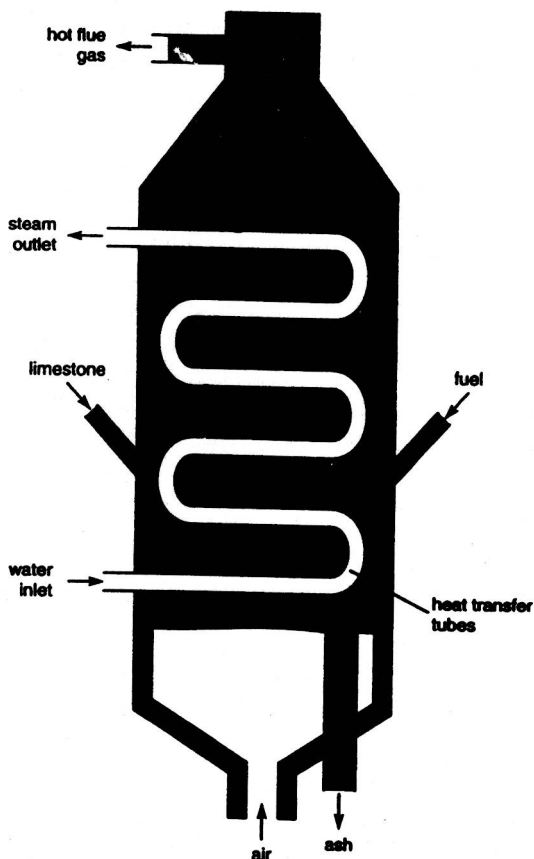


Fig. 1.1. A schematic view of a fluidised bed boiler fitted with limestone-based sulfur dioxide control.

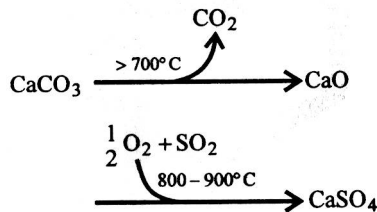
may be done on the basis of density, for the fuel has a lower specific gravity (1.1 to 1.8) than the impurities (from about 2 to about 5). In one process the raw coal is finely ground, so that most of the mineral particles become distinct from the fuel. The ground raw coal is then agitated in a mixture of air, water, oil and surfactant. The denser particles sink, while the others are held by surface tension at the interface between the liquid and the air. The cleaned coal is then isolated in a settling tank, where the air/oil/water mixture is allowed to separate, causing the fuel to sink.

Processes such as this may remove much of the inorganic sulfur fraction ( $\text{FeS}_2$  has a specific gravity of 4.5). In a typical

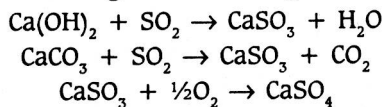
British coal, about half of the sulfur is inorganic, the rest forming part of the organic matrix of the fuel. It is now technologically possible to remove some of this also, though it is currently not economically viable to do so.

Vast amounts of coal are consumed worldwide, particularly during the production of electricity. This, coupled with the relative inefficiency of the routine coal cleaning process, makes this fuel by far the largest single contributor to anthropogenic sulfur dioxide emissions. There is therefore considerable interest in the removal of sulfur dioxide prior to the release of the flue gases.

Sulfur dioxide removal rates of 90% can be achieved from the combustion zone in boilers that are based on *fluidised bed combustion* (FBC) technology. In such systems the fuel is added in a pulverised form to a bed of inert material (e.g. sand or coal ash). This is kept in a state of agitation (i.e. fluidised) by a strong updraught of air, which acts as the oxidant. Such systems allow the coal to be burnt efficiently at relatively low temperatures ( $\sim 900^\circ\text{C}$ ). On addition of limestone (essentially  $\text{CaCO}_3$ ), they also provide an excellent environment for the sequestering of sulfur dioxide:



As an alternative, sulfur dioxide can be removed downstream of the boiler after the fly ash has been removed, a process called *flue gas desulfurisation* (FGD). FGD can be highly efficient: 90% removal rates are generally achievable. In a typical system, an aqueous slurry of an alkaline absorbant, commonly lime, or limestone, is passed in a fine spray through the flue gases. Sulfites and sulfates are therefore generated during this 'scrubbing' process:



The last of these reactions can be encouraged by the injection of air into the sump of the scrubbing tower. This yields high-quality gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) which can be sold for use in plasterboard and other building materials.

### $\text{NO}_x$ , Carbon Monoxide and Unburn Hydrocarbons

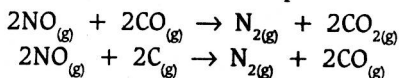
The burning of fossil fuels in air produces nitric oxide (NO) and, to a lesser extent, nitrogen dioxide ( $\text{NO}_2$ ); these are collectively known as  $\text{NO}_x$ . They are formed by the reaction of atmospheric oxygen with nitrogen at the high temperatures reached during combustion. The nitrogen may originate from either the air or the fuel, thereby producing thermal- $\text{NO}_x$  and fuel- $\text{NO}_x$  respectively.

The problem of fuel- $\text{NO}_x$  is primarily associated with coal because it has relatively high levels of nitrogen (1-2%) compared with other fossil fuels. For example, natural gas is virtually nitrogen-free, while fuel oil contains <0.5% N.

Clearly, thermal- $\text{NO}_x$  formation occurs whenever fuels are burnt in air. This allows transport to be a major contributor to  $\text{NO}_x$  emissions. For example, in the country about half of  $\text{NO}_x$  is traffic-related. The remainder originates from stationary producers, particularly electricity generating stations.

Reduction in the emissions of  $\text{NO}_x$  can be achieved by alterations to the combustion process. The reactions that produce thermal- $\text{NO}_x$  are endothermic and are therefore favoured by high temperatures. Lowering the temperature of combustion by, for example, recycling exhaust gases will therefore diminish  $\text{NO}_x$  emissions. Unfortunately, this will also reduce the Carnot efficiency of any heat-to-work device driven by the fuel. If used in a motor vehicle,  $\text{NO}_x$  reduction by this method will therefore be at the expense of fuel economy.

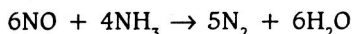
Fuel- $\text{NO}_x$  emissions can also be controlled by adjustments to the combustion process. Fuel nitrogen that has been oxidised to nitric oxide may then be reduced to molecular nitrogen by either fuel-derived volatiles or char, for example:



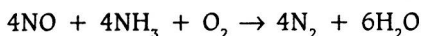
These reactions can be encouraged by allowing the early stages of the combustion process to be carried out under fuel-rich conditions, followed by an injection of air into the flame when it is more mature, allowing the char to be oxidised. This approach, called staged combustion, when used alone can result in the removal of up to 50% of  $\text{NO}_x$  in coal-fired stations.

The treatment of flue gases can also lead to  $\text{NO}_x$  removal. The approach used is dependent on whether the source is static or mobile. In the former case, either ammonia,  $\text{NH}_3$  (with or without

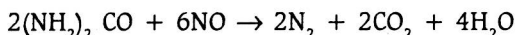
a catalyst), or urea,  $(\text{NH}_2)_2\text{CO}$ , is injected into the stack gases, causing the  $\text{NO}_x$  to be reduced:



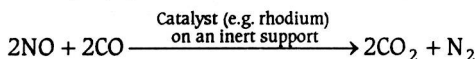
and



or



The treatment of vehicular emissions may be achieved by the catalytic reduction of  $\text{NO}_x$  to molecular nitrogen at the expense of carbon monoxide (CO) present in the exhaust gases:



Then, air may be injected and the gases allowed to pass over an oxidation catalyst such as platinum or palladium on an inert support. This will facilitate the conversion of any residual carbon monoxide to carbon dioxide and any unburnt hydrocarbons present in the waste stream to carbon dioxide and water.

### Particulates

Both stationary sources and Diesel-powered vehicles produce significant amounts of particulates. Where attempted, the recovery of these contaminants from the stack gases of the former source is generally very successful. The technologies used are based on cyclones, electrostatic precipitators and/or fabric filters (bag filters).

During the operation of a cyclone, the exhaust gases enter the top of its essentially cylindrical body, at a tangent. This causes them to move downwards in a helical fashion, generating centripetal forces that drive the particulates to the walls, from where they fall, exiting the cyclone at the bottom. The cleaned gases then leave the top of the cyclone via the pipe at its centre.

Electrostatic precipitators (ESPs) operate by virtue of a potential difference of 30 to 60 kV between the wires and plates that they contain. This causes a very steep gradient in the electric field around the wires and a concomitant high concentration of ions. These charge the particles of the effluent stream, which are then accelerated towards the plates by the potential difference. The dust may then be dislodged from the plates by agitation, allowing it to fall into a collection hopper.

Fabric filters (bag filters) physically remove particulates from the exhaust gases that are made to pass through them. The filters

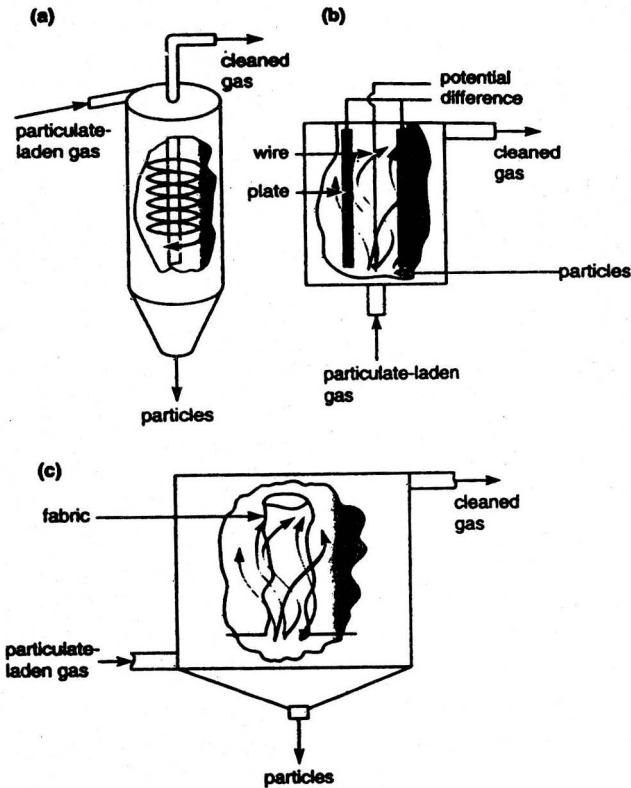


Fig. 1.2. Schematic representations of particulate control devices used with static sources: (a) a cyclone, (b) an electrostatic precipitator, (c) a fabric filter.

may be of many designs, although tubular constructions are common. The dust burden is periodically removed by either mechanical shaking and/or the reversal of the direction of gas flow.

There is increasing concern over the sooty particulates from Diesel engines, as epidemiological studies indicate that these contaminants may cause a range of health problems including heart disease. Currently, in the UK, Diesel engines account for about 40% of all black smoke emissions. It seems likely that this percentage will go up as the popularity of Dieselpowered vehicles increases.

Control of Diesel particulates is technologically difficult, though two approaches seem promising. The first involves improving the



homogeneity of the fuel-air mixture at the time of firing, so ensuring a more complete burn. The second relies on ceramic filters that may be cleaned either physically, by compressed air, or chemically, by heating in the presence of air.

### **Residual Solids**

The combustion of finely ground coal in electricity generating stations produces very large quantities of residual solids. These are ashes and, more recently, the products of limestone-based desulfurisation.

Two types of ash are generated, namely pulverised fuel ash (PFA) and furnace bottom ash (FBA); together these amount to about 12-13 Mtea<sup>-1</sup> in England and Wales alone. PFA is collected as a particulate from the flue gases and accounts for 80% of the total. Both of these products are used in cementitious materials. Despite this, in areas where production outstrips demand, considerable quantities are sent to landfill.

As previously mentioned, lime- or limestone-based desulfurisation post PFA removal can yield highquality gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). Clearly this has commercial value. However, the vast amounts produced may be sufficient to swamp the market, necessitating other disposal routes including landfill.

### **Carbon dioxide**

All fossil fuel combustion leads to the generation of carbon dioxide. Many exotic means of diminishing the contamination of the atmosphere with this gas have been suggested. Included amongst these is the possibility of increasing the primary productivity of the oceans. It is thought that this may be achieved by adding relatively small amounts of iron to areas that are deficient in this element. According to this hypothesis, the consequent increased rates of photosynthesis will result in the absorption of carbon dioxide. Recent large-scale experiments in the Pacific demonstrated that a single addition of iron salts did indeed promote productivity, at least in the short term. However, a fully concomitant net consumption of carbon dioxide did not occur. One possible explanation of this is that an increased biomass of photosynthetic plankton encouraged the activity of grazing zooplankton, and that the respiratory activity of these organisms recycled a large proportion of the carbon dioxide originally absorbed. It seems doubtful that the seeding of oceans with iron represents a feasible means of controlling atmospheric levels of