Umweltbundesamt
Austrian Federal Environmental Agency

BY–PRODUCT UTILIZATION AND WASTE MANAGEMENT FROM FUEL TREATMENT AND COMBUSTION

Status Report

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Abstract

By–products and wastes produced by various emission control systems for stationary combustion sources, are described. Beside the state of the art also a survey on R & D projects is given. Processes discussed include fuel treatment (coal, oil, gas), conventional fuel combustion (coal, oil, biomass, peat), flue gas desulphurization, nitrogen oxides control, fluidized bed combustion, coal gasification and municipal waste incineration. Included are generation data and standards for the utilization and disposal of by–products for various countries as well as related national laws. Generation data are figures based on the situation in the 80's, but also a prognosis for the year 2000 is given.

KEYWORDS: Wastes, by–products, combustion, air pollution, environmental protection, fuel treatment, disposal, utilization, flue gas, clean technology.

Summary

I. BACKGROUND

As a result of international agreements initiated by the United Nations Economic Commission for Europe (ECE), and of more stringent standards adopted by member countries to control atmospheric emissions from stationary sources, an increasing number of air pollution control measures and systems are being used. These processes, aimed inter alia at controlling emissions of particulates, sulphur dioxide and nitrogen oxides from stationary combustion sources, produce by–products in the form of solids and/or liquids. These by–products must either be utilized or disposed of as waste.

The ECE Working Party on Air Pollution Problems, in implementation of the work plan of the Executive Body for the Convention on Long–range Trans–boundary Air Pollution, appointed a Task Force to examine by–product utilization and waste mangement from fuel preparation and combustion emission control systems. The Task Force included experts from Austria (lead country), Canada, Czechoslovakia, Federal Republic of Germany, Finland, Italy, Netherlands, Sweden, United Kingdom, United States, Yugoslavia, and the International Energy Agency (IEA).

This report presents data on the amounts of fuel and by–products managed by countries in the ECE region during the late 1980's together with forecasts for the year 2000.

Information is provided on processes and by–products associated with fuel treatment (coal, oil, gas), conventional fuel combustion (coal, oil, biomass and peat), flue gas desulphurization (FGD), nitrogen oxides control (deNO$_x$), fluidized bed combustion (FBC), integrated coal gasification combined cycle (ICGCC), and municipal waste combustion. Policies, technical standards and legal requirements are included for the utilization and disposal of by–products by various countries. The Task Force's conclusions and recommendations are also presented.

II. BY–PRODUCT QUANTITIES

Available data on by–products and waste produced by countries in the ECE region are presented; so too are current generation rates and projected rates for the year 2000. Residues are produced from fuel cleaning, combustion and flue–gas cleaning.

Concerning data used in forecasts for the year 2000, it should be remembered that these will be influenced by factors (e.g. energy consumption, fuel mix, energy–conversion efficiency, pollution standards) that mean the values given have a significant degree of uncertainty.

These influencing factors include the increase or decrease of nuclear power, reflections and actions in connection with the CO_2 problem, different national strategies concerning the obligatory use of coal or gas.

Furthermore, changes in the data of the forecasts may also result from increases in energy–conversion efficiency by conventional and/or new measures and techniques.

In countries contributing data, by–products generated in recent years were projected by the year 2000 as follows:

Oil and gas treatment	by about 15 %
FGD products	by about 200 %
Conventional combustion	by about 50 %
FBC	by about 60 %.

For municipal waste combustion plants, an increase of about 20 % compared to the late eighties is expected.

Elemental sulphur (mainly for the chemical industry and for pulp mills), coal fly ash (for building purposes) and FGD gypsum (for the cement and gypsum industry) are the most commonly utilized by–products. Utilization of other by–products are of environmental concern and most are still at the research, development and demonstration stage.

Disposal of waste in landfills can be expected to become increasingly socially unacceptable due to environmental concern, and it is anticipated that environmentally acceptable options for the utilization of by–products will become increasingly important.

In addition, new treatment and cleaning processes as well as new combustion systems producing less by–products or waste and/or more usable by–products must be developed, and existing procedures must be improved.

III. FUEL TREATMENT

Physical and chemical processes are used to treat fuels to lower the sulphur content and, in the case of hard coal, to improve also the heating value. These processes are state of the art.

Cleaning wastes from hard coal (which may be acidic for higher sulphur coals) represent on average about 30 % of the coal produced. Cleaning is only usually done for bituminous coals, and the residuals are disposed of at the mine site.

Hydrogen sulphide is removed from "sour" natural gas. The hydro–desulphurization process (HDS) via Clauss treatment produces elemental sulphur which can be used for the production of sulphuric acid and other sulphur products.

Sulphur is removed by the HDS process from the lighter fractions of the crude oil. It is more difficult and expensive to remove sulphur from heavy fractions by special HDS processes. The by–product of this technique via a Clauss treatment is also elemental sulphur. However, this technique will become increasingly important in the future when crude oils with higher sulphur contents have to be processed.

IV. CONVENTIONAL COMBUSTION OF FUELS

Bottom ash and fly ash are produced from coal–fuelled boilers. Most of the ash is fly ash which may be of environmental concern because of the leachability of metals and salts which may contaminate ground water and surface water. Fugitive dust from fly ash is also of some concern. Bottom ash is of less environmental concern because contaminants are relatively immobile in this material, which is also relatively coarse and heavy.

The combustion of heavy oil and heavy residues also produces fly ash to some extent. This fly ash contains relatively high concentrations of heavy metals, especially vanadium and nickel.

Various national standards exist for the use of fly ash in cement. The pozzuolanic properties of many fly ashes effectively immobilize environmental polluting metals. Due to lack of pozzuolanic properties, coal and peat ash from grate–firing as well as ashes from oil and biomass combustion do not normally meet technical requirements for utilization in construction.

V. BY–PRODUCTS AND WASTE FROM DESULPHURIZATION PROCESSES

Wet working processes for FGD may be divided into processes generating throw–away products as waste for disposal and those which generate a usable and salable by–product. The large majority of FGD installations with a sludge process operate in the United States, dumping the generated sludge in lagoons or ponds nearby. Nearly all FGD plants in European countries use processes which generate salable by–products. This trend is mainly influenced by difficulties in obtaining sites and permission for disposal areas and by increasing waste–management costs.

About 90 % of the FGD plants in operation in Europe generate gypsum. In a few plants, for technical and/or local marketing reasons, processes were installed which generate pure SO_2 or elemental sulphur.

Spray–drying procedures which are comparatively simple to install and operate, still have the disadvantage that, in most cases, the by–product cannot yet be used for further industrial application and has to be disposed of. Therefore research and development (R & D) work is carried out in some countries to find and prove a treatment by which these by–products (especially calcium–based by–products) can be improved or used for special applications.

Like the wet working processes, dry working processes can generate usable by–products or waste for disposal. In general, dry additive procedures for both furnace or ductwork injection and FBC generate non–usable by–products, unlike most of the downstream desulphurization processes, e.g. the activated carbon process which generates salable sulphur or sulphur compounds. Application of this process has been limited to date.

VI. BY–PRODUCTS AND WASTE FROM deNO$_X$ PROCESSES

Low NO$_X$ combustion by primary measures lowering the formation of nitrogen oxides may be accompanied by an increased amount of unburnt carbon in slag and fly ash (and of the carbon monoxide concentration in the flue gas). The unburnt carbon content in the solid by-products could cause difficulties when disposed of, by further chemical reaction, and in the utilization of the fly ash in the cement industry. However, these effects occur mainly in those cases in which primary measures are driven up to a relatively high $deNO_X$ effect.

Secondary measures already remove nitrogen oxides contained in the flue gas generated. Selective catalytic reduction (SCR) is the most commonly applied process. This does not generate a by-product itself. However, depending on the position of the SCR unit, ammonia, used as a reducing agent, can be adsorbed on the surface of the fly ash, thus causing possible difficulties for the utilization of the fly ash. The used, deactivated catalysts would cause a minor disposal problem if they were not accepted back by the catalyst producers.

Contamination of fly ash by the reducing agent could constitute a particular problem when a selective non-catalytic reduction procedure (SNCR) is applied. However, in most cases the SNCR technique is applied for lignite-fired boilers, and in particular for municipal waste incinerators, where fly ash is not utilized.

VII. BY-PRODUCTS AND WASTE FROM SIMULTANEOUS AND COMBINED SYSTEMS

Most of these processes are at the development stage or in pilot plant testing. The activated carbon process, in commercial operation since 1988 for simultaneous desulphurization and $deNO_X$, generates sulphur but no $deNO_X$ by-products or waste. Others, like the e-beam process or the ammonia-ozone process, generate a mixture of ammonium, sulphate and ammonium nitrate which could be utilized as fertilizer.

VIII. BY-PRODUCTS AND WASTE FROM FLUIDIZED BED COMBUSTION (FBC)

Although much effort has been devoted to R & D to utilize the by-products from the different types of FBC (e.g. for synthetic gravel), the wide variability of their composition hinders industrial utilization. Furthermore, the comparatively low combustion temperatures of FBC generate ashes with significantly different physical and chemical properties compared with conventional combustion systems.

For desulphurization, lime/limestone is added to the fluidized bed. A mixture of calcium compounds and fly ash is deflected by this in the dust collector. The utilization of this by-product is not yet state of the art.

Circulating and rotating FBC systems have the advantage that the content of unburnt carbon in the ashes is lower than in atmospheric FBC and in conventional combustion systems. Pressurized FBC residues seem to be more utilizable in construction work than those from atmospheric FBC, though little experience of this exists.

IX. BY-PRODUCTS FROM GASIFICATION PROCESSES

Gasification processes generate, inter alia, the following by-products and waste: gasifier slag and fly ash, sludge and solid waste (salts) from liquid effluent handling and process wastes. Elemental sulphur, generated by desulphurizing the gas produced, is a by-product that is salable for industrial use. Because of the early stage of application of these techiques, investigations and tests to ensure proper handling of the materials involved have to be continued and results have to be consolidated. At the moment, gasifier slag shows potential for utilization in, inter alia, the field of road construction and maintenance, in industrial applications like filter media and mineral wool, and for resource recovery, taking advantage of, for instance, it's high aluminium content. Only a few leaching tests with gasification products have been made. Care must therefore be taken with regard to a potential environmental impact when the slag is in contact with ground water. However, the properties and quality of slag very much depend on the coal gasified and the process used for gasification.

Waste from liquid effluent treatment may be either a sludge which can be incinerated or, after a spray–drying treatment, a mixture of dry but soluble salts which at present are packed in large bags and disposed of.

Process waste is generated by some process units. Spent catalysts and, in some processes, used solvents have to be handled. Catalysts should be taken back by the manufacturers. In some processes, gas–treating units using periodical solvent blow–downs are sources of secondary emissions which should be incinerated.

X. BY–PRODUCTS AND WASTE FROM MUNICIPAL WASTE COMBUSTION

Solid by–products and waste from incineration and advanced flue–gas cleaning and waste–water treatment include slag, boiler and fly ash and filter cakes. When a dry or spray–drying procedure is used, a mixture of ash and reaction products is produced.

Depending on different standards in different countries, slag can be a by–product used, for example, for road construction as base or sub–base aggregate, or as a waste to be disposed of. According to new developments, the alkali content of the fine fraction of the slag can be utilized to improve the efficiency of the FGD section.

Boiler and especially fly ash containing heavy metals and toxic organic compounds often have to be disposed of after solidification. The technical possibility of eluting the heavy metals by acidic washing and destroying the organic compounds by thermal treatment is carried out in a few plants. The flue–gas cleaning system and products from dry or spray–drying procedures contain heavy metals and soluble salts. The relatively small amount of filter cakes from wet flue–gas cleaning systems and the comparatively larger amount of solid products from dry or spray–drying procedures have to be disposed of, in some cases after solidification.

New developments offer the possibility of melting the solid substance to produce a glassy mass without leaching effects. Such a substance could be used for industrial purposes.

XI. LEGAL INSTRUMENTS

Brief overviews show how countries in the ECE region regulate the use of by–products and the disposal of waste from fuel treatment, combustion and from flue–gas treatment.

XII. CONCLUSIONS

As efforts to reduce SO_2 and NO_X emissions from stationary sources and thus comply with environmental objectives (e.g. fuel cleaning and flue–gas treatment) are increased in the countries of the ECE region, the quantities of by–products will also increase.

Because of changing energy scenarios in different countries, it is difficult to make an accurate forecast of the future volumes of by–products generated. Data is therefore uncertain.

Volumes of by–products are now substantial. Within countries contributing data, by–products generated in the late 80's are projected to increase until the year 2000,

from oil and gas treatment	by about 15 %
from FGD	by about 200 %
from conventional combustion	by about 50 %
from FBC	by about 60 %
and from municipal waste combustion plants	by about 20 %.

The reclamation and decommissioning of emission control waste disposal sites warrants careful investigation, so that the land may be suitable for the beneficial use of future generations, unrestricted by environmental and health concerns.

If by–product management is to be successful, it is important that no product be considered in isolation and that no generalized decisions be made. As a result of differences in fuel quality, the origin and types of raw materials, treatment processes, combustion systems and flue–gas treatment technology, the physical and chemical properties of by–products vary considerably. Therefore, generalized decisions in favour of specific forms of utilization and disposal are meaningless.

Environmental concerns associated with by–products from flue–gas emission control systems can be reduced or eliminated by the application of available environmental protection technologies and practices.

Certain by–products may require disposal. Many countries have classification systems and legislation governing the utilization and disposal of waste.

Conventional coal–cleaning produces a waste which is usually disposed of. Treatment of liquid and gaseous fuels results in a usable by–product (sulphur).

Conventional coal combustion processes produce large amounts of ash and slag which may be utilized. However, under some conditions, ash cannot be utilized.

In all member countries, the utilization of these ashes must generally be considered as state of the art. In some member countries, up to 80 % and more of the amount produced is utilized.

The number of FGD installations is increasing rapidly within the ECE region. Currently, the lime/limestone gypsum processes are the most commonly used. By–products and waste from desulphurization processes are:

Usable:	*Gypsum* *Magnesium compounds* *Sulphur, sulphur dioxide and sulphuric acid* *Ammonium sulphate*
Probably usable (R & D):	*Mixtures of* $CaSO_3$, $CaSO_4$, $CaCO_3$ *and fly ash*
Not usable:	*Condensates* *Waste water* *Sludges from waste–water treatment*

The decision on the technology to be used for the desulphurization of flue gases has far–reaching and long–term consequences. The environmental impact, caused by the technology chosen depends to a great extent on the manner of utilization and the disposal of the by–products of the selected technology.

The only commercially available combined system for SO_X and NO_X

removal is the activated carbon process, which generates usable by–products.

$DeNO_X$ processes (primary and secondary) may influence fly ash in a negative manner with regard to utilization (e.g. carbon and NH_3 content).

FBC is a technology available for the reduction of both SO_2 and NO_X emissions. At present, there is no large–scale utilization of its by–products.

At IGCC plants, the sulphur content of the fuels is recovered in a usable form. The main residues are slag and sludge from waste–water treatment. Data on the uses and properties of these substances are sparse. However, this technique will not contribute significantly to the total formation of by–products till the year 2000.

By–products from municipal waste incineration plants are to be considered separately on account of their content of toxic compounds. In some countries, slag is utilized for road construction, while in others it has to be disposed of, sometimes after treatment. In some countries, by–products from flue–gas treatment and filter cakes from waste–water treatment have to be handled in the same way as toxic materials.

In all contributing countries, enhanced R & D is carried out in most of the following fields:

- Improving the quality of usable products;
- Development of further processes to generate usable by–products;
- Treatment of by–products that are still unusable, to obtain usable ones;
- Treatment of toxic by–products to produce less toxic or non–toxic ones.

The practical utilization of by–products from dry FGD systems, sorbent–injection systems and FBCs warrants further research, development and demonstration. Full consideration should be given to all environmental and health concerns.

The appropriate management of by–products from thermal power emission control systems provides practical opportunities to apply the principle of "sustainable development" as advocated by the World Commission on Environment and Development. The United Nations Economic Commission for Europe can play an important role in promoting these opportunities.

XIII. RECOMMENDATIONS

By–product utilization and waste management from fuel treatment and combustion systems should be consistent with sustainable development.

The process of energy production and consumption has to be viewed by all parties as one system, whereas fuel treatment and flue–gas treatment are only parts of the whole. Considerations concerning by–products are strongly influenced by energy–saving measures and energy–conversion efficiency. Therefore, these parts of the energy life cycle have to be handled with priority; they will also result in lower amounts of by–products.

An integrated approach to environmental protection should be adopted and the management and fate of by–products should be considered for the whole cycle at the earliest possible stage of the selection, planning and operation of any energy–conversion system.

The aim should be to avoid where possible the production of waste.

Where residuals are generated, they should be produced and/or treated in a way that will encourage their utilization rather than disposal. By–products should be used in an environmentally acceptable manner.

The concept of clean technologies should be enforced in power plants and other industrial installations. This has been shown to produce long–term economic and environmental benefits in many cases.

The decision on the utilization of by–products should be based on chemical and physical properties and environmental goals. Today, different test methods are available which could be used to classify residuals and to evaluate environmental effects.

To ensure the proper management of residuals in the long term, new utilization possibilities should be explored and R & D should be implemented. This applies not only to by–products now utilized (e.g. FGD gypsum), but especially to residuals not yet widely utilized (e.g. FBC ash).

In many cases, the utilization of residuals is still governed by economic considerations. Residuals often compete with natural materials. One must ensure that the utilization of residuals is not hampered by inappropriate product norms. Fiscal and regulative measures can be used to promote the replacement of natural materials by the utilization of by–products.

The use of residuals for landfilling, land reclamation, soil conditioning or other applications with characteritics similar to those of disposal has to comply with environmental goals and long–term land uses. Environmental pollution by long–term processes (e.g. leaching) must be considered. Methods for the analysis and assessment of landfill products should reflect the actual and long–term behaviour of substances in a landfill as accurately as possible. The leaching methods, for example, have to be reviewed from this angle.

Even where a high degree of utilization can be achieved, it will still be necessary to have contingency plans for storage and disposal.

The primary aim of complying with environmental criteria should be to minimize and contain the waste and not solely to dilute the residue with other material.

If utilization is not possible, the aim should be to produce residuals that have a minimum impact on the environment. If material has to be disposed of, the siting and design of the site must take account of all the relevant physical and chemical characteristics of the waste, the future uses of the site and environmental goals. The aim should be to avoid long–term technical intervention, but technical (e.g. monitoring) and financial provision should be made, as appropriate, to ensure that future generations are protected.

With the use of advanced disposal techniques, the cost of disposal can be expected to rise, thereby encouraging the utilization of by–products and the adoption of clean technologies. Disposal sites should be carefully regulated by the responsible authorities.

Further R & D and exchange of information between countries in the ECE region should be undertaken to help achieve these recommendations.

The subject of "By–product Utilization and Waste Management from Fuel Preparation and Combustion" should be a major topic at the Fifth Seminar on Emission Control Technology for Stationary Sources.

CONTENTS

1 INTRODUCTION

The 4th seminar on Emission Control Technology for Stationary Sources held in May 1986 in Graz, Austria, had a special topic "By-Product Utilization and Waste Disposal". On basis of the presented papers and the connected discussions the delegates formulated and adopted, inter alia, a recommendation, that more information should be collected and presented on the utilization of by-products from primary and secondary measures for desulphurization, ecological aspects of disposal of wastes from these processes including research and development in this field. At the 16th meeting of the Working Party of Air Pollution Problems in Geneva in June 1987, Austria made the proposal to keep the function of a lead country for preparing a status report on by-product utilization and waste disposal, dedicated to be presented at the 5th seminar on Emission Control Technology for Stationary Sources 1990 or 1991. The Working Party accepted this proposal and the meeting of the Executive Body in November 1987 gave his agreement.

The first meeting of experts nominated by the member countries was held in Vienna, Austria, on March 3 and 4, 1988. The list of experts present at this and/or following meetings is as follows:

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Furthermore, a delegate from an international organisation took part in the process:

Mrs. Irene Smith
IEA Coal Research
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Reports and studies on problems and solutions for utilization and/or disposal of by-products from flue gas cleaning systems were delivered to the Working Party also from:

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After the presentation of the general structure of the Status Report to be elaborated at the 17th session of the Working Party in June 1988 the second meeting of the Task Force was held in Vienna on November 17 - 18, 1988. On basis of the information given to the Working Party and the results of discussions within the Task Force it was decided to change the title of the report on the final wording: "By-Product Utilization and Waste Management from Fuel Treatment and Combustion" regarding the fact that fuel treatment and fuel cleaning - also one of the topics of the 4th seminar in Graz and an important strategy for reducing emissions - also generates by-products and wastes. Furthermore the Working Party and the Executive Body asked to add a prognosis on by-product utilization and waste generation from the concerning sources for the year 2000. Finally it was decided that special chapters concerning by-products and wastes from municipal waste incinerators, from fluidized bed combustion and gasification processes should be part of the report.

The 3rd meeting of the Task Force took place in Salzburg on May 17 - 18, 1989. The experts formulated a preliminary version of conclusions to be presented at the 18th Working Party session in June 1989 in Geneva and to be adopted in the 4th meeting of the Task Force in December 4 - 5, 1989.

This meeting has to conclude the content of the short version of the status report and beside the conclusions also the recommendations to be forwarded in February 1990 to the ECE secretariat in Geneva and finally to the 5th seminar in June 1991. In February 1989 the Chairman and the delegate from Sweden of the Task Force joined the first meeting of the UNDP/ECE Task Force on utilization and disposal of by-products in Malta, reporting on ongoing work and giving advice on liaison between the two Task Forces.

The summary (short version of the status report) including the conclusions and recommendations, published under United Nations ENVWA/WP.1/R.21, 23rd April 1990, was presented to the 19th session of the Working Party in June 1990 in Geneva. The Working Party adopted the summary, but formulated, that the missing data for the increase of by-products and residues by the year 2000, which have to be added at the Task Force meeting in October 1990, have to be added and delivered before the November-meeting of the Executive Body. The E.B. should then discuss and adopt the final version of the summary including the prognosis-data.

During the last meeting of the Task Force, 17th to 19th October 1990 in Vienna, the Task Force elaborated the tables concerning the prognoses for 2000 and made improvements on the actual values with more accurate data.

The Status Report will then be printed in the original english version at the begin of 1991 and presented at the 5th seminar in June 1991 in Nürnberg.

The Task Force also concluded that reflecting the big change in the political and economical situation in Europe since the last year and taking into account not only the rapid development in techniques for utilization and treatment of by-products and wastes but also the aspects of the global warming discussion the present Status Report should be updated by a Follow-up Report which has to be presented at the 6th seminar. The Task Force recommends and asks for such a conclusion of the 5th Seminar.

2 GENERAL DESCRIPTION

2.1 General Introduction

Since the improved understanding of the reasons of acidification and of increasing air pollution in total, measures have been taken to reduce emissions to the atmosphere, especially from electric power plants and industrial sources.

Measures have taken to reduce particulates, SO_2 and NO_x. Since the start of such programmes an enormous reduction of emissions concerning these pollutants (or groups respectively) has been achieved.

As a result of the enforced measures for flue gas cleaning the load for the environment changed. Environmental polluting substances are transfered from the flue gases to water and/or soil. The reason is that most of the processes lowering emissions cause by-products or wastes. As the reduction of emissions will go on the amounts of by-products will increase.

To avoid any confusion with respect to the meaning of the term "hazardous waste", the terms "potentially harmful" or "environmentally polluting" will be used in this report or in special cases "toxic". The term "hazardous waste" will be restricted to use in connection with legal matters and national law.

This report deals with the generation, characteristics, handling, treatment and utilization of usable by-products from fuel treatment and emission control systems. Furthermore, the characteristics, handling, treatment and disposal of nonusable by-products are discussed. Residuals from other environmental protection technologies other than those associated with the conversion of energy, are not covered in this report.

There are three ways to produce usable by-products (Arbeitsgemeinschaft Nachwachsende Rohstoffe, 1986):

a) Substitution of a source using known production techniques. This means, that the new product has to compare economically with existing standard products.

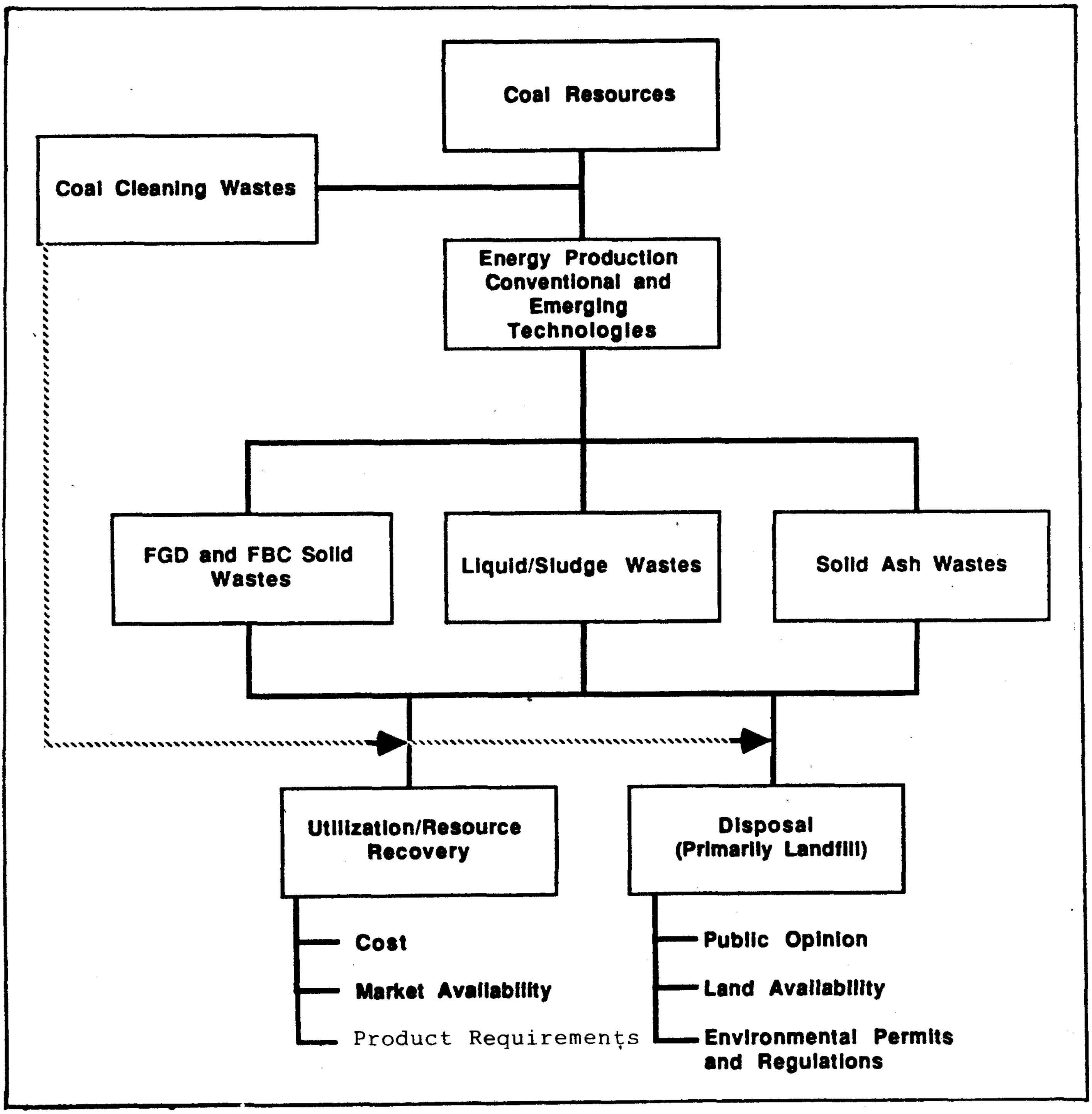


Figure 2.1: Fossil Fuel Cycle Waste Management Programme Perspective (U.S. Department of Energy, 1987; adapted)

b) Replacement of a resource combined with the use of a new technology to produce existing products. As a result both - source and technology - have to be economically compared with traditional production.

c) Development of new products and/or markets with known methods or methods have to be developed. Taking this way a lot of research and development (R & D) has to be done.

In addition to physical and chemical properties which have to be satisfied for a possible utilization, there are other factors which influence utilization. Examples are distances between the points of generation and utilization and (therefore cost of transportation), public acceptance of the "new" products, availability of raw materials and national structure of industry, as well as environmental aspects.

By-products generated arising during fuel preparation, combustion and flue gas treatment may be classified as follows (Hackl, 1986a):

1. utilizable by-product
    1.1. for commercial product
    1.2. as an alternate resource
    1.3. for internal recycling
2. not usable by-products
    2.1. disposal waste
    2.2. hazardous waste

<u>Commercial products</u> can be sold with economic profits for both sides. The market may request this product because of a better quality, fewer changes in quality, no national or nearby source for such a product, thus bringing more benefit than cost. As long as the production of such a by-product does not exceed the

regional or national volumes of market, these by-products can be utilized with economic profits. Sulphur, as a by-product of flue gas desulphurization, for example, is such a commercial product.

Substituting products can in principle be used as an alternate resource. Although they are usable there is no guarantee in general that they will be accepted on a regional or national market. According to the name of this group these products can substitute others. To get a certain share of the market it is necessary to reduce the share of the conventional products which should be substituted. This target can be met easily, when such a product will substitute products which have to be imported or have to be brought over a long distance. In case of national sources and a nearby production only high qualities and profitable costs could bring some chances for utilization. A typical example of a substituting product is gypsum produced by flue gas desulphurization.

Products for internal recycling are by-products which can be reused within the same plant in which they are generated. That means that less raw material, less energy, no external transportation and no disposal are necessary. Beside economic advantages in most cases this brings also ecological advantages. For example in case of the magnesium oxide process for flue gas desulphurization internal recycling is practised.

For the second group "not usable by-products" some forms of classifications can be developed, for example as proposed by the Landesamt für Wasser und Abfall (1987):

Class 1: inert material with no effect on ground water or surface water
Class 2: mineral substances with neglectable and temporary impacts
Class 3: disposal for municipal waste, treatment of leachate is necessary

Class 4: disposal for industrial waste, treatment of leachate is necessary

Class 5: disposal for toxic waste.

As national acts and standards define most of the terms for substances with relevance to disposal one may find these definitions in chapter 11 and the relevant chapters.

A lot of factors influence the composition and quantity of by-products and therefore also the possibilities of utilization and the amounts of waste which has to be dumped. The most important parameters influencing by-products of fuel treatment and combustion are:

- kind of fuel, its composition and specific characteristics
- kind of combustion process
- kind of flue gas treatment process
- (necessary) percentage of contaminant removal.

The choice of the fuel is first of all a matter of resources. When planning or operating a plant and comparing the costs for different fuels one must keep in mind the expense of flue gas treatment and for the management of the by-products.

The type of combustion process influences not only the quantity and composition of the by-products but also the necessity of flue gas treatment processes to meet the emission standards.

Flue gas treatment processes may result either only in cleaned gases (as in most processes for denitrification) or in a liquid, solid or slurry by-product. The choice of the process introduces possibilities of utilization depending also on the quantities of the wastes.

It is necessary to say that with a very high rate of purification often an non-linear increase in the amount of residuals is introduced.

In many cases, depending on the technology used, the higher the percentage of purification of the flue gas the bigger are the quantities of residuals. However, in some cases (e.g. dry processes) also the opposite is possible.

In conclusion to the above mentioned classifications the two principal possibilities of discharging by-products are utilization and disposal.

Utilization avoids the necessity of finding suitable disposal sites and preserves natural resources. In future increasing difficulties in further disposal have to be expected. The choice between utilization and safe disposal of by-products can only be made after careful consideration of all factors pertaining to a specific set of circumstances.

In some European countries flue gas cleaning processes, especially flue gas desulphurization (FGD) have been applied for just a few years. In the forthcoming years an extensive expansion will take place (ECE/EB.AIR/18, 1988; ECE/UNDP, 1989; UN, 1979). The target of the Helsinki Protocol for lowering SO_2 emissions is to be met at the latest by 1993. At the same time the quantities of by-products will increase requiring the investigation of new fields of utilization. Additionally municipal waste incineration programs, in combination with district heating, will cause increasing quantities of by-products in some countries.

2.2 Formation and Annual Quantities

2.2.1 Main Sources of Generation of By-Products

According to the state of the art there are five possible ways to reduce air pollution from combustion:

- fuel cleaning
- low emission combustion processes
- flue gas treatment
- increasing the conversion efficiency
- change in the fuel mix.

Depending on the kind of fuel and the desired or required efficiency of purification, one or a combination of processes can be chosen. An example is given by figure 2.2. The example shows how a reduction of emitted NO_x can be achieved and the effect of combining different methods on the total emitted amount of NO_x.

Nearly all of the fuel cleaning and flue gas treatment processes generate by-products and/or residuals. By-products will be reduced by increasing the conversion efficiency and switching of fuels, eg. coal to gas.

To provide an indication of the relationship between the amount of used raw energy and the produced by-products, table 2.1 to 2.4 give a short look over the used raw energy in the contributing countries. In some countries the data include not only power generation, but also heat generation for district heating and industrial purposes.

Table 2.5 gives an outlook for the projected amounts of raw energy for energy production in the year 2000. The prognosis is based on data available in September 1990.

A	excess air level reduction
B	air staging
C	flue gas recirculation
D	fuel concentration
E	condensation separation

pointed barr: no measures

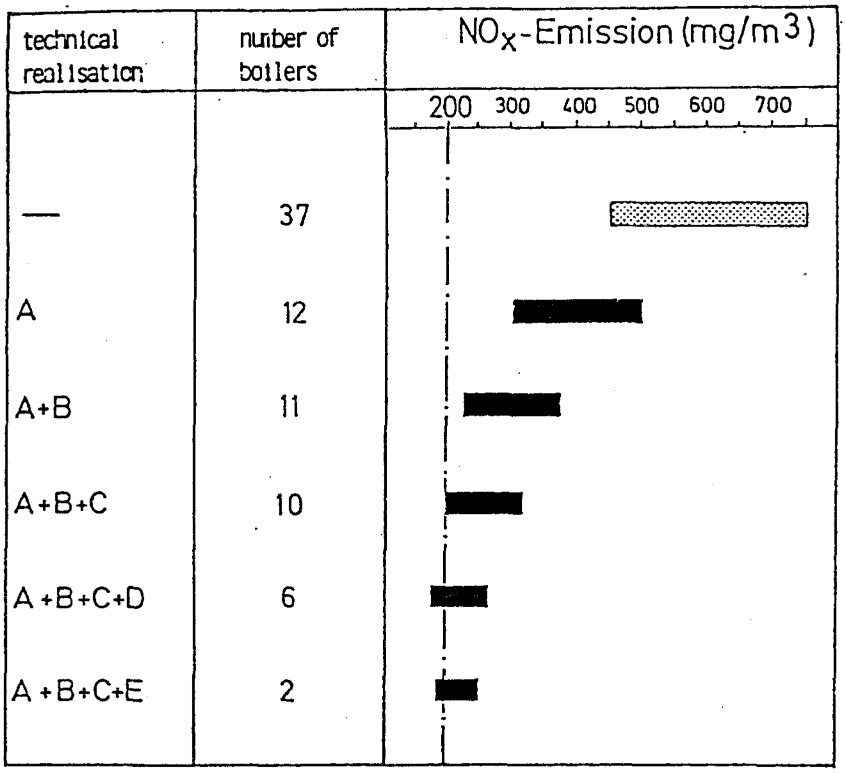


Figure 2.2: NO_x Reduction by Combustion Modifications at Brown Coal Firing Systems in the FRG. Results from Selected Boilers (150 - 600 MWe) (König and Hein, 1988). The resulting emissions show a marked decrease when the different methods are combined.

Table 2.1: Coal Consumption for Power and Heat Generation in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA*)	845.202	t	1987	hard coal2)
	1.760.109	t	1987	brown coal2)
CANADA	36.900.000	t	1987	bituminous and sub-bituminous coals1)
	8.300.000	t	1987	lignite1)
FEDERAL REPUBLIC OF GERMANY	1.236	PJ	1986	hard coal1)
	833	PJ	1986	brown coal1)
FINLAND	5.500.000	t	1988	hard coal2)
ITALY	12.300.000	t	1987	solid fuels except biomass1)
MALTA	350.000	t	1988	hard coal1)
NETHERLANDS	6.200.000	t	1987	hard coal1)
SWEDEN	2.700.000	t	1988	hard coal2)
UNITED KINGDOM	82.460.000	t	1988	hard coal1)
UNITED STATES OF AMERICA	618.400.000	t	1988	bituminous and sub-bituminous coals1)
	69.300.000	t	1988	lignite1)

*) The Austrian use of fossil raw energy depends to a large extent on the degree of power generation from water power plants. The hydroelectric generation of electricity by its own depends strongly to climatic conditions (e.g. rainfall).

1) Power generation
2) Power and heat generation

Table 2.2: Oil and Gas Consumption for Power and Heat Generation in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA*)	516.325	t	1987	oil2)
	1.211.914	kNm^3	1987	gas2)
CANADA	2.850,4	PJ	1987	oil1)
	1.823,9	PJ	1987	gas1)
FEDERAL REPUBLIC OF GERMANY	155	PJ	1986	oil1)
	286	PJ	1986	gas1)
FINLAND	2.500.000	t	1987	heavy fuel oil2)
	1.570.000	kNm^3	1987	natural gas2)
ITALY	19.400.000	t	1987	oil1)
	6.400.000	Nm^3	1987	natural gas1)
MALTA	227.435	t	1987	oil1)
NETHERLANDS	10	PJ	1987	oil1)
	300	PJ	1987	gas1)
SWEDEN	284	PJ	1988	oil2)
	14	PJ	1988	gas2)
UNITED KINGDOM	9.100.000	t	1988	coal equivalent oil1)
	10.000	t	1988	coal equivalent gas1)
UNITED STATES OF AMERICA	33.550.000	t	1988	oil1)
	74.609.000.000	m^3	1988	gas1)

*) The Austrian use of fossil raw energy depends to a large extent on the degree of power generation from water power plants.

1) Power generation
2) Power and heat generation

Table 2.3: Municipal Waste Incinerated in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	216.000	t	1987	(9,4 % of total arising amount)
CANADA	1.280.000	t	1987	
FEDERAL REPUBLIC OF GERMANY	9.100.000	t	1988	
FINLAND	55.000	t	1987	
ITALY	3.200.000	t	1990	(20 % of total)
MALTA	none			
NETHERLANDS	3.100.000	t	1988	
SWEDEN	1.700.000	t	1989	(60 % of municipal waste)
SWITZERLAND[1)]	2.000.000	t	1986	(80 % of total)
UNITED KINGDOM	800.000	t	1988	
UNITED STATES OF AMERICA	18.000.000	t	1987	

1) Bundesamt für Umweltschutz, Switzerland, 1987

Table 2.4: Other Fuels Used for Power and Heat Generation in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	175.163	t	1987	biomass 2)
	7.150.000	Nm^3	1987	landfill gas 2)
CANADA	518	PJ	1987	biomass 1)
FEDERAL REPUBLIC OF GERMANY	none			
FINLAND	4.000.000	t	1987	peat 2)
	2.170.000	t	1988	black and sulphite liquors 1)
	863.000	t	1988	wood 2)
ITALY	none			
MALTA	none			
NETHERLANDS	none			
SWEDEN	60 *)	TWh	1988	biomass 2)
	2	TWh	1988	peat 2)
UNITED KINGDOM	1.000.000	t	1988	biomass 2)
	50.000	t	1988	peat 2)
UNITED STATES OF AMERICA	146.000.000	t	1987	biomass 1)

*) inclusive 44 TWh used as a fuel in industry

1) Power generation

2) Power and heat generation

Table 2.5: Prospected Amount for the Year 2000 for Used Fuels in Member Countries (data provided by member countries; data from Federal Republic of Germany are for 1995)

Country	Amount	Unit	Remarks
AUSTRIA	1.500.000	t	hard coal
	2.100.000	t	brown coal
	400.000	t	oil
	230.000	PJ	gas
	500.000	t	biomass
CANADA	47.500.000	t	hard coal
	10.700.000	t	lignite
	3.138,7	PJ	oil
	2.371,1	PJ	gas
	750.000	t	municipal waste
	589,6	PJ	biomass
FEDERAL REPUBLIC OF GERMANY	1.323	PJ	hard coal
	966	PJ	brown coal
	75	PJ	oil
	283	PJ	gas
	13.000.000	t	municipal waste
FINLAND	10.700.000	t	hard coal
	9.200.000	t	peat
ITALY	28	Mt	hard coal
	14	Mt	oil
	30.000	Mm^3	gas
MALTA			
NETHERLANDS	10.000.000	t	hard coal
	0	PJ	oil
	200	PJ	gas
	7.000.000	t	municipal waste
SWEDEN	400	PJ	solid fuels except municipal waste
	300	PJ	oil
	100	PJ	gas
	2.000.000	t	municipal waste
UNITED KINGDOM	data not available		coal, oil, gas
	1.500.000	t	municipal waste
	1.500.000	t	biomass
	80.000	t	peat
UNITED STATES OF AMERICA	850.000.000	t	hard coal
	54.320.000	t	oil
	159.000.000.000	m^3	gas
	22.100.000	t	municipal waste

2.2.1.1 Fuel Cleaning

Before firing, conventional fuels (coal, oil and natural gas) are sometimes treated to reduce transportation costs, improve combustion characteristics and/or to lower the content of contaminating components, e.g. sulphur, ash.

Hard coal is usually treated by physical processes to reduce the ash-content. A partial removal of inorganic sulphur is often reached as a simultaneous effect. The residual is disposed in land-fills, in many cases in mines.

Table 2.6: Fuel Treatment of Solid Fuels in Member Countries
(data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	none			
CANADA	32.700.000	t	1987	bituminous coal
	none	t	1987	lignite
FEDERAL REPUBLIC OF GERMANY	132.560.000	t	1988	hard coal
FINLAND	none			
ITALY	very little			
MALTA	none			
NETHERLANDS	none			
SWEDEN	none			
UNITED KINGDOM	data not available			
UNITED STATES OF AMERICA	316.000.000	t	1985	hard coal and brown coal (approx. 42 % of coal produced is subjected to some form of physical coal cleaning)

Table 2.7: By-Products from Solid Fuel Treatment in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	none			
CANADA	7.200.000	t	1987	cleaning wastes disposed at mine
FEDERAL REPUBLIC OF GERMANY	58.786.000	t	1988	hard coal cleaning
FINLAND	none			
ITALY	none			
MALTA	none			
NETHERLANDS	none			
SWEDEN	none			
UNITED KINGDOM	data not available			
UNITED STATES OF AMERICA	72.000.000	t	1985	coal

Oil may be desulphurized by adding hydrogen (HDS), forming H_2S in high concentrations. Within a Claus plant H_2S is transformed to marketable elemental sulphur. Therefore for desulphurizing oil, only catalysts used for the chemical processes remain as residuals. Natural gas is often found as "sour gas". It is cleaned by physical and chemical washing processes, finally leading to elemental sulphur too. Table 2.8 gives an overview over generated sulphur in member states.

Table 2.8: Sulphur as a By-product from Crude Oil Fraction and Gas Treatment (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	50.000	t	1989	gas treatment[1)] oil treatment
CANADA	5.900.000 140.000	t t	1986 1986	gas treatment oil treatment (light oil)
FEDERAL REPUBLIC OF GERMANY	952.000 182.000	t t	1988 1986	gas treatment oil treatment
FINLAND	data not available			
ITALY	data not available			
MALTA	none			no treatment
NETHERLANDS	120.000	t	1987	
SWEDEN	40.000	t	1989	oil treatment
UNITED KINGDOM	108.000	t	1986	refinery production
UNITED STATES of AMERICA[2)]	6.200.000	t	1987	

1) BBU included
2) Data provided by Sulphur Institute (Fike, 1989)

In some countries efforts are on the way to separate hazardous components from the waste, for instance mercury containing components, in order to incinerate a less harmful waste.

2.2.1.2 Combustion

The main waste by-product of traditional combustion is slag and/or ash. Furthermore in the case of fluidized bed combustion (see chapter 2.2.1.3) the ash is mixed with the bed material. An overview of amounts of by-products from conventional combustion is given in table 2.9.

Table 2.9: By-Products from Conventional Combustion Systems for Fuels in Member Countries (data provided by member countries, all units metric tons)

Country	Amount		Year	Remarks
	Hard Coal	Brown Coal		
AUSTRIA	80.000	296.000	1989	fly ash
		25.000	1989	total bottom ashes
		20.000	1989	biomass ashes
BELGIUM	1.000.000			
CANADA	910.000	510.000	1987	bottom ash
	2.450.000	1.380.000	1987	fly ash
FEDERAL REPUBLIC OF GERMANY	3.000.000	1.120.000	1989	bottom ash incl. granulates from wet bottom boilers and coarse ashes from dry bottom boilers
	3.000.000	4.480.000	1989	fly ash
FINLAND	550.000		1988	total coal fly ash
		90.000	1987	peat fly ash
ITALY	1.200.000		1989	total ash production
MALTA	6.000		1988	bottom ash
	44.000		1988	fly ash
NETHERLANDS	80.000		1988	bottom ash
	700.000		1988	fly ash
PORTUGAL				
SWEDEN	200.000		1988	fly ash
	150.000		1988	bottom ash
	4.000		1988	fly ash from oil combustion
		40.000	1988	bottom ash
		100.000	1988	fly ash biomass & peat
SWITZERLAND	none		1988	
UNITED KINGDOM	13.000.000		1988	total ash amount production
UNITED STATES OF AMERICA	12.300.000		1984	bottom ash total by-products
	46.300.000		1984	fly ash
	3.800.000		1984	slag

2.2.1.3 Low Emission Combustion Processes

Low emission combustion processes will generate less contaminating components in the flue gas than conventional combustion processes. This can be achieved by different ways such as lowering or rising combustion temperature and/or adding sorbents. These procedures lead to different properties of both the flue gas (not further discussed in this paper) and the products of any following flue gas treatment.

Residuals caused by Fluidized Bed Combustion (FBC) consisting of "bed material" and fly ash have very specific characteristics and have to be evaluated case by case.

By-products can be generated by separating the contaminating components themselves chemically unchanged or by formation of components which contain the contaminating components chemically or physically bound. Table 2.10 shows generated by-products from Fluidized Bed Combustion Systems.

Table 2.10: By-Products from Fluidized Bed Combustion Systems in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	55.000	t	1989	total by-products
CANADA	16.000	t	1989	total by-products
FEDERAL REPUBLIC OF GERMANY	500.000	t	1989	ash and slag
FINLAND	11.500	t	1988	FBC ash
ITALY	none		1988	
MALTA	none		1988	not performed
NETHERLANDS	3.800	t	1984	ash
SWEDEN	60.000	t	1988	fly ash
	20.000	t	1988	bottom ash
UNITED KINGDOM	50.000	t	1986	ash
UNITED STATES OF AMERICA	1.380.000	t	1989	total by-products

Table 2.11 shows the amounts of generated by-products from the coal gasification process.

Table 2.11: By-Products from Gasification Processes in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	none			
CANADA	none			
FEDERAL REPUBLIC OF GERMANY	20.000	t	1987	slag
	7.000	t	1987	fly ash and filter cake
	1.800	t	1987	sulphur
FINLAND	none			
ITALY	none			
MALTA	none		1988	
NETHERLANDS	40.000	t	1994	assumed
SWEDEN	none			
UNITED KINGDOM	none			
UNITED STATES OF AMERICA	data not available			

2.2.1.4 Flue Gas Treatment (FGT)

The following flue gas treatment processes cause by-products having to be utilized or disposed of:

- precipitation of fly ash
- flue gas desulphurization
- flue gas denitrification
- flue gas dehalogenation.

Precipitation of fly ash in the case of solid fuels currently causes the largest amount of residuals from FGT-processes. The quantities and characteristics of fly ashes depend on the properties of the fuel and the conditions of combustion. Very often utilization is possible. Generated amounts can be found in table 2.9.

Wet flue gas desulphurization is the most applied desulphurization process. Its advantages are a high sulphur dioxide removal and, in most cases, a usable by-product.

Dry and quasi-dry desulphurization are also applied in some plants in the USA and in Europe. Possibilities of utilization of by-products caused from this systems are being investigated in some countries.

Catalytic reduction of nitrogen oxides by adding ammonia causes no direct solid or liquid residual. But it must be mentioned that the catalyst itself after the loss of activity has to be renewed, disposed or recycled. Additionally, the properties of fly ash can be influenced in a negative way because of an unavoidable ammonia-slip which could be adsorbed on it.

The following tables 2.12 to 2.13 give a survey of quantities of by-products produced by flue gas treatment processes in some ECE-member nations.

Table 2.12: By-Products from FGD Systems in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA*)	61.000	t	1989	gypsum
	38.000	t	1989	FGD-mixture
	10.000	t	1989	sulphur
	16.000	t	1989	sodium compound
	30.000	t	1989	SO_2
	12.000	t	1989	sulphuric acid
BELGIUM	none		1987	
CANADA	none		1987	
FEDERAL REPUBLIC OF GERMANY	3.000.000	t	1989	gypsum
	500.000	t	1989	FGD-mixture
	30.000	t	1989	sulphuric acid
	40.000	t	1989	SO_2
	60.000	t	1989	sulphur
	4.000	t	1989	ammonium sulphate
FINLAND	30.000	t	1988	FGD-mixture from wet-dry process
	10.000	t	1988	FGD-mixture from LIFAC-process
ICELAND	none		1987	
ITALY	none		1988	
IRELAND	none		1986	
MALTA	none		1988	no process employed
NETHERLANDS	180.000	t	1988	gypsum
	190.000	t	1989	gypsum
NORWAY	none		1987	
PORTUGAL	none		1987	
SWEDEN	80.000	t	1988	FGD-products
TURKEY	none		1987	
UNITED KINGDOM	none		1988	
UNITED STATES OF AMERICA	14.000.000	t	1985	wet lime/limestone scrubbers
	90.000-700.000	t	1985	estimated amounts of utilized by-products, incl. H_2SO_4 from Wellman-Lord, MgO scrubbers and gypsum
YUGOSLAVIA	none		1987	

*) As the Austrian power supply mainly relies on hydro-electric generation, data are not very representative for the long-time average.

Table 2.13: Residues from Combustion, Flue Gas and Waste Water Treatment from Municipal Waste Combustion in Member Countries (data provided by member countries)

Country	Amount	Unit	Year	Remarks
AUSTRIA	15.000	t	1989	fly ash
	120.000	t	1989	slag
CANADA	320.000	t	1987	ash
FEDERAL REPUBLIC OF GERMANY	2.730.000	t	1989	slag
	370.000	t	1989	fly ash and filter cake
	57.000	t	1989	residues from waste water treatment
	3.000	t	1989	recycling salt (NaCl)
FINLAND	20.000	t	1987	slag and fly ash
ITALY	1.000.000	t	1989	
MALTA	none		1988	
NETHERLANDS	900.000	t	1988	slag
	100.000	t	1988	fly ash
SWEDEN	425.000	t	1989	slag
	15.000	t	1989	fly ash
	4.000	t	1989	filter cake
	25.000	t	1989	fly ash and lime products
SWITZERLAND	600.000	t	1987	slag
	40.000	t	1987	fly ash
	6.000	t	1987	slime from flue gas treatment (dry matter)
UNITED KINGDOM	900.000	t	1989	slag
	65.000	t	1989	fly ash
UNITED STATES OF AMERICA	5.000.000	t	1987	slag
	500.000	t	1987	fly ash

2.3 Utilization

The use of by-products as a resource is very important, especially in the long term perspective. It is possible to save natural resources, and areas for disposal sites. Therefore by-product utilization, if possible, should be the first choice.

Any possibility for the utilization of by-products depends on their physical properties and chemical behavior. The following properties of the by-products should be known before making a decision as to which process of flue gas treatment (FGT) is chosen and by this a possible utilization or disposal of the by-product.

Table 2.14: Physical and Chemical Properties of By-Products which should be Examined

Physical Properties	Chemical Properties
moisture content	chemical composition
morphology	trace element content
specific weight	salt content
bulk density	content of hazardous substances
particle size distribution	reactivity
freezing resistance	unburnt carbon
compressive strength	leaching characteristics
shear resistance strength	pozzolanic properties
permeability	toxic effects
deformation	content of buffering subtances
capillarity	pH
radioactivity	
colour	

It is also necessary to be aware not only of the average or typical value of the properties, but also the extent of their variability (Cope and Dacey, 1984). This extent of variability is important for three reasons:

(i) It indicates the degree of flexibility which a disposal or utilization system will need to display, in order to cope with the waste as it arises.

(ii) The extremes of the range of variability may indicate where materials could arise which require special treatment.

(iii) It contributes to the uncertainty involved in any predictions or economic evaluations.

Table 2.15 and table 2.16 list key significant characteristics for by-products of the combustion of coal.

Table 2.15: Key Characteristics for Different End-Products from Coal Combustion (Cope and Dacey, 1984)

	SOLID PRODUCTS								LIQUID PRODUCTS		
Characteristics	Gypsum	Blended cement	Lightweight aggregate	Concrete	Building blocks	Bituminous filler	Lime/cement stabilised fill	Bricks	Sluice water	Pond decant	Landfill/ pond leachate
Physical											
Particle size	/	/	/								
Specific surface area		/									
Bulk density			/	/	/	/	/	/			
Permeability			/	/	/	/	/	/			
Compressive strength	/	(/)	/	/	/	/	/	/			
Rate of strength development				/	/		/	/			
Moisture content	/	/	/	/	/	(/)	/				
Colour	/	/		/							
Chemical											
pH									/	/	/
Trace heavy metals						(/)	(/)		/	/	/
Radioactive trace elements	(/)	/	/	/	/	(/)	(/)	/	/	/	/
CaO	/	/		/							
MgO	/	/	/	/	/						
SO_3	/	/	/	/	/		/		/	/	/
Chloride	/	/		/							

Table 2.16: Key Characteristics for Derived Products from Coal Combustion and FGD-Processes (Cope and Dacey, 1984)

Characteristic	Fly ash	Furnace bottom ash	Boiler slag	Stoker grate ash	FBC bed ash	FBC spent sorbent	FGD scrubber sludge	Dry powder FGD waste	Gasifier ash	Gasifier slag	Liquefaction residues
Physical											
Particle size	/	/	/	/	/	/	/	/	/	/	/
Specific surface area	/				/	/		/			
Mineralogical phases	/	/	/	/	/	/	/	/	/	/	/
Bulk density	/	/	/	/	/	/	/	/	/	/	/
Permeability	/	/	/	/	/	/	/	/	/	/	/
Viscosity							/				(/)
Compressive strength	/	/	/	/	/	/	/	/	/	/	/
Shear strength	/	/	/	/	/	/	(/)	/	/	/	(/)
Moisture content	/	/	/	/	/	/	/	/	/	/	/
Slurry pH	/	/	/	/	/	/	/	/	/	/	/
Colour	/				/	/	/	/			
Chemical											
Major elements:											
SiO_2	/	/	/	/	/	/	(/)	/	/	/	/
Al_2O_3	/	/	/	/	/	/	(/)	/	/	/	/
Fe_2O_3	/	/	/	/	/	/	(/)	/	/	/	/
CaO	/	/	/	/	/	/	/	/	/	/	/
MgO	/	/	/	/	/	/	/	/	/	/	/
Na_2O, K_2O	/	/	/	/	/	/	/	/	/	/	/
SO_3	/	/	/	/	/	/	/	/	/	/	/
Trace heayy metals	/	/	(/)	/	/	/	/	/	/	(/)	/
Radioactive trace elements	/	/	(/)	/	/	/	(/)	/	/	(/)	/
Unburnt carbon	/	(/)	(/)	/	(/)	(/)		/	(/)	(/)	/
Pozzolanicity	/		(/)		(/)	(/)		/		(/)	
Free lime content	/					/	/	/			
Trace organics (PAH etc)					(/)				(/)		(/)

The importance of these and other individual characteristics depends on the specific residual (e.g. if it is fly ash or a FGD-product) as well as on its utilization or deposition potential.

Beside the chemical and physical - in sum technical - requirements five more factors influence a possible utilization (Cope and Dacey, 1982). They were called institutional factors and may be described as follows:

- initiatives from local, national or supranational authorities
- requirements created by standards and codes of practice
- competition from other materials
- matching supply and demand
- attitudes of potential users.

Furthermore the availability of efficient transport and storage systems is a factor which influences the competiveness on the market.

Also environmental aspects are to be considered when the waste material is used e.g. in soil construction works.

In countries with cold climate an additional problem is caused by the production of these products in wintertime, when the conditions for e.g. construction works are not favourable. Moreover, the small power plants produce these products so slowly that buffer storages are requried when wastes are used in soil construction works. This involves additonal costs to the power plant.

Table 2.17 gives an overview about the possibilities of utilization and the state of development.

byproduct disposal/ utilization options	fly ash from hard coal	ash from FBC	fly ash from DAP	product from SAP	gypsum from FGD	residue from WWT	ammonia-sulphate
gypsum industry	filler D				plaster/wallboard gypsum boards S mining mortar D/S		
cement industry	raw material, intergrinding material S			technical anhydrite D	additive S		
concrete and construction material industry	ingredient lightweight aggregate S	ingredient for gas concrete S	ingredient for gas concrete and sand-lime brick D	filler for building brick D	ingredient for gas conrete S		
road building	filler, ingred. S road construction base D/S		road construction base D/S		additive D		
landfilling	fill material D	fill material D	fill material D/S		additive D		
mining	ingredient (mortar) D/S	fill material D		ingredient (mortar) D	fill material D		
fertilizer industry		soil amendment D			soil amendment D		fertilizer S
industrial production	chem. industry (adsorbent) mineral recovery D		sludge neutralization D/S	chem. industry (SO_2-richgas) D			
disposal	disposal is technically feasible for all byproducts						

S... state of the art; D... under development; D/S... suitable, single application

FBC... fluidized bed combustion; DAP... dry additive process; SAP... spray absorption process; FGD... flue gas desulfurization; WWT... waste water treatment

Table 2.17: FGD By-Products and their Utilization/Disposal Options (Rentz, 1988)

2.4 Disposal

2.4.1 General Aspects

Disposal is necessary if utilization of the residuals is not possible or would be too expensive. In the case of utilization by conditioning the residuals often by-products are often created, which have to be removed in a non-hazardous way. So it is obvious that one way will be disposal (Figure 2.3).

Technical criteria for choosing a disposal system are comprehensivly covered by sources such as the U.S. Electric Power Research Institute (EPRI) Coal Ash Disposal Manual (Bahor et al., 1981), the EPRI FGD Sludge Disposal Manual (Baker, 1980) and the EPRI Atmospheric Fluidized-Bed Combustion Waste Management Design Guidelines (Lees et al., 1988). These are particulary oriented towards US practices and reflect the regulatory constraints applicable in the US as well as EC codes, but the technical aspects and range of options available are similar in other countries. For by-products from waste combustion the criteria may be different. Figure 2.4 shows possibilities for the controlled disposal of wastes. Furthermore national standards may influence the way of disposal. (Annex III gives some definitions on terms related to waste and disposal.)

The choice of the convenient kind of disposal for a special not usable by-product mainly depends on the by-product properties. A scheme for the election of a special kind of landfill, which is perhaps the most common form of solid waste disposal currently in practice, is shown in figure 2.5. Careful site selection is the major concern with landfills, and improper site selection is often cited as the major cause of environmental problems with land disposal operations (Department of Energy, 1987). Table 2.18 gives a summary of criteria to be considered in selecting a site.

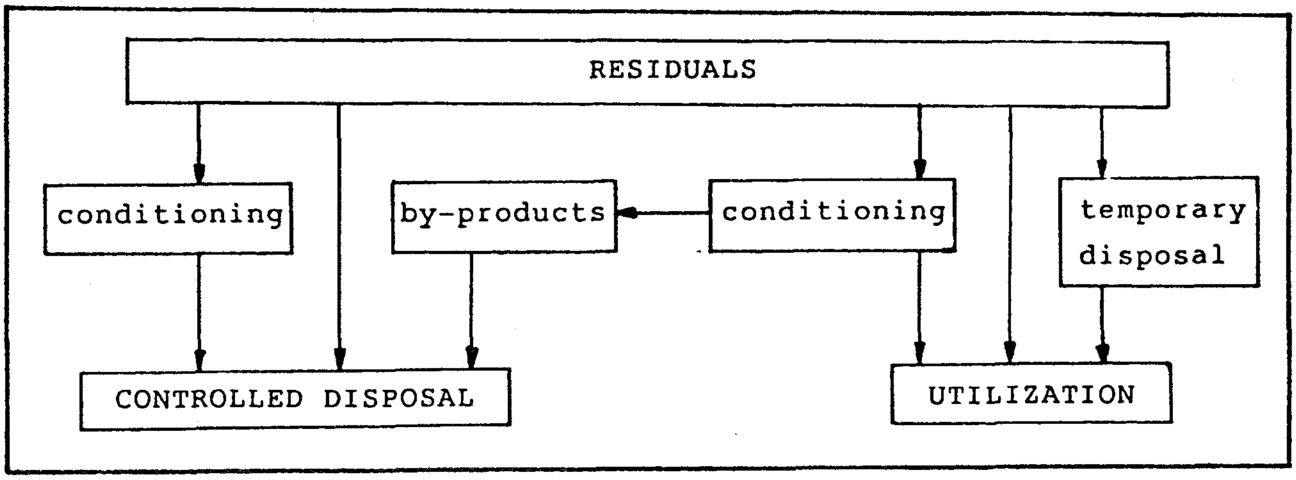


Figure 2.3: Survey of Different Possibilities of Discharging By-Products

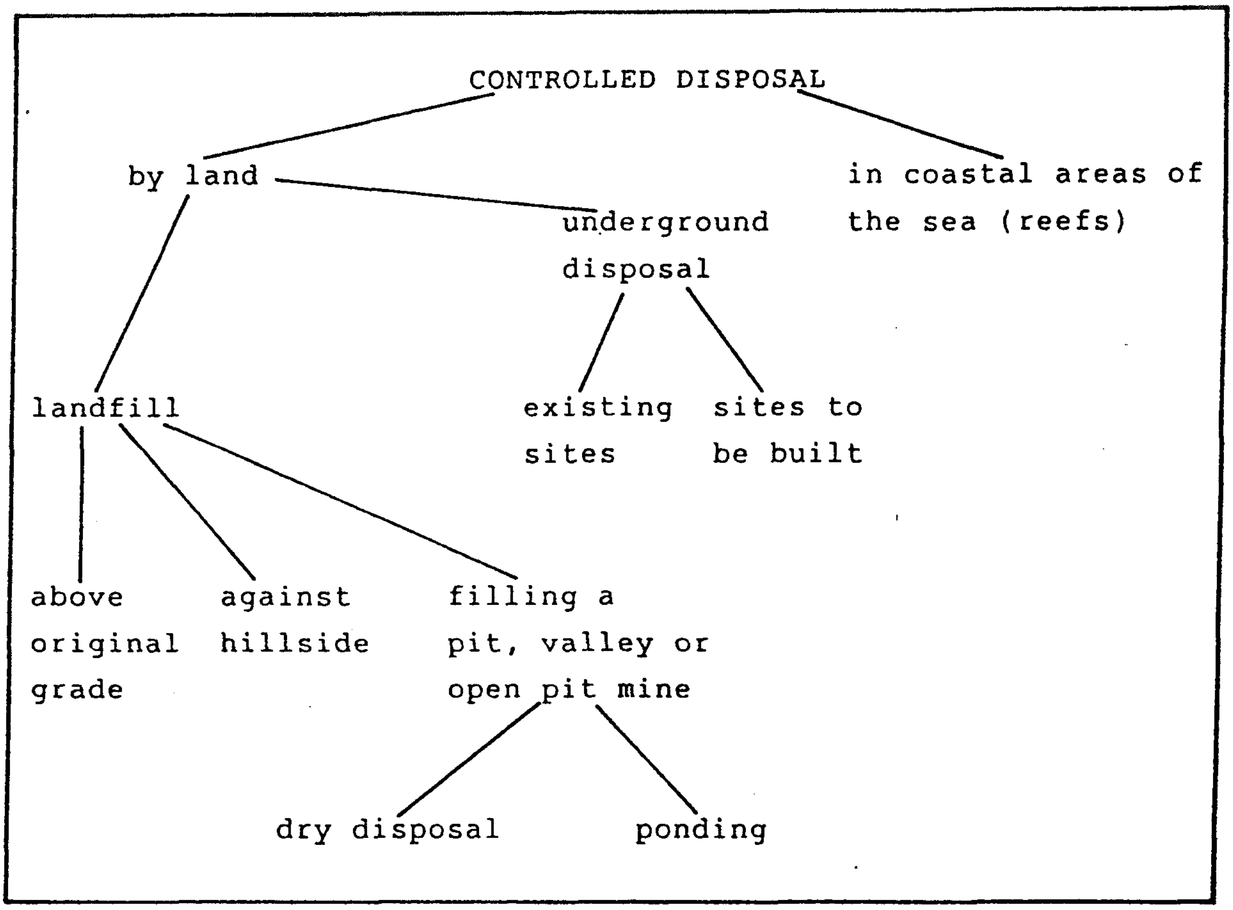


Figure 2.4: Survey of Different Kinds of Depositions According to their Localities

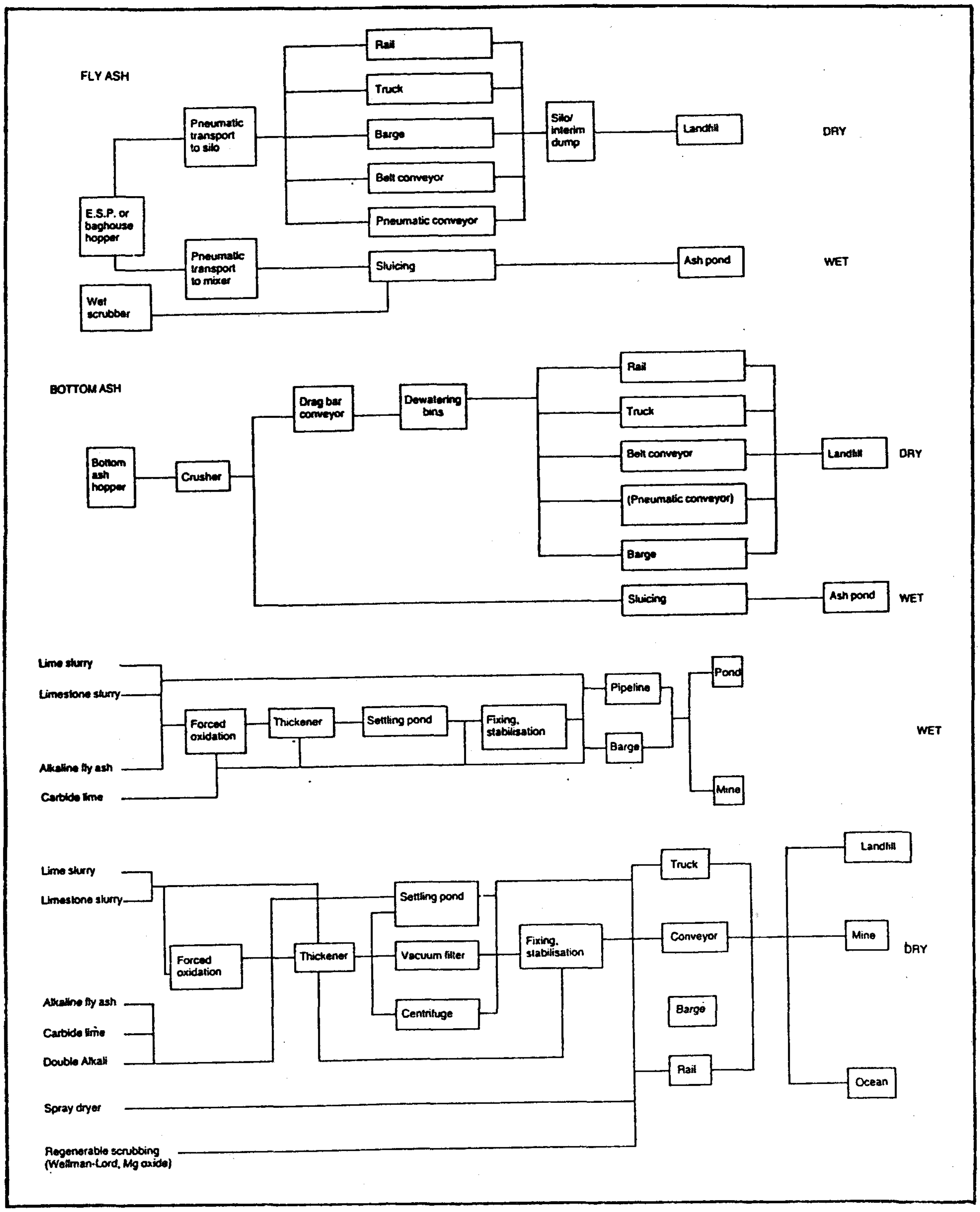


Figure 2.5: Processing, Handling, Transport and Disposal Options for Combustion By-Products (Cope and Dacey, 1984)

Table 2.18: Summary of Criteria Involved in Siting a Deposit (Lundgren and Elander, 1987a)

Siting criteria

- Size, necessary area
- Disposal height
- Transport distance
- Accessibility (e.g. road standard)
- Topography
- Geology (e.g. type of ground and depth of soil cover)
- Geotechnique (e.g. bearing capacity)
- Supply of native soils for covering material

Environmental criteria

- Surface water situation
- Groundwater situations
- Wind conditions
- Terrestric and limnic ecology
- Noise
- Ground use
- Natural amenities
- Landscape value
- Recreation
- Historical interests

Economic criteria

- Ground costs
- Construction costs
- Cost for finishing off deposit
- Operating costs
- Annual cost
- Value of completed deposit

Legal criteria

- Environmental legislation
- Physical land use planning
- Authorities' opinion
- Nearby residents' opinion
- Administrative responsibility

The choice of the convenient kind of deposition for a special residual with its necessary expense depends mainly on the by-product's properties. The following environmental impacts have to be avoided or minimized:

- release of salts to ground and surface water
- release of trace elements to ground and surface water
- radon emission from the deposit
- particle emission from the deposit
- impact on surrounding landscape
- limitation on further land use
- noise emission from vehicles and machines

Figure 2.6 shows possible pathes of toxic substances from a deposit with special emphasis on ways of possible uptake for man.

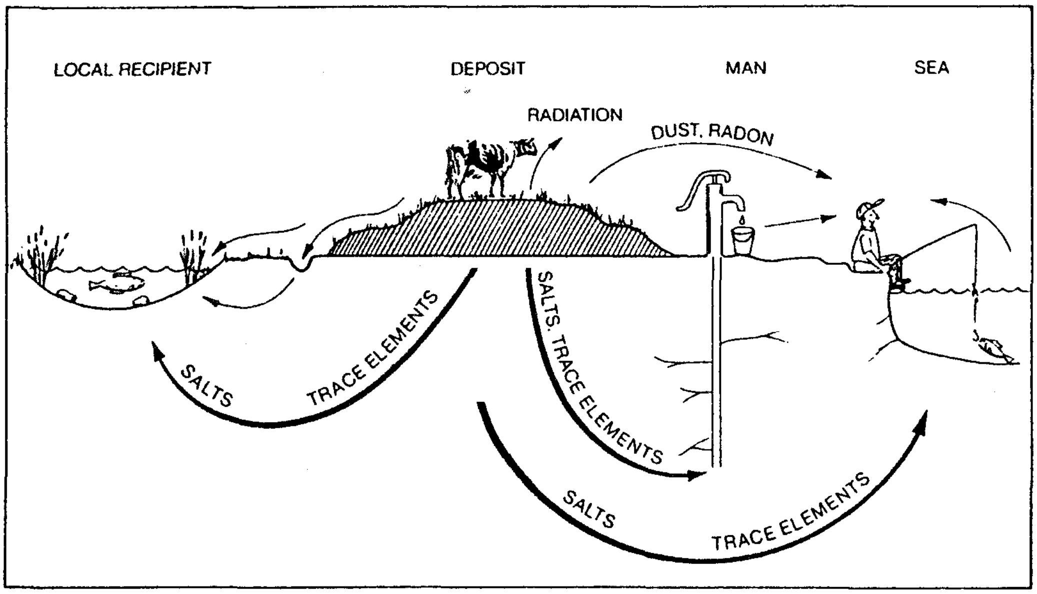


Figure 2.6: Possible Effects of a Deposit on Human Health and Environment (Lundgren and Elander, 1987a)

Besides landfills underground disposal is in use for hazardous waste. Worked out mines, especially saltmines out of work, are of interest for this use as there is no contact with ground water (Sattler, 1982). In the FRG for example parts of the wastes from flue gas treatment of municipal waste combustion are filled in salt mines (Mühlenweg and Brasser, 1990). For liquid wastes impoundments are in practice too (U.S. Department of Energy, 1987).

Additionally ocean dumping is practiced in some countries. Desulphurization by-products and coal fly ash can be disposed in embarkments near the coast in order to get more area in the harbour. The desulphurization waste should be mixed with fly ash and suitable additives to achieve a sufficient stability. Direct contact with the sea water should be avoided until the mixture has hardened (Miljöministeriet, 1985; Johannessen, 1988).

The construction of a subsurface ocean reef of stabilized brick like solids of desulphurization wastes mixed with suitable additives has been studied in the USA and the UK. The physical and chemical behaviour of the blocks in sea water as well as the biological impacts have been studied (Seligman and Duedall, 1979; Woodhead and Parker, 1984). The CEGB (Central Electricity Generating Board) and Southampton University in the UK also are conducting trials in which 8 mini reefs were put in place in Poole Bay in June 1989. The materials tested are

5 : 1 PFA/gypsum and 10 % cement
2 : 1 PFA/gypsum and 10 % cement
PFA/FGD scrubber sludge and 10 % cement concrete.

Although these reefs have only been in place for a couple of months some colonization by fish, crabs and lobsters has already taken place. The results of three preliminary studies in connection with this project show (Kyte, 1989) that

- small pieces of the test materials were placed in Southampton Dock. These were colonized rapidly by a fauna typically of the primary colonizers in the area. There was no evidence of transfer of metal ions from the substrate to the epifauna.

- Diatom bioassay experiments: Samples of concrete or cement stabilized gypsum/PFA and gypsum/PFA/FGD waste water treatment sludge were broken up and 60 g of material which passed a 500 µm sieve shaken with 600 ml seawater for 24 hours, settled for 48 hours and the filtered leachate used to culture diatoms

(Phaeodactytum tricornutum). This represents an extreme worst case for the toxic effects of the leachates. The concrete sample showed some inhibitory effect on diatom growth (due to high pH) but the other materials produced similar growth to the controls.

- Settlement of oyster (Ostrea edulis) larvae on blocks in the laboratory showed concrete to be a less suitable substrate than gypsum/fly ash or gypsum blocks stabilized with cement. The high pH of concrete leachate may again account for the difference.

Artificial reefs of PFA/FGD wastes are colonized rapidly and develop a fauna which will have an increased biomass, compared to a flat seabed, due to the increased structural diversity offered. There is no evidence to suggest that toxicity of the materials will cause problems (Kyte, 1989).

Discussion of the environmental impacts associated with this disposal method is ongoing.

2.4.2 Disposal and Effects on Water

Probably the biggest environmental influence of disposal is that of polluting surface and underground waters. Especially ground water has to be protected in the long run as a possible source of drinking water. Protection of the ground water against contamination is necessary. Though by conditioning of the waste, careful choice of the disposal's position, proper realization of drainage and sealing, and other measures the hazardous effects can be minimized. It must be said, that the potential effects of a controlled tipping to the ground water are in quality just like those of uncontrolled tipped landfills, only much smaller in quantity. Therefore it is of special importance that the position of the landfill be chosen in such a way that the ground water beneath is not already used as drinking water and is not considered as potential source of drinking water for the future.

Considering long term effects it should also be kept in mind that ground water sooner or later will become surface water. Ground water pollution should therefore not exceed ecological effect guidelines which are lower than drinking water criteria (see also table 2.20). Locations near ocean shores often fulfil the requirements that the aquifer be relatively insensitive to moderate levels of contamination by leachate (Hjelmar and Thomassen, 1989).

The pollution can be affected by superficial run-off and leachate during the filling of the site or after closing the landfill.

The amount of leachate that will be produced is affected by the design of the landfill, the pozzolanic properties of the filled by-product, its capillarity and permeability as well as by climatological factors and the way of closing the landfill. In general the rate of leachate flow will increase with time towards a maximum when stationary conditions have arisen and the deposit is more or less saturated with water. Stationary conditions are usually considered only as they cover the longest period and represent the most unfavourable case. In this case the water balance in a landfill, as shown in figure 2.7 can be expressed by the equation

$$\Delta M = P - A - E \text{ (mm/year)}$$

where ΔM = net percolation (equal to leachate flow)
P = precipitation
A = superficial run-off and
E = evaporation

Unfortunately, most of the included parameters are difficult to measure. Only a rough calculation can be made.

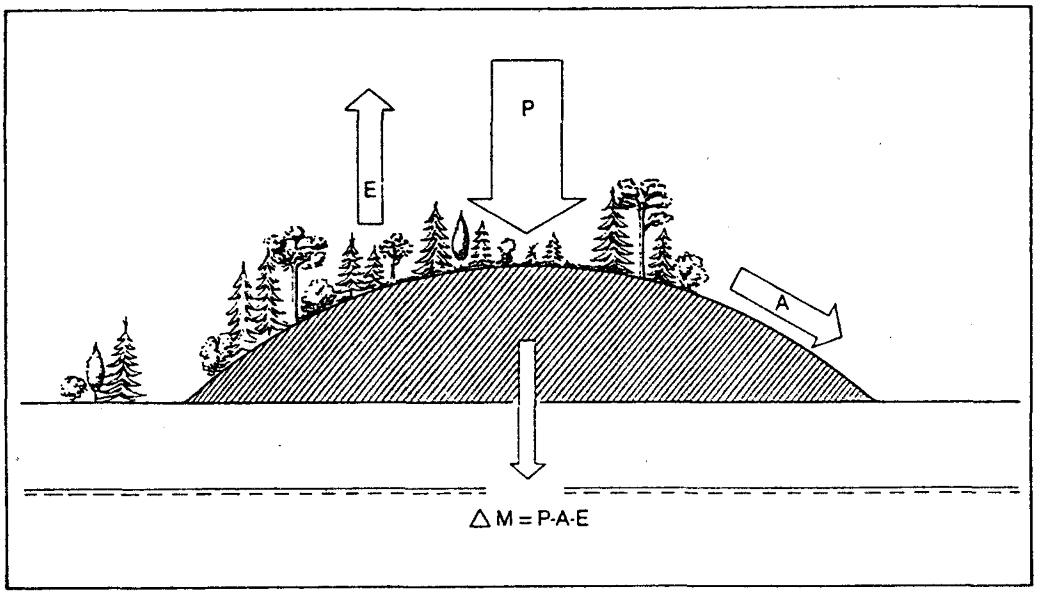


Figure 2.7: Factors Effecting the Water Balance of a Landfill (Lundgren and Elander, 1987a)

Means to reduce leaching and/or run-off and to avoid contact of leachate and water are:

- A mineral layer (e.g.clay) built in the bottom of the deposition. Materials used for it should have a k_f -value below 10^{-9}m/s (Bundesamt für Umweltschutz, 1988; Lechner and Mostbauer, 1989).

- A synthetic material.

- A sealing of good quality can be obtained by a combination of a mineral layer with a synthetic sealing. For municipal waste, for example, two layers of clay (each about 30 cm, k_f 10^{-9}m/s) with a foil above are a good combination of sealings.

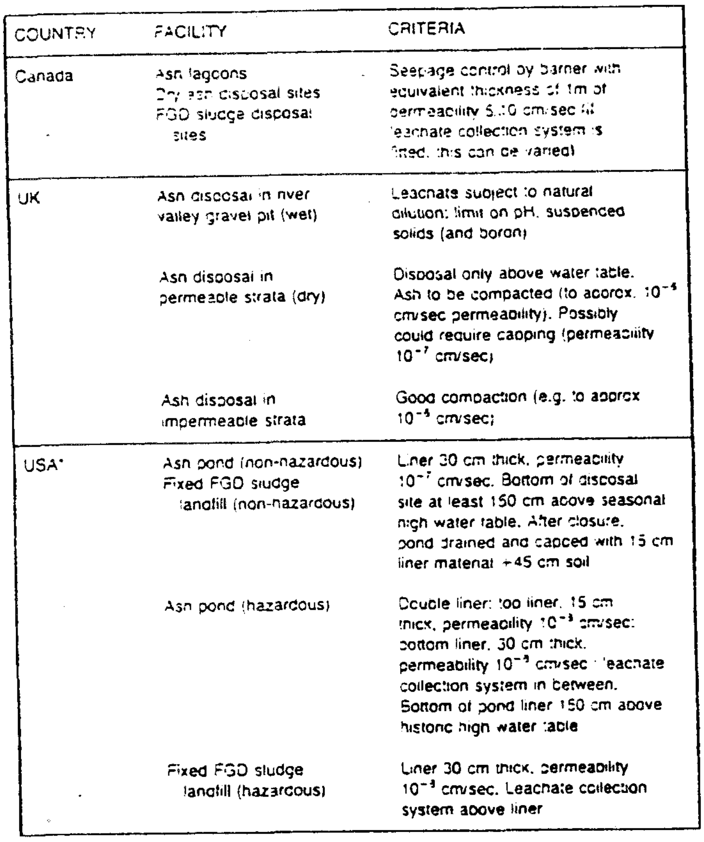
- Surface covering with a capillary layer.

- Drainage above ground sealing and/or under surface sealing.

- Chemical change of the by-products.

Table 2.19 shows how in some countries criteria are set for waste disposal sites to prevent ground water contamination.

Table 2.19: Examples of Containment Criteria for Waste Disposal Sites to Prevent Ground Water Contaminations (Cope and Dacey, 1984)



COUNTRY	FACILITY	CRITERIA
Canada	Ash lagoons Dry ash disposal sites FGD sludge disposal sites	Seepage control by barrier with equivalent thickness of 1m of permeability 5.10 cm/sec (if leachate collection system is fitted, this can be varied)
UK	Ash disposal in river valley gravel pit (wet)	Leachate subject to natural dilution; limit on pH, suspended solids (and boron)
	Ash disposal in permeable strata (dry)	Disposal only above water table. Ash to be compacted (to approx. 10^{-5} cm/sec permeability). Possibly could require capping (permeability 10^{-7} cm/sec)
	Ash disposal in impermeable strata	Good compaction (e.g. to approx 10^{-5} cm/sec)
USA*	Ash pond (non-hazardous) Fixed FGD sludge landfill (non-hazardous)	Liner 30 cm thick, permeability 10^{-7} cm/sec. Bottom of disposal site at least 150 cm above seasonal high water table. After closure, pond drained and capped with 15 cm liner material +45 cm soil
	Ash pond (hazardous)	Double liner: top liner, 15 cm thick, permeability 10^{-9} cm/sec; bottom liner, 30 cm thick, permeability 10^{-9} cm/sec : leachate collection system in between. Bottom of pond liner 150 cm above historic high water table
	Fixed FGD sludge landfill (hazardous)	Liner 30 cm thick, permeability 10^{-9} cm/sec. Leachate collection system above liner

The way, how sealing and drainage are applied has a big influence on the water balance. Figure 2.8 gives an overview how waterflow changes with different measure in disposals situated in an inflow or outflow area for ground water. It can be seen from the drawings that disposals at inflow areas are preferable in view of the reducing quantities of leachate is produced.

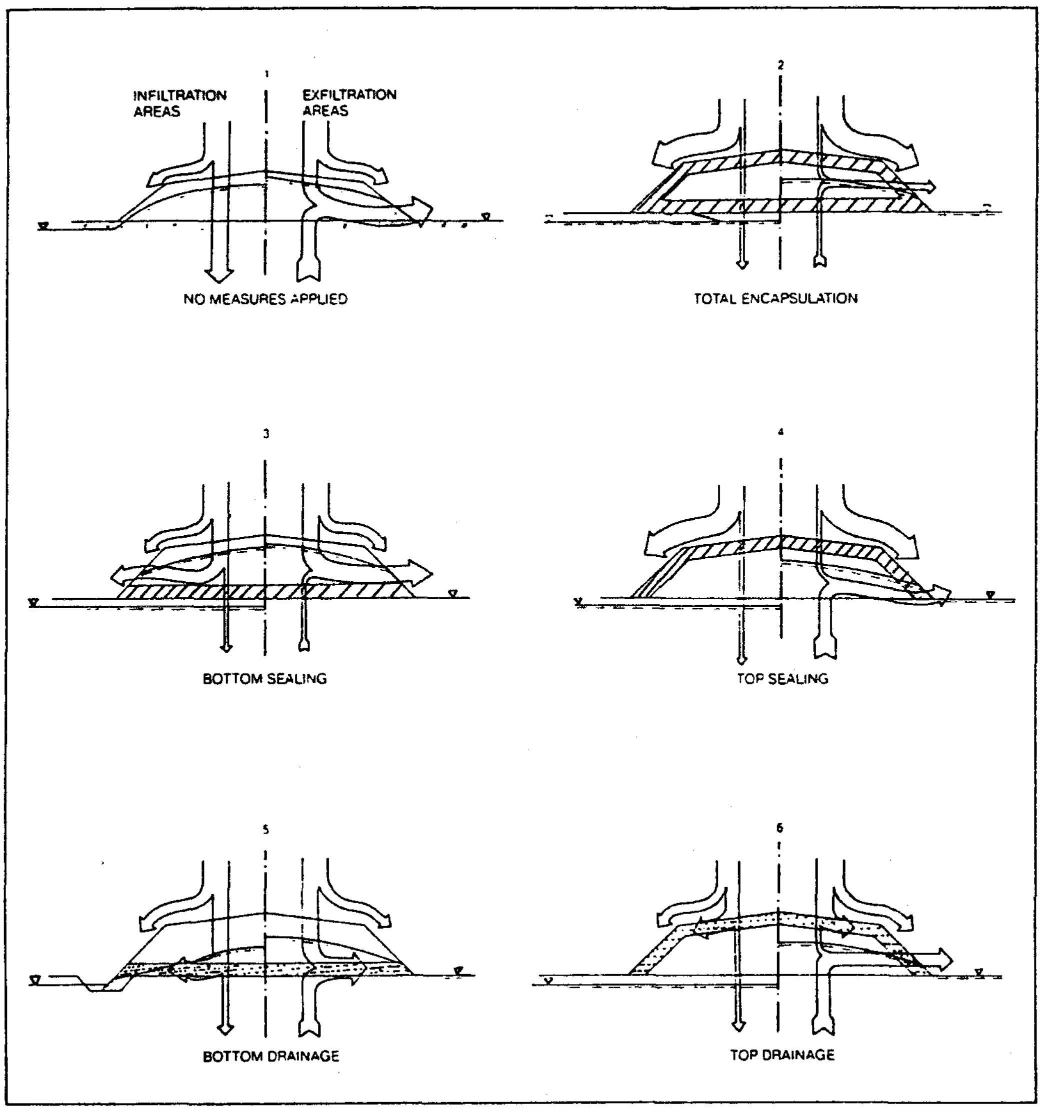


Figure 2.8: General Influence on the Water Balance in a Deposit According to the Type of Site and Different Measures (Lundgren and Elander, 1987a)

Another influence concerning water pollution is the way a disposal site is filled up. One important parameter of filling a deposition is, how thick the layer of residuals tipped into the landfill should be. To get better compression characteristics it is sometimes useful to sprinkle the products with water before they are compacted.

Due to the large quantities of the residuals most depositions are filled segment by segment. One of the advantages of running a landfill in this way is, that segments can be capped and reclaimed thereby minimizing the generation of leachate within a short time.

According to the kind of filling covering can occur in segments or for the whole landfill all at once. In addition a temporary sealing, for every day use, would reduce the quantity of leachate during the period of running.

At least during the reclamation phase it must be decided if further measures are required to minimize fugitive emissions and the negative visual impression of a landfill.

The environmental impacts of a landfill do not end after the period of filling. A forecast of future effects and behavior of a landfill is given in table 2.20. Measures must be taken including the disposal to minimize its hazardous effects. Just after the landfill (or segments of the landfill) has been filled, its surface should be sealed (e.g. with a layer of clay) to reduce the quantity of water trickling into the wastes (in the case of organic waste causing the production of landfill gas, the problem of sealing the surface has also to be considered. This is not further discussed in this report).

Table 2.20: Time Scale of Effects on Water. The forecast is valid on the assumption that recommended measures are applied. Apparently, chlorid and sulphate contents together with pH will be particularly high in a couple of hundred years, while the content of trace elements will be enhanced in thousands of years. Time scales and mechanisms shown below connected with leaching in a dry deposit, 10 m high. Not applicable to colliery deposits or acid washes (KHM). (Lundgren and Elander, 1987a)

Deposit age (years)	Water situation	Leachate formation	pH situation	Leachate situation
0-2	Water is chemically bound, with exothermic reactions producing upward migration of free water.	None or very little.	pH reduction only in the surface layer as a result of carbonate formation.	Leaching from the deposit surface, primarily from exposed areas. Leachate runs off as surface water.
2-100	Unsaturated, non-stationary flow. Formation of wet fronts which move down until complete saturation conditions are established.	Probably insignificant. Capillary forces attempt to produce uniform water content and retain the water until full saturation is established.	Surface pH has fallen noticeably, but only a small amount of the buffer capacity has been utilized.	Leaching taking place, primarily in alkaline environment. Precipitation may occur close to surface of the deposit.
100-1,000	Deposit saturated, with largely stationary flow pattern in the lower parts of the tip.	Maximum leachate formation, balancing infiltration of precipitation in the deposit (50 mm/year).	Predominantly alkaline environment in the deposit, at least in the lower part.	Certain metals enter solution as ion complexes, and can reach relatively high concentrations. Relatively high salt concentrations.
1,000	Deposit saturated, with largely stationary flow pattern in the lower parts of the tip.	Maximum, possibly increasing, due to erosion of the covering layer.	pH reduction has stopped and stabilized at pH 5-8. This value may be higher in deposits with high buffer capacity.	Metal concentrations progressively decrease as pH falls to the neutral level. Moderately high salt concentrations.

2.4.2.1 Leachate

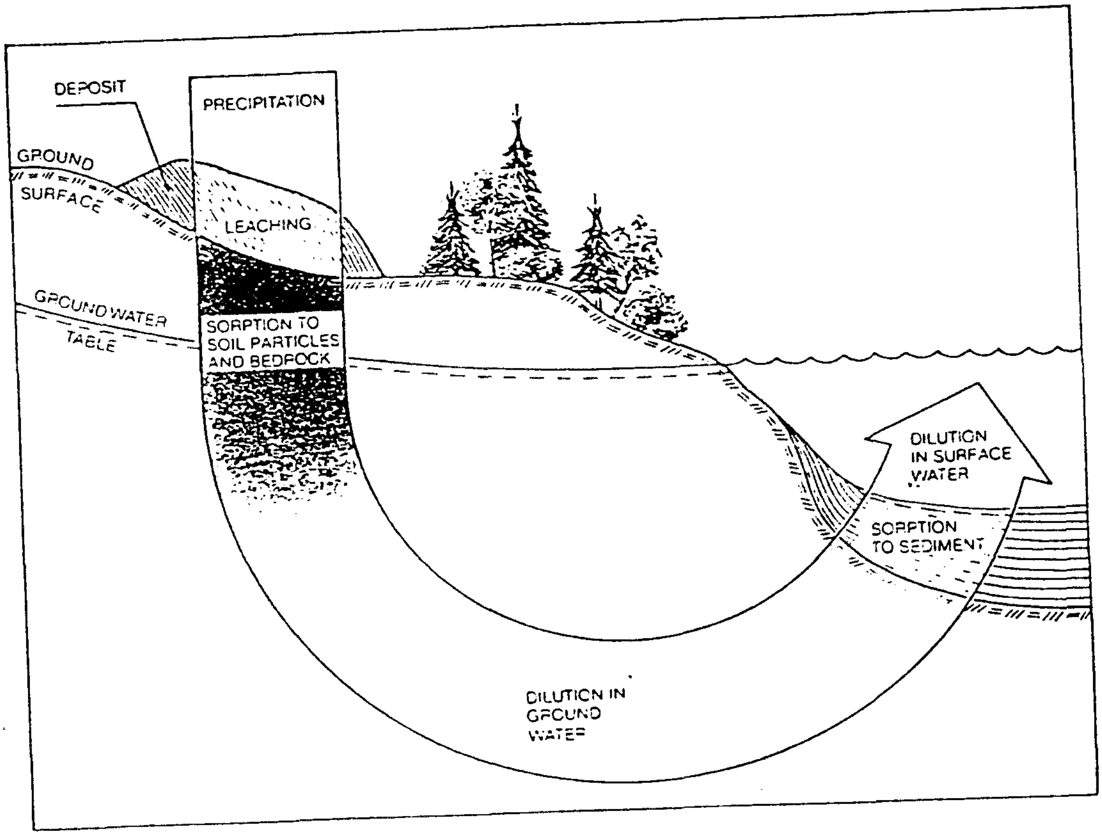


Figure 2.9: Principle Mechanisms which Influence Disposal of Pollutants from a Deposit (Lundgren and Elander, 1987a)

When collecting the leachate arising in a disposal by a drainage system the question may arise how it might be treated to remove its hazardous substances before discharging it into natural surface water. Possible ways are dicussed below.

- No treatment is required or possible: Sometimes it seems advantageous to leave small amounts of leachate to drain naturally.

- Treatment in common with municipal waste water: If the leachate is mixed with municipal waste water there is the risk that the hazardous elements are only diluted in spite of the following sewage plant before inducting into a surface water.

- Treatment in common with industrial waste water: The possibility of co-treatment with industrial waste water must be evaluated case by case, examples having realized this alternative are not available.

- Treatment of the leachate alone: In most cases the treatment of the leachate alone has to be prefered because of its specific characteristics.

Basic informations about choice of applied cleaning technology has to be received from analyses of leachate. The following parameters have to be examined:

- inorganic pollution: dissolved salt concentration
  trace elements concentrations
  radioactive trace elements concentration
- organic pollution: COD, TOC, BOD, EOX
- other physical and chemical parameters: pH-value
  electric conductivity
  toxicity
- biological pollution

Comparing the different characteristics of deposition's waste water it must be said that the leachate of municipal waste depositions contain a large amount of organic pollution, while a negligible portion of organic substances is in the water after trickling through the residuals of a flue gas cleaning process.

On the other hand in most cases the dissolved or, at least under special circumstances, soluble heavy metals are of predominant importance considering the leachate of by-products from flue gas treatment. To give some data table 2.22 lists chemical analyses of leachates of raw by-products. Table 2.23 gives chemical analyses of leachates from the by-products as given in table 2.22 mixes as described in table 2.21. The tables were taken from Roeder et al., 1987. The used leaching procedure is (DEV-S4) to be found in annex I.

Table 2.21: Composition for Two Mixtures for Monodisposals (Roeder et al., 1987)

Monodisposal with dry by-products from dry additive process and spray drying (with $CaSO_3$ and $CaSO_4$)	Monodisposal with waste combustion particulates and fly ashes (with $CaCl_2$)
50,0 parts dry by-product	50 parts of particulates
37,5 parts FBC-ashes	28 parts FBC ashes
12,5 parts cement	22 parts cement
40 % water for binding	42 % water for binding

Table 2.22: Metallic Components of By-Products in mg/kg and in Leachates According to DEV-S4 in mg/l (Roeder et al., 1987)

	FBC Ash		Fly Ash from Dry Additive		Municipal Waste Incineration Dust	
	Remain	Leachate	Remain	Leachate	Remain	Leachate
pH-value	13.2	13.0	n.a.	12.6	12.6	12.7
conductivity (mS/m)	2,870	750	n.a.	945	2,965	1,980
Sb	2.2	< 0.001	5.5	< 0.001	132	0.008
As	14.1	0.001	3.9	0.002	5.8	0.001
Ba	655	0.41	13	0.35	707	3.77
Be	4.5	< 0.01	0.7	< 0.001	< 1.0	< 0.01
Pb	142	< 0.05	222	< 0.05	2,918	17.3
B	262	< 0.01	32	0.66	174	0.09
Cd	< 0.5	< 0.005	< 0.5	< 0.005	188	< 0.005
Cr total	73	0.04	54	< 0.01	106	0.02
CrVI		0.03		< 0.01		< 0.01
Fe solved		< 0.1		< 0.1		< 0.1
Co	18.6	< 0.01	38	< 0.01	7.2	< 0.01
Cu	110	< 0.01	123	0.09	462	0.01
Mn	521	< 0.01	268	< 0.01	482	< 0.01
Ni	63	< 0.05	88	< 0.05	77	< 0.05
Hg	1.41	< 0.0002	0.5	< 0.0002	6.6	0.0017
Se	0.07	0.001	0.2	0.004	0.16	0.006
Ag	< 1.0	< 0.01	2.3	< 0.01	5.6	< 0.01
Tl	0.74	0.004	< 1	< 0.01	< 1.0	0.008
V	157	< 0.01	14	< 0.001	27	< 0.01
Zn	258	< 0.01	280	< 0.01	6,833	4.75
Sn	< 10	< 0.1	46	< 0.1	402	< 0.1

n.a. ... not analyzed

Table 2.23: Analyses of Leachates of Pressed Blocks from the Two Mixtures for Monodisposals According to Table 2.19. Values if not declared in mg/l. (Roeder et al., 1987)

	Mono-deposition for Fly Ash of Powerstations (with $CaSO_3$)		Mono-deposition for Fly Ash of Waste Incineration (with CaCl)	
	Leachate (DEV-S4)	Leachate (pressed block)	Leachate (DEV-S4)	Leachate (pressed block)
pH-value	12.34	11.55	12.91	12.2
conductivity (mS/m)	492	61	1,635	417
COD mg O_2/l	< 15	< 15	< 15	< 15
PAH	0.0008	0.0001	0.0006	0.0004
phenols	n.a.	n.a.	< 0.005	< 0.005
hydrocarbons	n.a.	n.a.	< 0.1	< 0.1
EOX (Cl)	n.a.	n.a.	< 0.1	< 0.01
Ba	0.06	0.05	9.06	1.6
Pb	< 0.05	< 0.05	0.77	< 0.05
Hg	0.0004	0.0003	0.0002	< 0.0002
Zn	< 0.01	< 0.01	0.09	0.04
fluoride	0.76	0.14	0.93	0.27
ammonium	0.23	0.18	0.25	0.11
chloride	745	75	4,300	1,075
cyanide total	< 0.01	< 0.01	< 0.01	< 0.01
cyanide l.f.			< 0.01	< 0.01
NO_3	4.8	< 0.5	0.7	< 0.5
NO_2	0.8	0.47	0.07	0.03
PO_4	0.1	0.21	0.16	0.15
SO_4	< 5	< 5	3.5	< 5
SO_3	7.0	6.0	n.a.	n.a.

n.a. ... not analyzed

As in this paper beside the German DEV-S4 leaching procedure the Swedish leaching test is used, this procedure is also found in annex I. The Swedish leaching test procedure represents a period of about 2000 years leaching in a deposit. Additionally the leachate used in the test is distilled water acidified with sulphuric acid to pH 4 (0,05 mMol) to resemble acid precipitation (Hartlen and Elander, 1986).

Judgement of environmental consequences of the disposal and utilization of by-products cannot be made on the basis of a single batch test extraction alone. Methods based on the determination of intrinsic properties of the materials concerned are more versatile in many respects (van der Sloot and de Groot, 1988).

The release of hazardous compounds from by-products is reduced by a high alkalinity of the products. Unless there is no certainty that ashes will not come in contact with water it would be practical to avoid the formation of acidic ashes by blending the fuel (van der Sloot et al., 1982).

2.4.3 Management of Disposals

Disposal operations can be divided into four stages according to Cope and Dacey (1984):

a) removal from immediate boiler environs
b) transportation to the disposal sites
c) processing (either prior to or after transportation)
d) emplacement at the disposal site.

For all types there is the choice of "wet" or "dry" disposal. Wet disposal would be a redundant option for selfhardening fly ash collected dry.

One question is to be answered before taking a disposal choice: Is the disposal the ultimate choice or is a utilization later on expected. Connected to this is the way of setting up and running a site.

If utilization is planned later on storing in silos may be the first choice for a short time. By-products without any conditioning may be stored at disposal sites without mixing with other wastes.

Co-disposal with other wastes may be an economic advantage. Shortfalls in the production which may result in idle equipment or during summertime can be compensated for by accepting "spot" disposals of other wastes. The possibilities and problems of co-disposal of combustion by-products and other industrial and public wastes - especially non-hazardous inert wastes - are factors to be considered in any waste management evaluation (Cope and Dacey, 1984).

Potential problems from co-disposal arise from two sources:

a) The added complexities which may arise from operating a system which requires the integration of different waste types.

b) The possibility of interactions between by-products and other wastes disposed on sites.

The integration of combustion wastes (especially coal and biomass) collection with other wastes at the same points of waste production already occurs widely with domestic and small commercial waste. Waste disposal operators express generally favourable attitudes (Cope and Dacey, 1984) in handling.

Co-disposal may also give environmental problems. Synergistic effects may occur especially with respect to leachate. In Italy a study concerning co-disposal of coal ash and municipal waste has been performed for fifteen months. According to the results published (Cossu and Serra, 1989), the coal ash reduced the release of heavy metals to the leachate. However, the long term effects are not discussed in the paper.

Some by-products may be disposed without special conditioning. Most of the residuals get better properties for disposing by conditioning. Measures of conditioning include:

- dewatering (e.g. by-products of wet flue gas treatment)
- mixing
- special conditioning
- condensing
- sprinkling
- chemical treatment
- physical treatment

Waste materials, which have pozzolanic properties need to be compacted after conditioning in order to achieve good strength development.

Beside emplacement decisions like siting, preparation, way of filling and final site restoration the measures taken to prohibit environmental damage have to be supervised. The most important items are:

- monitoring of ground water (ground water quality has to started to be examined during initial planning of a landfill)
- monitoring of sealing and draining (starting during construction and going on for operation)
- chemical and physical properties (have to be monitored to avoid tipping if not suitable by-products)
- control of proper draining off of both the leachate and the surface run-off leading it to an appropiate treatment
- dust control

Costs which may arise by avoiding environmental impacts from by-product disposal will facilitate possibilities of utilization.

3 FUEL TREATMENT

Fuel treatment processes as a measure for reducing the concentration of environmental polluting or contaminating substances in the fuel have been applied for many years. Commercially used are treatment processes for hard coal, oil and natural gas.

The main reasons for treatment had been economical and technical ones. For example, treatment of coal increases the heating value per unit and therefore reduces transportation costs per heating value unit. Another example is treatment of sour-gas to protect pipelines from corrosive damage. However, because of the reduction of sulphur components within the fuel, which is a side effect of fuel cleaning processes, this treatment becomes also an environmental one.

3.1 Coal (Hard Coal, Lignite, Brown Coal)

Mainly applied are those processes which reduce the ash content of the coal. Because of the necessity to reduce the SO_2-emissions of firing systems which depend on the content of sulphur in the fuel, technologies have been developed for removal of sulphur compounds in hard coals. The raw coals characteristics and the intensity of treatment will determine the quality of the final product.

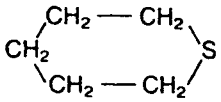
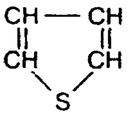
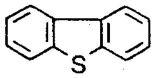
The following principal types of processes for sulphur removal are in industrial application or in research and development:

	Ind. Appl.	R & D
1. physical processes	x	x
2. chemical processes		x
3. biotechnological processes		x
4. combined processes		x

An overview over processes is given by the International Energy Agency/OECD (1985).

Sulphur occurs in coal in both inorganic and organic compounds. The inorganic forms mainly consist of metallic sulphides and sulphates. A major compound is FeS_2 which is either present as pyrite or marcasite. Sulphate may occour from oxidation. Organic sulphur compounds are an integral part of the molecular structure of the coal. Table 3.1 gives an overview over main occuring organic sulphur compounds.

Table 3.1: Main Groups of Organic Sulphur Compounds Present in Coals (Kargi, 1982)

Compound	Chemical composition
ethanethiol	CH_3CH_2SH
2-propanethiol	$(CH_3)_2-CHSH$
benzenethiol	C_6H_5SH
diethyl sulphide	$CH_3CH_2S\ CH_2CH_3$
thiocyclohexane	
diethyl disulphide	$CH_3CH_2SS\ CH_2CH_3$
dimethyl disulphide	$CH_3SS\ CH_3$
thiophene	
dibenzothiophene	

Coals vary, as does the amount of sulphur. Both, inorganic and organic sulphur can be present in variable proportions and in different chemical and physical forms. Therefore it is essential to characterize fully any coal before considering the most appropriate method of desulphurization (Couch, 1987).

3.1.1 Physical Processes

By physical processes the inorganically bound sulphur can be removed to a certain extent. About 20 to 80 % of pyritic sulphur is removable. The site specific value has to be estimated case by case and is dependant on the different coal properties. Pyrite which is in most cases the inorganic substance containing sulphur has a higher specific weight than the other parts of the coal. Therefore by physical processes done by

- settling down
- cyclones
- jigs
- tables

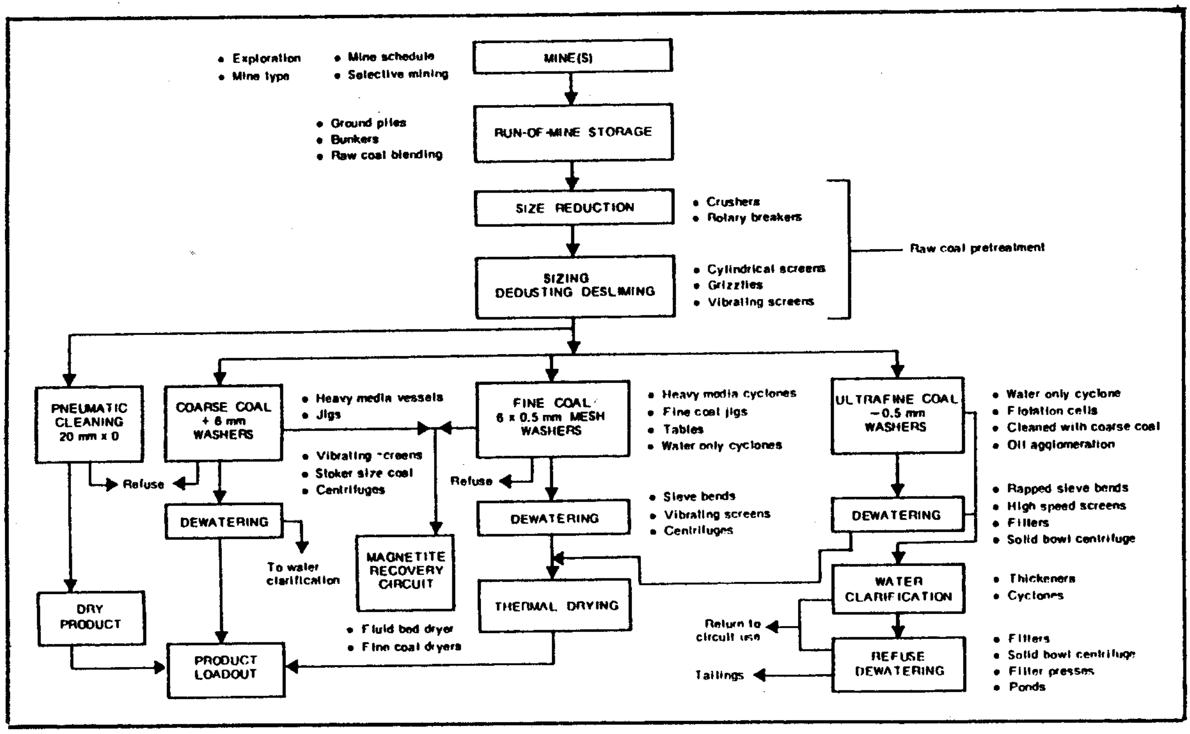
most of the pyritic fraction can be separated from coal. Parameters of these processes are

- the dispersion of the pyritic parts in the coal
- the degree of coal crushing.

Another physical process, flotation, depends first of all on different surface properties.

Figure 3.1 shows the range of options of physical coal cleaning. The raw coal will be crushed and together with the coalfines from a classifier led to a centrifugal separation in cyclones. The heavy fraction then goes to a vibrating table where the coal particles are separated from the ash containing and pyritic particles which are deposited. The lighter fractions go to a flotation unit separating the small coal particles from where they are led to a drumfilter, dewatered and combined with the pile of concentrated coal.

In its application to pyrite removal one has to overcome the problem that pyrite has similar surface properties to coal. Therefore conditioning of the coal (or pyrite) would be necessary for using this removal procedure. Flotation can be applied for the separation of very small coal-particles.



<u>Figure 3.1:</u> Physical Coal Cleaning - Range of Options (International Energy Agency/OECD, 1985)

The advantages of the physical processes are:

- comparatively cheap
- increasing heating values
- lowering transport volume, weight and cost.

The disadvantages of desulphurizing coal by physical processes are:

- organically bound sulphur is not removed
- the higher the pyrite removal rate the higher the cost (e.g. for the necessary degree of coal crushing)
- with the pyritic particles also some coal particles will be removed causing a considerable loss of fuel.

Physical coal treatment processes are applied in several countries for reducing the ash-content having a simultaneous effect in removing the pyritic sulphur content.

The residuals are usually disposed in any kind of landfill, often filling a mine.

Table 3.2 lists some data on amounts of coal subjected to physical coal cleaning processes in the United States. Table 3.3 shows the achievable reduction of SO_2 by actual physical coal cleaning in the U.S.A. Table 3.4 shows the effect of the float-sink separation for different elements. Table 3.5 gives projected amounts of treated fuels for the year 2000, table 3.6 projected amounts of by-products of solid fuel treatment.

Table 3.2: Amounts of Coal Physically Cleaned in U.S.A (Science Application International Corporation, 1987)

NORTHERN APPALACHIAN COAL PREPARATION (1983)

Area	Quantity Produced[a,b]	Percentage Mechanically Cleaned	Percentage Crushed and Screened	Percentage Not Prepared
Maryland	5,39	58	26	16
Ohio	33,39	82	14	4
Pennsylvania	64,35	65	25	10
TOTAL	103,13	70	22	8

CENTRAL APPALACHIAN COAL PREPARATION (1983)

Area	Quantity Produced[a,b]	Percentage Mechanically Cleaned	Percentage Crushed and Screened	Percentage Not Prepared
Eastern Kentucky	50,7	57,4	26,8	15,8
Tennessee	4,2	80,0	20,0	0,0
Virginia	25,0	76,8	15,6	7,6
West Virginia	121,0	79,5	18,6	1,9
TOTAL	200,9	73,5	20,3	6,2

MIDWESTERN COAL PREPARATION (1983)

Area	Quantity Produced[a,b]	Percentage Mechanically Cleaned	Percentage Crushed and Screened	Percentage Not Prepared
Illinois	63,0	93	6	1
Indiana	33,7	78	17	5
Western Kentucky	36,5	72	18	10
TOTAL	133,2	83	12	5

[a] Quantity is in millions of raw metric tons.

[b] All values include only mines producing more than 90,700 (100,000) metric tons of coal per year and reporting on Form EIA-7A Supplement.

Table 3.3: Current Reduction of SO_2 Achievable by Pysical Coal Cleaning (U.S.A)
(Science Application International Corporation, 1987)

Region State	Quantity of Coal Cleaned* (Thousand of Clean Metric Tons)	Quantity of SO_2** in the Raw Coal* (Thousands of Metric Tons): Input to Mechanical Cleaning Plants	Removed Through Mechanical Cleaning	Remaining in the Clean Coal
Appalachia				
North:				
Ohio	19.317	2.175	741	1.434
Pennsylvania	29.689	1.838	894	944
West Virginia	62.745	2.875	943	1.932
South:				
Alabama	13.377	397	55	342
Eastern Kentucky	18.067	431	185	246
Tennessee	1.919	81	58	23
Virginia	11.186	243	45	198
TOTAL	156.300	8.040	2.921	5.119
Midwest:				
Illinois	43.448	3.877	1.463	2.414
Indiana	19.588	1.466	204	1.262
Western Kentucky	19.599	2.163	848	1.315
TOTAL	82.635	7.506	2.515	4.991
West:				
Colorado	1.434	27	10	17
Missouri	2.362	363	130	233
New Mexico	145	3	1	2
Utha	1.367	24	12	13
TOTAL	5.308	417	153	265
Grand Total	244.243	15.963	5.589	10.375

* ..... includes only coal and SO_2 produced by operations at mines over 90.700 metric tons (1983)

** ..... SO_2 equivalent of the sulphur content assuming that all sulphur contained would be released as SO_2 upon consumption

Table 3.4: Distribution of Elements in Float-Sink Separation of Illinois Coals at Varying Specific Gravity to Achieve 75 Percent Weight Recovery (Buhl and Perlsweig, 1988)

	Concentration (ppm unless otherwise stated)			Concentration Factor	
Element	Raw Coal	Clean Coal	Refuse	Clean Coal(1)	Refuse(2)
Al	2.3 %	0.5 %	7.8 %	0.22	3.39
Ca	0.38 %	0.07 %	1.32 %	0.19	3.47
Fe	2.9 %	0.80 %	9.3 %	0.28	3.21
K	0.28 %	0.09 %	0.87 %	0.32	3.11
Mg	81.2	34.5	215.1	0.42	2.65
Na	400	200	1000	0.50	2.50
P	20.9	19.2	26.2	0.92	1.25
S	4.4 %	1.6 %	12.9 %	0.36	2.93
Si	4.2 %	0.9 %	14.2	0.21	3.38
Ti	1300	450	3900	0.35	3.00
As	11.5	1.5	41.0	0.13	3.57
B	28.7	31.7	19.8	1.10	0.69
Be	3.0	2.9	3.3	0.97	1.10
Cd	2.0	0.2	7.2	0.10	3.60
Co	5.8	3.0	14.2	0.52	2.45
Cr	14.0	8.7	29.9	0.62	2.14
Cu	29.1	16.2	68.1	0.56	2.34
Ga	3.0	2.7	4.1	0.90	1.37
Ge	6.7	8.1	2.3	1.21	0.34
Hg	0.28	0.07	0.92	0.25	3.29
Mn	69.6	7.4	258	0.11	3.71
Mo	11.5	3.8	34.8	0.33	3.03
Ni	30.5	19.6	63.5	0.64	2.08
Pb	110	22	377	0.20	3.43
Sb	0.57	0.34	0.87	0.60	1.53
Se	2.8	1.3	7.3	0.46	2.61
V	15.2	9.1	33.4	0.60	3.67
Zn	510	12.0	2019	0.02	3.96
Zr	3.6	1.9	8.8	0.53	2.44

(1) Ratio of contaminant concentration in clean vs. raw coal

(2) Ratio of contaminant concentration in refuse vs. raw coal

Table 3.5: Projected Amounts of Treated Solid Fuels for the Year 2000 (data provided by member countries, all values given in metric tons)

Country	Actual Amount	Amount 2000	Remarks
AUSTRIA	(no fuels are treated)	none	
CANADA	32.700.000	42.000.000	only bituminous coals are cleaned
	none	none	lignite
FEDERAL REPUBLIC OF GERMANY	132.560.000	130.000.000	hard coal
FINLAND			
ITALY	very little	1.800.000	lignite
MALTA	(no fuels are treated)		
NETHERLANDS	none	none	
SWEDEN	none	none	
UNITED STATES OF AMERICA	316.000.000	data not available	hard coal and brown coal (approx. 42 % of coal produced is subjected to some form of physical coal cleaning)

Table 3.6: Projected Amounts for the Year 2000 for By-Products Resulting from Solid Fuel Treatment in Member Countries (data provided by member countries, all values given in metric tons)

Country	Actual Amount	Amount 2000	Remarks
AUSTRIA	none	none	
CANADA	7.200.000	9.260.000	hard coal cleaning
FEDERAL REPUBLIC OF GERMANY	58.786.000	57.000.000	hard coal cleaning
FINLAND			
ITALY	none	data not available	
MALTA	not applicable	not applicable	
NETHERLANDS	none	none	
SWEDEN	none	none	
UNITED STATES OF AMERICA	72.000.000	data not available	coal

3.1.2 Chemical Processes

There are chemical techniques for the reduction of sulphur compounds in coal available as well, but these are generally energy-intensive or economically unattractive. Oxidative methods involve oxidation with air, which causes soluble sulphates. Reduction methods achieve reduction to hydrogen sulphide (H_2S). Other possible chemical processes involve reaction at high temperature with alkali carbonates, bicarbonates or hydroxides to produce soluble salts.

Much of the organic sulphur can be removed by hot diluted sodium carbonate containing dissolved oxygen under moderate pressure (Monticello and Finnerty, 1985; Markuzewski et al., 1981). Sulphur which is tied to organic ring structures is difficult to remove even by chemical methods.

Contrary to the physical processes chemical processes are not applied in commercial plants. But the necessity of enhanced desulphurization (alternatively by fuel treatment and/or by flue gas treatment) causes considerable activities in R & D of chemical processes for coal desulphurization. The most promising chemical process investigated in bench-scale tests is an alkali leaching of the sulphur with a possible application to lignites with high sulphur content.

Compared to flue gas desulphurization at present chemical coal cleaning is more expensive on lower degree of sulphur removal achievable. Therefore chemical coal cleaning probably is profitable only for low price coal with rather high sulphur content (Couch, 1987). Table 3.7 lists some chemical coal cleaning processes which have been developed recently.

Because of the early stage of development consideration of residuals of chemical and biotechnological coal treatment processes is difficult. However, it is expected that the quantities caused by these processes are much smaller than those caused by physical processes for coal cleaning.

Table 3.7: Chemical Coal Cleaning Processes (Umweltbundesamt Berlin, 1980)

Process	Short Description of Process	Sulphur Reduction Phyrit	Sulphur Reduction Org. Sulphur	State of Development
Meyers TRW Inc. Redondo Beach, California	oxidizing leaching by ferrous(III)sulphate regeneration of ferrous(III) sulphate by oxygen	90 - 95 %		pilot plants
Ledgemont Kennecoll Copper Co.	oxidizing leaching by oxygen in aqueous solution at high temp. and pressure	95 %		pilot size
GE General Electric Co	irradiation by microwaves and formation of soluble sulphid by reaction with NaOH	75 %	75 %	pilot size
Batelle Batelle Columbus	alkaline leaching	95 %	25-50 %	pilot plant 9 kg/h Ohio
JPL Jet Propulsion Pasadena, Calif.	oxid. by chlorine in presence of organic solvents	90 %	70 %	pilot size
IGT Institute of Gas Technology, Chicago	oxidizing pretreatment hydrodesulphurization	95 %	85 %	pilot size
KVB KVB, Inc. Tustin	oxid. by nitrous gas and subsequential scrubbing of generated sulphates	95 %	40 %	laboratory size
ERDA ERDA, Bruceton Pa.	oxid. by air leaching under high pressure and temp.	95 %	40 %	pilot size
Syracuse Syracuse Research Co, Syracuse, N.Y.	"chemical crushing" by wet ammonia, subsequential physical separation	50 - 70 %		pilot plant
Magnex Hazen Researach Golden, Colorado	treatment of coal by iron pentacarbonyl increases magnetizability of phyrite	90 %		pilot plant 90 kg/h

3.1.3 Biotechnological Processes

Some bacteria species are able to reduce both the inorganic and/or organic sulphur content by oxidation. It is possible to remove about 90 % of the pyritic sulphur from finely milled coal. Figure 3.2 gives a short scheme for microbial action on coal. Alternatively, microorganisms can improve the separation of pyrite in a conventional flotating process in a matter of minutes. Beneficial side-effects of microbial desulphurization can be the simultaneous removal of certain metal ions and of ash, and increased ash fusion temperatures (Couch, 1987).

A possible advantage may be that extracted sulphur can be recovered and used as raw material.

No commercial plant has yet been planned but an economical attractive microbial desulphurization process for certain coals could well emerge during the next years.

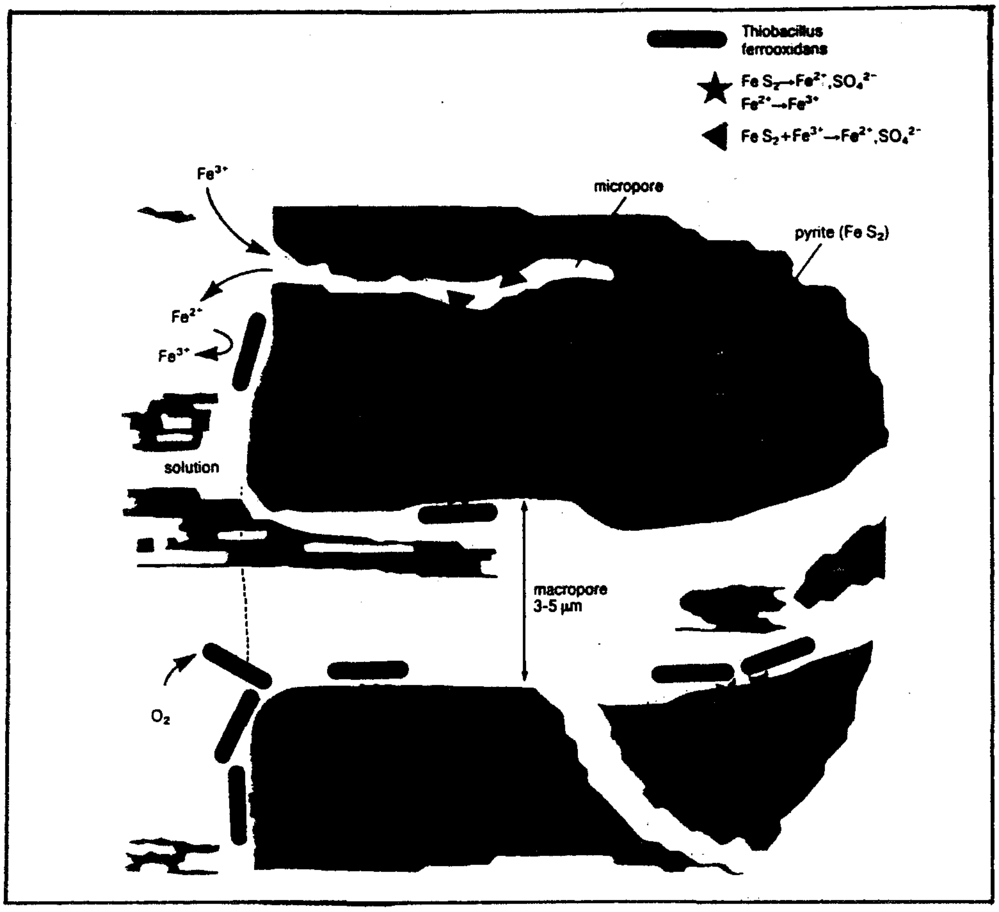


Figure 3.2: Possible Process Scheme for Microbial Coal Desulphurization (Kargi, 1982)

The figure shows the oxidation of pyrite through attack by Thiobacillus ferrooxidans *and through chemical attack. Although some pores and transport channels in coal are accessible to the smaller organisms, the evidence to date is that the reaction rates are a function of the external surface area. This may be partly because most of the desulphurisation work has been done on bituminous coals where much of the pore structure is below 1.2 nm diameter.*

Thiobacillus *and* Sulpholobus *have diameters around 200 to 500 nm which means that they are too large to penetrate anything other than large cracks on the coal surface.*

Whilst work at Bergbau-Forschung has indicated the possibility of reaction inside pores, there is little evidence that coal porosity has any contribution or effect on the bio-reactions observed to date.

3.2 Oil

Desulphurization of oil usually works with a hydrodesulphurization process (HDS) within the refinery. A flow sheet of a refinery processing crude oil including the HDS-technique is given in figure 3.3. The sulphur content of the light and middle oil destillates is thereby transformed into H_2S gas at high pressure with the help of catalysts (the heavy oil fractions content of heavy metals often is removed before). With the exception of the exhausted catalysts no residuals are caused by this process.

A study made in Canada in 1983 gives a possible reduction of 43.800 tonnes/year sulphur in light fuel oil and lighter products with investment costs of total 52.4 million dollars to receive 0,1 weight% in this product (Environment Canada, 1983).

Desulphurization of heavy residues (atmospheric and vacuum residues) from destillation is done in some Japanese oil refineries and in a few refineries in the U.S.A. (see table 3.8), but not yet in Europe.

Table 3.9 gives data on present and projected amounts of by-products generated by for gas and oil treatment.

Table 3.8: U.S. Heavy Oil Treatment Capacity
(Perlsweig, 1989)

Hydrocracking	1.025.400	Barrels/day
Hydrorefining/Hydrotreating	4.167.450*	Barrels/day
Coking	1.267.500**	Barrels/day

* Approximately 50 % of capacity is utilized for heavy oil. Oil and Gas Journal Report, March 21, 1988.

** Coke production capacity is on the order 70.000 tons per day. Nearly all the coke is utilized either as a fuel or for anodes for aluminium manufacture. Two thirds of the coke produced in the U.S. is exported.

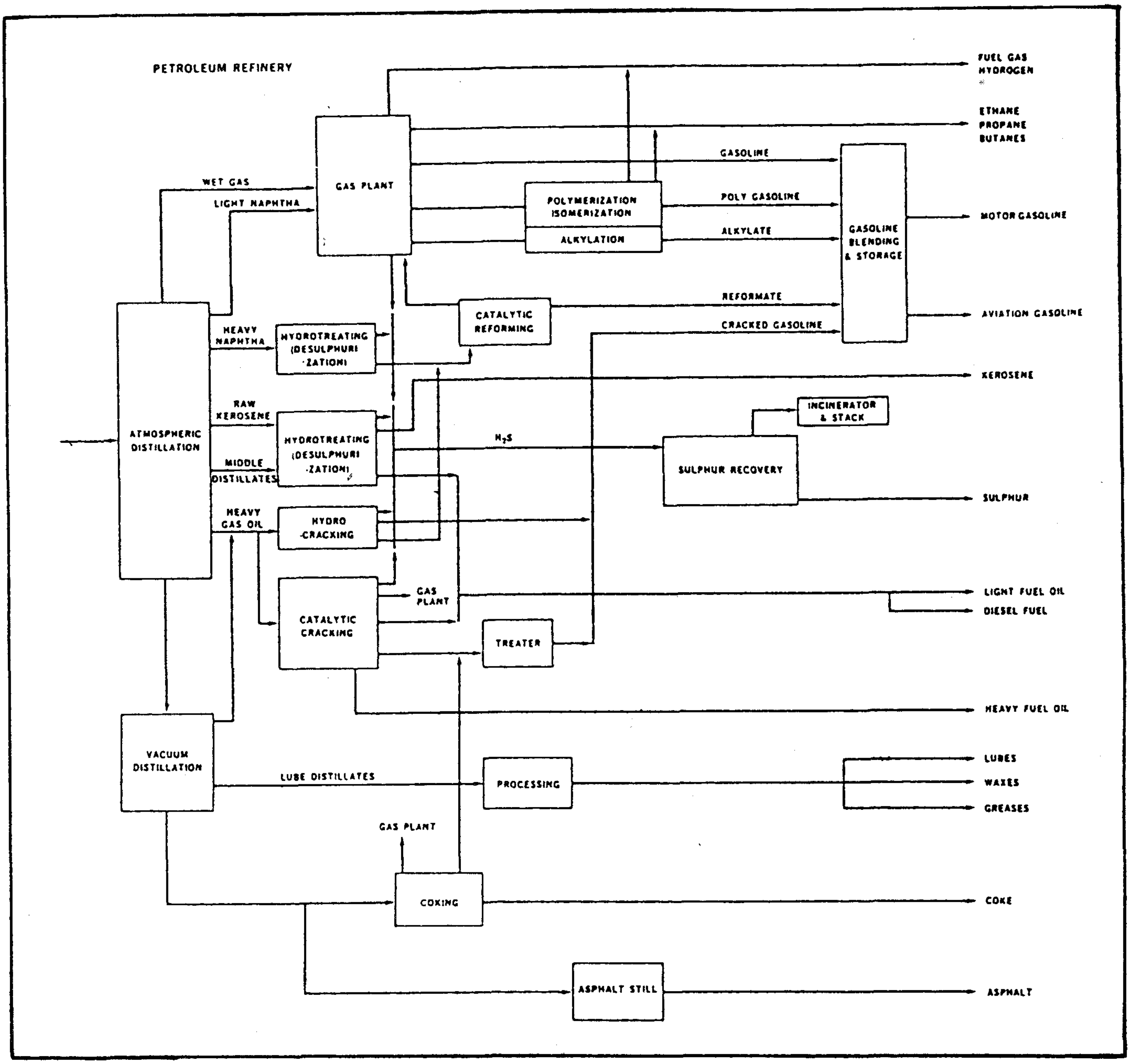


Figure 3.3: Desulphurization of Light and Middle Destillates in a Simplified Petroleum Refinery Process Flow Diagram (Environment Canada, 1987)

Table 3.9: Projected Amounts for the Year 2000 for Sulphur from Crude Oil Fractions and Gas Treatment in Member Countries
(data provided by member countries, all values are given in metric tons)

Country	Actual Amount	Amount 2000	Remarks
AUSTRIA	50.000 (total)*)	20.000 20.000	gas treatment sulphur oil treatment sulphur
CANADA	5.900.000 140.000	7.670.000 170.000	gas treatment sulphur oil treatment sulphur
FEDERAL REPUBLIC OF GERMANY	952.000 182.000	900.000 160.000	sulphur from gas treatment sulphur from oil treatment
FINLAND	41.000	data not available	sulphur from oil treatment
ITALY	data not available	data not available	
MALTA	not applicable	none	
NETHERLANDS	120.000	data not available	
SWEDEN	40.000	data not available	sulphur from oil treatment
UNITED KINGDOM	108.000	108.000	refinery production
UNITED STATES OF AMERICA	6.200.000	6.200.000	

*) value inclusive flue gas treatment of BBU

3.2.1 R & D Projects

Biotechnological processes must be kept in mind as a possible technology in the future for desulphurization of oil. Because of the enormous development of biotechnology and genetics it might be possible that special microorganisms are selected or produced which enable biotechological commercial plants for at least special types of crude-oil and/or products.

Another process for desulphurization of petroleum being investigated works with plasma oxidation. The sulphur compounds are oxidized and form a second phase which can easily be separated on the basis of its higher specific gravity (Suhr et al., 1987). Further investigations had been stopped in 1988.

3.3 Gas

The different types of natural gas vary greatly in their properties. Most of them have to be treated before they are pipelined to the consumer. The most frequent impurities of a so called "sour gas" are

CO_2
H_2S
COS
mercaptanes.

The concentration of H_2S, for example, should not exceed a few ppm in the treated gas, as there could occur problems with corrosion in the pipeline systems.

Most common for gas treatment are washing processes, i.e.

physical washing
chemical washing.

Thereby H_2S is separated from the "sour" gas and concentrated enabling the production of pure sulphur by a Claus plant. A flow sheet of such a cleaning procedure is given in figure 3.4. Sulphur is a marketable product used in the chemical industry.

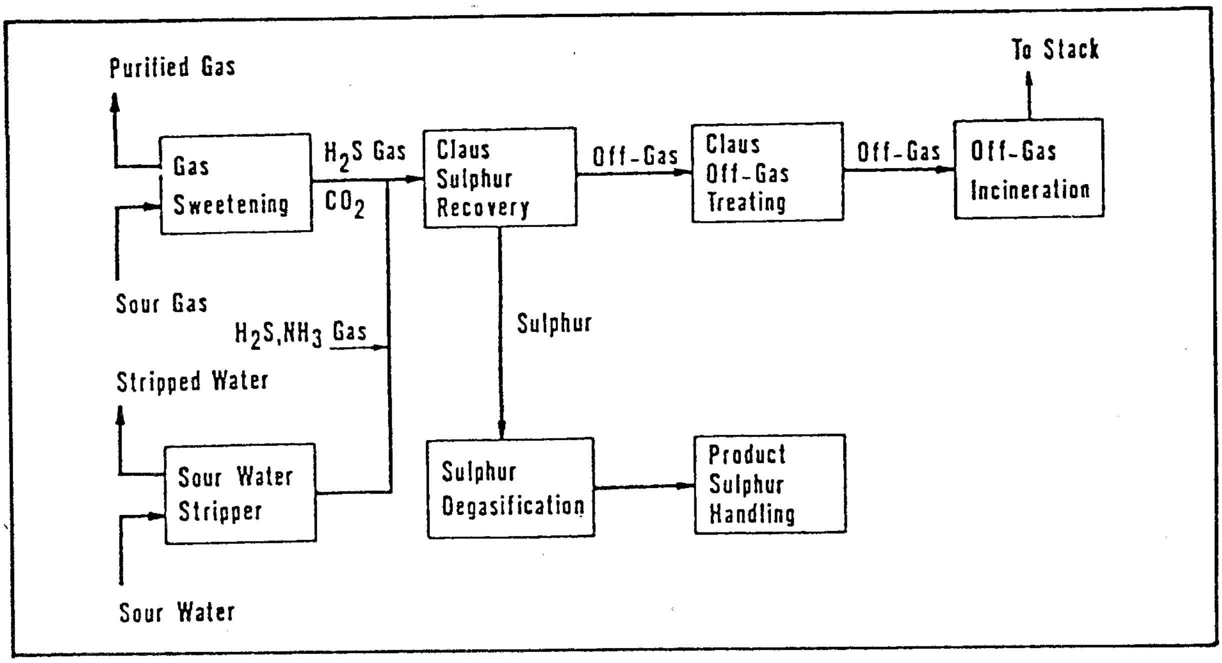


Figure 3.4: Simplified Flow Sheet of Gas Cleaning (Snepvangers, 1983)

4 BY-PRODUCTS AND WASTE FROM CONVENTIONAL COMBUSTION OF FUELS

During the conventional combustion of solid or liquid fuels the main by-product beside untreated flue gas is any kind of ash. Actually the term "ash" may summarize various types of solid by-products. It is immediately obvious that there are a number of characteristics being similar for all these kinds of products. But due to at least slightly different origin there are some differences regarding both quality and quantity of particular types of ash within one fuel.

The term "ash" covers a variety of products. The two common categories of ashes which will be discussed within this chapter are:

- bottom ash which falls by gravity from the combustion zone to the bottom of the furnace

and

- fly ash which is light enough to be carried in the flue gas until measures are taken to separate it.

"Ash" can also be categorized by the area of the appliance it is collected from. Terms such as "stoker ash" and "pulverized fuel ash" (PFA) may be encountered. In addition, ashes from special combustion techniques will be discussed within the concerning chapters, such as fluidized bed combustion system ashes (see chapter 8), gasifier slag (see chapter 9) and ashes from municipal waste combustion (see chapter 10).

Data of the generation of ashes at present as well as a prognosis for the year 2000 is given in table 4.1.

Table 4.1: Projected Amounts for the Year 2000 for By-Products from Conventional Combustion in Member Countries (data provided by member countries, all values given in metric tons)

Country	Actual Amount	Year	Amount 2000	Remarks
AUSTRIA	25.000	1989	45.000	bottom ash
	80.000	1989	90.000	fly ash hard coal
	296.000	1989	320.000	fly ash brown coal
	20.000	1989	35.000	biomass ashes
CANADA	910.000	1986/87	1.170.000	bottom ash hard coal
	510.000	1986/87	660.000	bottom ash brown coal
	2.450.000	1986/87	3.160.000	fly ash hard coal
	1.380.000	1986/87	1.780.000	fly ash brown coal
FEDERAL REPUBLIC OF GERMANY	3.000.000	1989	3.000.000	bottom ash hard coal
	1.120.000	1989	1.100.000	bottom ash lignite
	3.000.000	1989	3.000.000	fly ash hard coal
	4.480.000	1989	4.500.000	fly ash lignite
FINLAND	740.000	1988	1.000.000	coal ash
	100.000	1987	450.000	peat ash
ITALY	1.200.000	1987	3.000.000	total ash
MALTA	44.000	1988	104.000	fly ash
NETHERLANDS	80.000	1988	130.000	bottom ash
	700.000	1988	800.000	fly ash
SWEDEN	150.000	1988	150.000	bottom ash from coal combustion
	200.000	1988	400.000	fly ash (incl. FGD-products)
	4.000	1988	4.000	fly ash from oil combustion
	40.000	1988	60.000	bottom ash from biomass and peat
	100.000	1988	150.000	fly ash from biomass and peat
UNITED KINGDOM	13.000.000	1988	10.000.000	bottom and fly ash
UNITED STATES OF AMERICA	62.400.000	1984	107.000.000	coal - total ash

4.1 Hard Coal and Brown Coal

Ash is an inescapable solid by-product arising from combustion of coal. For every ton of coal consumed in combustion or conversion between 40 and 300 kg of ash will inevitably arise. The quality and quantity of ash will be determined by the mineralogical composition of the fuel, its treatment and combustion system and operating conditions. However, there are a number of characteristics which will be relevant to all types of ash considering methods of utilization or disposal.

A survey of factors influencing ash characteristics is given in figure 4.1.

The decision whether ash should be utilized or disposed of will depend on a number of factors, not least the quality and structure of the material, the quantities involved, suitable outlets for utilization and the proximity of suitable disposal sites. Considerations of these factors will indicate the most viable options. Table 4.2 shows the operations involved in ash utilization or disposal.

FACTOR		ASH CHARACTERISTICS INFLUENCED	
		PHYSICAL	CHEMICAL
SOURCE	Coal composition (including ash)	Slurry pH Colour Mineralogical phases	Major element content Trace element content Radioactivity Free lime
PREPARATION	Size reduction, washing	Particle size Specific surface area	Major element content (washing) Trace element content Radioactivity Free lime
COMBUSTION CONDITIONS	PF firing: Temp T_1, Residence t_1 time Cyclone firing: Temp T_2, Residence t_2 time Stoker firing: Temp T_3, Residence t_3 time	Particle size Specific surface area Bulk density	Major element content Trace element content Radioactivity Free lime Unburnt carbon Trace organics
MINERAL CHANGES	Breakdown of original minerals Formation of melts Formation of new crystalline, glassy and amorphous phases	Mineralogical phases Particle size Specific surface area	Major and trace elements Radioactivity Free lime Pozzolanicity
CHEMICAL PARTITION OF ELEMENTS	Partition of major elements between new phases Incorporation of trace elements in new phases (Dependence on chemistry and temperature)		Major and trace elements Radioactivity Free lime Pozzolanicity
ADSORPTION	Condensation of volatile elements on particles during cooling		Trace metal content Trace organics
TYPE OF ASH COLLECTION EQUIPMENT	Baghouse E.S.P. Cyclone	Particle size Specific surface area Bulk density Compressive strength	Pozzolanicity Trace elements

Figure 4.1: Factors Influencing Ash Characteristics (Cope and Dacey, 1984)

Table 4.2: Operations Involved in Ash Utilization or Disposal (Cope and Dacey, 1984)

PHASE	DISPOSAL	UTILISATION
1. Removal from combustion system	Pneumatic or hydraulic conveying to hopper/sluice	Pneumatic conveying to hopper
		(Pneumatic conveying to storage site) (Short/medium term storage)
	Transport to processing	Transport to processing
		Transport off-site to user
2. Processing	(Conditioning) (Mixing with sludge for stabilisation)	(Size fractionation) (Handling/storage at processor) (Incorporation into products) (Quality control/testing)
3. End use	Deposition in pond/landfill (Dredging of landfill) Site maintenance and monitoring	Use of ash/ash product (Additional handling/storage at point of use) Marketing of ash/product

It is important to indentify those physical and chemical properties of the ash which will influence decisions as to the merits of utilization or disposal. Additionally an appreciation of the extent of variability of these properties is essential.

Physical properties which are of relevance include:

* particle size
* permeability
* moisture content
* bulk density
* compression strength
* slurry pH.

Chemically and mineralogically ash predominately consists of glassy particles of aluminosilicates and inorganic compounds. The crystalline fraction includes oxides of aluminium, silicon and iron, calcium compounds and small amounts of alkali and alkaline earth compounds, clay and heavy metals. As noted above the chemical composition of ash will vary considerably, depending on the type of coal, as given e.g. in figure 4.3, 4.4 and table 4.5, and the methods of pre-treatment and combustion.

Depending on its composition ash may be considered as a secondary raw material, suitable for utilization. Because of their different properties, fly ash and bottom ash should be considered seperately.

Table 4.3 shows different uses of bottom ashes and fly ashes and the distribution in the U.S.A.

Table 4.3: Relative Distribution of Utilized Coal Ash in the U.S.A. 1984 (Buhl and Perlsweig, 1988)

Bottom Ash Utilization (%)		Fly Ash Utilization (%)
1.3	Aggregate	0.7
24.5	Blasting grit	n.a.
9.7	Cement additive	18.6
2.5	Concrete admixture	35.6
0.9	Concrete block	3.6
0.0	Dam construction	1.8
13.8	Fill material	4.5
NA	Grouting	6.2
NA	Hazardous waste fixation	0.7
11.4	Ice control	0.5
13.6	Roofing granules	n.a.
10.4	Miscellaneous uses	25.1
100		100

n.a. ... not analyzed

4.1.1 Fly Ash

It is likely that there will be a practical limit to the quantities of fly ash that can be used. A report in 1982 suggested a figure of 100 kg/inhabitant as a likely limit (NEOM, 1982).

An overview of possibilities for utilization of fly ash is shown in figure 4.2.

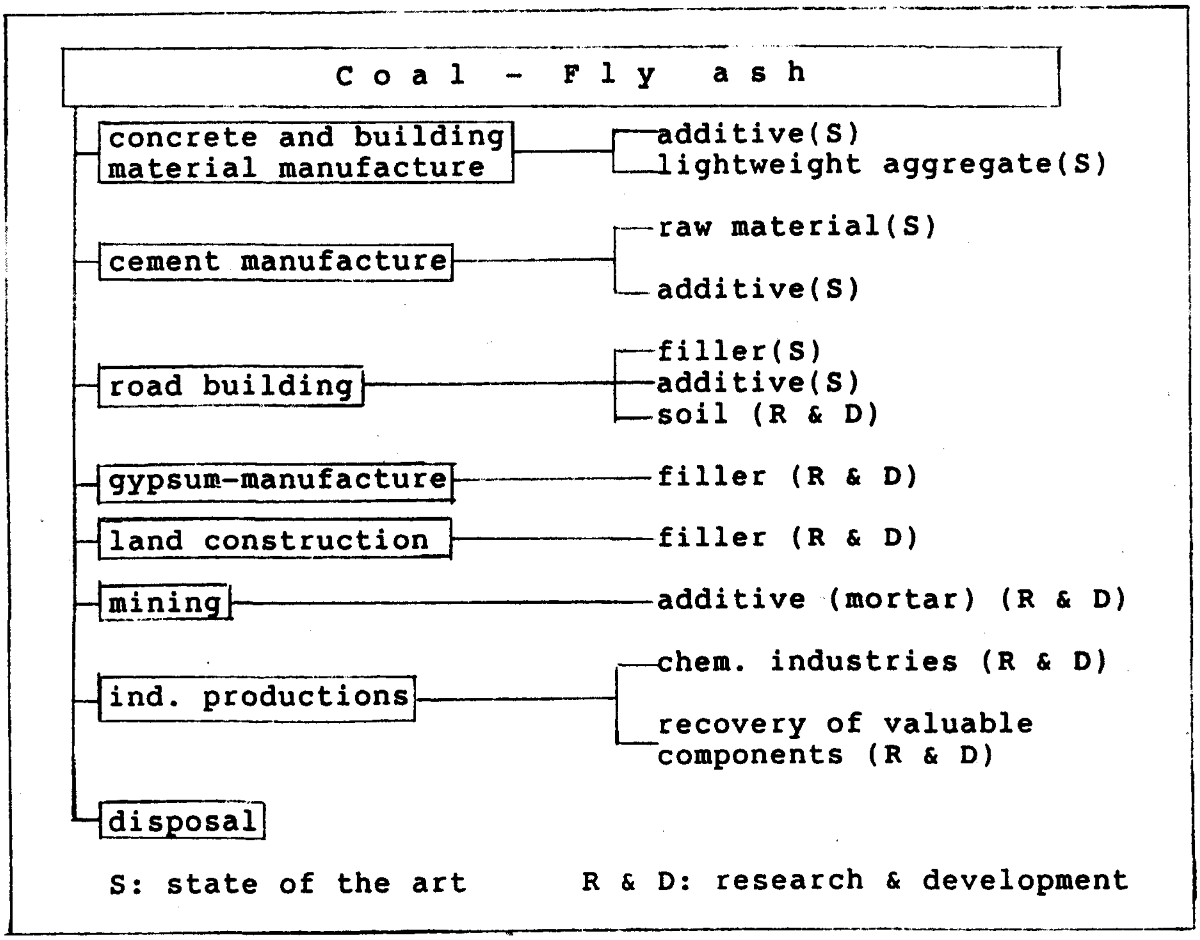


Figure 4.2: Possibilities of Utilization for Fly Ash Arising by Combustion of Hard-Coal Applied or Investigated in the FRG (Arbeitsgruppe Kraftwerksreststoffe, 1988)

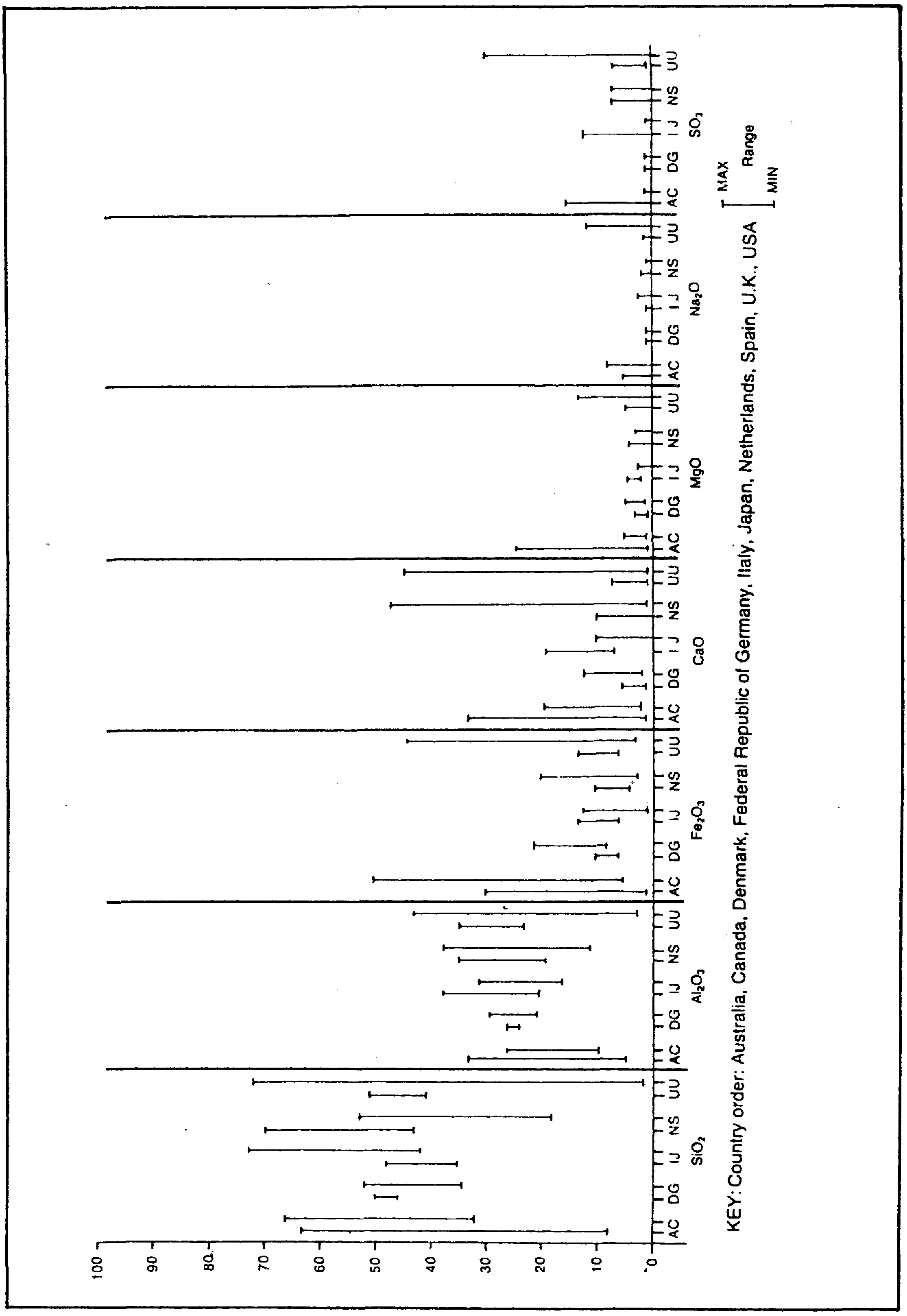


Figure 4.3: Major Element Composition Ranges for Fly Ash from Economic Assessment Service of IEA Coal Research Countries (Cope and Dacey, 1984)

Figure 4.3 shows the great variation of main components in fly ash in different countries, depending on the kind of coal used. Table 4.4 gives more detailed analyses of fly ashes from different sources.

Coal contains a wide range of trace contaminants at variable but generelly low concentrations. These include a variety of metals, the most abundant of which are aluminium and iron, and other elements such as selenium, arsenic and the halogens. The contaminants may be present in elemental form or in combination with, for example, oxygen. The degree to which they are lost to the environment via the combustion process depends largely upon the volatility of the species formed. For example, fluorine is considered to be almost entirely converted to hydrogen fluoride, and therefore the large majority of the fluoride would be in the gas phase and thus emitted to the atmosphere. By contrast a non-volatile element such as aluminium would be in the solid phase at the temperature conditions following combustion and would be retained in the bottom ash and fly ash. In this case loss to the environment would be limited to that associated with the small proportion of the ash solids that escape the electrostatic precipitation system.

Many elements are, however, only partially volatilised during combustion. The factors determining the volatility of individual trace elements during combustion are complex, but there is genereally partial correlation with the boiling points of oxides. This is probably attributable to the presence of many of the elements in coal in the form of oxides or the formation of oxides on heating. While elements or their oxide or other species are volatilised at the highest temperatures of the combustion process, there is subsequent condensation on the fly ash matrix as the temperature reduces from the maximum encountered in the furnace.

Table 4.4: Element Composition of Fly Ashes from Different Coal Sources (Van der Sloot et al., 1985)

Element	Unit	USA	Australia	Poland	Belgian/German
Ca	%	1.6 ± 0.7	1.2 ± 0.6	3.7 ± 0.9	1.9 ± 0.5
Mg	%	0.8 ± 0.13	0.68 ± 0.18	2.6 ± 0.4	1.6 ± 0.3
Ti	%	1.0 ± 0.16	0.68 ± 0.17	0.63 ± 0.08	0.65 ± 0.09
Si	%	21.6 ± 1.4	26.8 ± 3.8	21.5 ± 0.9	21.8 ± 1.3
Fe	%	5.3 ± 0.5	3.6 ± 0.8	6.8 ± 0.7	5.2 ± 0.56
Al	%	15 ± 2	11.8 ± 3.1	12.0 ± 1.0	13.5 ± 0.8
Na	%	0.41 ± 0.20	0.30 ± 0.12	0.60 ± 0.06	0.67 ± 0.21
K	%	1.8 ± 0.2	1.08 ± 0.37	1.8 ± 0.19	3.34 ± 0.20
S	%	0.32 ± 0.06	0.25 ± 0.05	0.47 ± 0.11	0.41 ± 0.13
P	%	0.14 ± 0.07	0.30 ± 0.15	0.17 ± 0.04	0.22 ± 0.07
As	ppm	68 ± 10	32 ± 17	32 ± 19	76 ± 61
B	ppm	193 ± 126	109 ± 60	200 ± 33	163 ± 66
Ba	ppm	1910 ± 760	1680 ± 1040	1940 ± 220	972 ± 342
Be	ppm	18 ± 3.3	16 ± 6	9.8 ± 1.9	7.4 ± 2.1
Br	ppm	5.6 ± 6.5	2.4 ± 2.6	8.7 ± 7.5	3.7 ± 4.8
Ce	ppm	258 ± 20	178 ± 36	165 ± 16	173 ± 11
Cd	ppm	0.81 ± 0.20	0.65 ± 0.19	1.2 ± 0.3	6.0 ± 4.8
Co	ppm	83 ± 21	63 ± 15	55 ± 9	69 ± 12
Cr	ppm	205 ± 40	97 ± 32	152 ± 24	224 ± 30
Cu	ppm	247 ± 33	128 ± 44	198 ± 19	260 ± 50
Cs	ppm	9.0 ± 1.5	6.5 ± 1.5	14.1 ± 2.1	26.5 ± 11.2
Eu	ppm	4.3 ± 0.42	3.1 ± 0.8	2.5 ± 0.7	2.7 ± 0.6
Ga	ppm	47 ± 3.7	42 ± 3.7	40 ± 3.3	55 ± 24
Hf	ppm	8.6 ± 1.8	11.6 ± 1.3	6.2 ± 1.5	5.4 ± 0.35
La	ppm	100 ± 8.1	68 ± 15	63 ± 6.3	67 ± 5.2
Mo	ppm	15 ± 7	9 ± 3.6	8.7 ± 6.3	16.6 ± 9.7
Mn	ppm	291 ± 123	383 ± 121	929 ± 410	764 ± 183
Nd	ppm	69 ± 6	56 ± 14	47 ± 9	42 ± 12
Ni	ppm	113 ± 26	85 ± 60	93 ± 12	156 ± 49
Pb	ppm	151 ± 32	125 ± 26	187 ± 29	505 ± 290
Rb	ppm	101 ± 24	46 ± 30	102 ± 20	202 ± 14
Sb	ppm	9.5 ± 1.1	10.5 ± 4.2	14.0 ± 2.1	20.3 ± 10
Sc	ppm	47 ± 8	30 ± 6	30 ± 3	39 ± 5
Se	ppm	22 ± 10	9.5 ± 13	13 ± 5.5	7.6 ± 7.9
Sm	ppm	23.3 ± 1.5	18.5 ± 3	15.4 ± 1.7	14.9 ± 1.8
Sr	ppm	1460 ± 680	1029 ± 390	800 ± 130	300 ± 100
Ta	ppm	2.1 ± 0.5	1.2 ± 0.5	1.3 ± 0.3	1.2 ± 0.4
Tb	ppm	4.0 ± 0.7	2.8 ± 0.8	2.0 ± 0.65	2.2 ± 0.7
Th	ppm	39 ± 5	32 ± 11	26 ± 3	24 ± 2
U	ppm	20 ± 4	17 ± 4.5	17 ± 2.6	14 ± 4
V	ppm	320 ± 70	230 ± 70	258 ± 36	400 ± 120
W	ppm	8.5 ± 1.7	8.7 ± 4.1	5.4 ± 1.2	4.9 ± 2.7
Yb	ppm	9.8 ± 1.2	9.3 ± 0.7	6.3 ± 0.8	4.9 ± 0.7
Zn	ppm	350 ± 60	400 ± 70	440 ± 90	890 ± 460

In the case of highest boiling species, condensation is rapid and is essentially complete before the flue gas reaches the electrostatic precipitators. The effects of this condensation process are particularly important in the case of the smallest particles of fly ash that are not trapped by the electrostatic precipitators. These particles have a much greater specific surface area than the larger particles in the bulk fly ash, and there is therefore a disproportionate degree of condensation of the volatile elements on these smaller particles. Concentrations of volatile trace elements have been reported (Natusch et al., 1973; Smith et al., 1979) to increase as particle size decreases in the 1 - 10 µm size range, but in the case of sub-micron particles to be independent of particle size.

This progressive increase in the concentration of the volatile elements in ash particles of decreasing diameter is known as enrichment and has been reported (Linton et al., 1977; Smith et al., 1979) as occurring in a surface layer of thickness 0.01 - 0.1 µm. The significance of enrichment for some of the more volatile trace elements is shown in table 4.5.

Average enrichment factors of fly ash particles have been calculated from data on Illinois coals and ashes (Cahill et al., 1976) and are given in table 4.6, table 4.7 shows the range of the distribution of trace elements in the separated fly ash. The remaining part of these amounts is in the flue gas and bottom ash.

Table 4.5: Concentrations of Some Elements in Emitted Fly Ash Particles as a Function of Particle Diameter (Natusch et al., 1973)

Particle Diameter (μm)	Concentration (mg kg^{-1})				
	Pb	Sb	Cd	As	Ni
> 11.3	1100	17	13	680	460
7.3 - 11.3	1200	27	15	800	400
4.7 - 7.3	1500	34	18	1000	440
3.3 - 4.7	1550	34	22	900	540
2.06 - 3.3	1500	37	26	1200	900
1.0 - 2.0	1600	53	35	1700	1000

Table 4.6: Average Enrichment of Fly Ash Particles from 70 Illinois Coals (Cahill et al., 1976)

Enrichment Factor	Enrichment	Elements
0.1	Depleted	Na, Mg, K, Ti, Mn
0.1 - 2	No trend	Al, Ca Fe, V, Sn, Ca, Co, Ni, Be*), Cr, Zn, Pb, Hg, Ga, U, Ba, Ag, Sc, W, La, En
2.0 - 10.0	Slightly enriched	Pb, As, Cl, Sb, Mo, Cd, Ge, Br
10.0	Highly enriched	Se

*) Elements underlined are those of particular environmental importance.

Table 4.7: Distribution of Heavy Metals During Dust Separation Procedure (Arbeitsgruppe Kraftwerksreststoffe, 1988)

Element	Raw Flue Gas Dust (%)	Fly Ash (%)	Dust from Cleaned Flue Gas (%)
As	100	60 - 90	10 - 40
Cd	100	80 - 90	10 - 20
Cr	100	85 - 90	10 - 15
Cu	100	85 - 95	5 - 15
Hg	100	0 - 10	90 - 100
Ni	100	80 - 95	5 - 20
Pb	100	85 - 95	5 - 15
Zn	100	80 - 90	10 - 20

There exist clear indications that some trace elements (heavy metals) concentrate in fly ash and thus are subject to increased leaching (see table 4.8). To prevent impairment on ground and surface water appropriate options of utilization and disposal have to be provided.

Coal (and peat as well) contain radioactive substances, though, in general, they have less natural activity than ordinary soil and rock (for instance granite and shale). Exceptions may be found among certain peat fuels with naturally enriched uranium or peat which has been exposed to cesium fall-out from Tjernobyl. The radiological exposure from fossil fuel plants is considered by several authors (e.g. Lim, 1979) to be of negligible public health significance.

In the combustion residues, however, especially in fly ash, where certain radioactive trace-elements may be enriched, the activity is normally higher than the average soil activity. This radioactivity may pose a problem, if the ash is used in building materials. A normal activity in coal fly ash is 200 and 150 bq/kg, respectively, of thorium and radium (Ericson, 1983).

Table 4.8: Leaching Percentages of Elements at Liquid-Solid Ratio 5 for the Pulverized Coal Ash Categories Acidic, Neutral and Alkaline (Van der Sloot et al., 1985)

Element		Acidic	Neutral	Alkaline
Ca	%	10 - 15	5 - 15	10 - 15
Mg	%	1 - 2	0.001 - 2	0.001
Si	%	0.01	0.005 - 0.01	0.005
Al	%	0.001 - 0.1	0.001 - 0.1	0.001
SO^{2-}	%	50 - 100	50 - 100	50 - 100
As^{4}	%	1 - 5	0.1 - 2	0.1
Sb	%	5 - 10	0.02 - 5	0.02
Sc	%	10 - 50	0.5 - 50	0.5
U	%	0.05	0.01 - 0.05	0.02
Mo	%	10 - 100	70 - 100	70 - 100
W	%	20	1 - 20	1
V	%	0.5	0.005 - 0.5	0.005
Cu	%	0.01 - 10	0.005 - 0.01	0.01
Zn	%	0.01 - 5	0.005 - 0.1	0.01
Pb	%	0.005 - 0.5	0.005 - 0.1	0.01
Cd	%	0.1 - 20	0.01 - 0.05	0.05
Cr	%	0.05	0.05 - 1	1
B	%	30	1 - 30	1

The radioactivity of radium-226 in building materials in Sweden, for instance, must not exceed 200 Bq/kg. For concrete, this corresponds to a radon emission of appr. 40 Bq/m^{2}h. The normal activity of radium in concrete is appr. 50 Bq/kg, corresponding to a radon emission of 10 Bq/m^{2}h.

Measurements of the radon emission from concrete with fly ash indicate that the added fly ash may decrease the total emission of radon. At a meeting with Nordic experts on atomic energy, it was concluded that the admixture of fly ash in concrete either decreases the radon emission or has no significant effect (Ericson, 1983).

A "worst case" calculation based on an average coal and on the assumption that all of the radon in fly ash is emitted and that the radon emission from the other components in fly ash is not influenced, would give an additional 2 Bq/m^2h, from appr. 10 to appr. 12 Bq/m^2h, if 10 % of the concrete is replaced by coal fly ash. The acitivity would of course be higher, when high activity coal or peat has been combusted.

4.1.2 Bottom Ash

This and similar material is generally utilized in the form in which the material is received and rarely treated extensively prior to utilization. It has a more limited range of uses than fly ash. In many countries there is higher percentage of utilization of bottom ash and some individual users are able to achieve a 100 % utilization.

Referring to disposal and the utilization as a landfiller or for road building relative low leachability of coal ashes (due to high specific surface area and high contents of glassy phases) has to be taken into account. Figure 4.4 shows the range of trace metals in different bottom ashes.

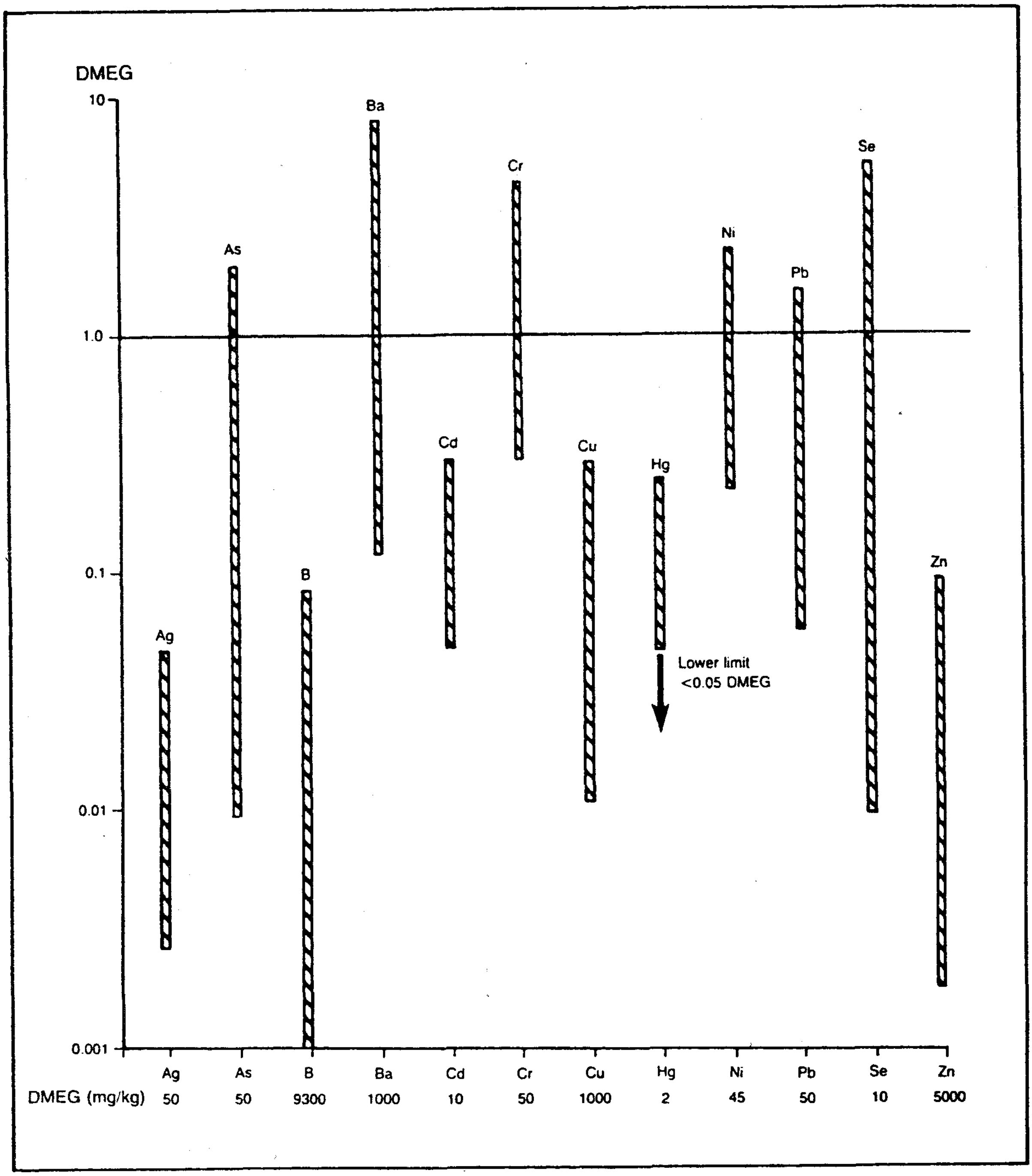


Figure 4.4: Range of Trace Metal Contents in Bottom Ashes from Economic Assessment Service of IEA Coal Research Countries (Cope and Dacey, 1984)

DMEG ... Trace metal contents are expressed in terms of the Discharge Multimedia Environmental Goal for human health,* as determined by the US EPA

4.1.3 Requirements and National Standards

As requirements created by National Standards strongly influence the possibility of utilization of by-products an overview about some standards concerning ashes is given in table 4.9. Table 4.10 shows the comparison of standards for portland and modified cements while table 4.11 concerns related materials.

Five types of standards relate to combustion residue utilization. These standards concern

* fly ash itself
* portland and blended cements
* lightweight aggregate
* concrete
* plaster and wallboard.

Table 4.9: Comparison of National Standards - Fly Ash (Cope and Dacey, 1984, supplemented)

COUNTRY	STANDARD	YEAR	TITLE		PARAMETERS								
					% SiO_2	% Al_2O_3	% Fe_2O_3	% CaO	% MgO	% Na_2O	% SO_3	% LOl	% Cl
AUSTRALIA	AS 1129	(1971)	PFA for use in concrete								<2.5	<8.0	
AUSTRIA	ÖNORM B 3319	(1981)	Concrete additive		42-60	16-32	3-12	5-20 (2%)	0-5	-	<5.0	<5.0	<0.1
CANADA	CAN/CSA- A23.5-M86	(1986)	supplementary cementing materials	(F)	-						5.0	12.0	
				(C)	-						5.0	6.0	
DENMARK	DS 411 (Part 3.1.2.4)	(1982)	Fly ash for addition to concrete or cement						<5.0	<1.5	<4.0	<5.0	<0.1
FRG	(DIN 1045)		(Concrete additives)								<4.0	<5.0	<0.1
JAPAN	JIS A6201	(1958)	Fly ash for use as an admixture in portland cement mortar and concrete		>45							<5.0	
	(Unofficial)		(Cement companies specifications)		45-70	15-30	2-10	0-10	<1.5	<2.5*	<1.25		<0.003
NETHERLANDS	(Unofficial)		Fly ash for portland cement				5-10					<5.0	
UK	BS 3892	(1965)	PFA for use in concrete						<4.0		<2.5	<7.0	
	BS 3892 Part 1	(1982)	(Revision of above)						<4.0		<2.5	<7.0	
USA	ASTM C593	(1981)	Fly ash and other pozzolan material for use in plastic mortars										
	ASTM C618	(1980)	Fly ash or calcined natural pozzolan for use as mineral admixture in concrete	(F)	70				<5.0+	<1.5*+	<5.0	<12.0	
				(C)				(can be <10%)	<5.0+	<1.5*+	<5.0	<6.0	

* ... $Na_2O+0.658K_2O$

F ... Ashes from anthracite and bituminous coals

\+ ... Optional requirement

C ... Ashes from sub-bituminous and lignite coals

Table 4.9: Comparison of National Standards - Fly Ash (Continued) (Cope and Dacey, 1984, supplemented)

COUNTRY	STANDARD	YEAR	TITLE	PARTICLE SIZE	m^2kg^{-1} FINENESS	% MOISTURE	OTHERS
AUSTRALIA	AS 1129	(1971)	PFA for use in concrete	>90% passing 150 µm >50% passing 45 µm		<1.5	
AUSTRIA	ÖNORM B 3319	(1981)	Concrete additive			<1.0	3% carbon
CANADA	CAN/CSA-A23.5-M86	(1986)	Supplementary cementing materials	>66% passing 45 µm		<3.0	Pozzolanic activity index F+C: 68% of control Density 5%
DENMARK	DS 411 (Part 3.1.2.4)	(1982)	Fly ash for addition to concrete or cement	60% passing 45 µm		<1.5	
FRG	(DIN 1045)		(Concrete additives)	65-90% passing 40 µm	240-430 (<200)		Glass content 80-100%
JAPAN	JIS A6201	(1958) (1977)	Fly ash for use as an admixture in portland cement mortar and concrete	>75% passing 44 µm	>240	<1.0	Density >1950 kg/m^{-3}
	(Unofficial)		(Cement companies specifications)				TiO_2<1.5%, P_2O_5<0.5%
NETHERLANDS	(Unofficial)		Fly ash for portland	>40% passing 16 µm >60% passing 32 µm			Glass content >80%
UK	BS 3892	(1965)	PFA for use in concrete		A) 125-275 B) 275-425	<1.5	
	BS 3892 Part 1	(1982)	(Revision of above)	>87.5% passing 45 µm	C) >425	<0.5	Water demand <95% of OPC control

USA	ASTM C593	(1981)	Fly ash and other pozzolan material for use in plastic mortars	>98% passing 600 μm >70% passing 75 μm		Maximum 10% water soluble material. Lime-pozzolan mix to have 7-day strength >4.1 MPa
	ASTM C618	(1980)	Fly ash or calcined natural pozzolan for use as mineral admixture in concrete	>66% passing 45 μm	<3.0	Pozzolan activity 75% of OPC control at 28 d. Compressive strength + lime - 5.5 MPa after 7 d. Water requirement <105% of OPC control. Maximum variation in particle size (% passing 45 μm) ± 5%
				>66% passing 45 μm	<3.0	

Table 4.10: Comparison of National Standards - Portland and Modified Cements (Cope and Dacey, 1984, supplemented)

				PARAMETERS									
COUNTRY	STANDARD	YEAR	TITLE	% PFA in cement	% SiO_2	% Al_2O_3	% Fe_2O_3	% MgO	% CO_2	% SO_3	% LO1	% Cl	% insoluble residue
AUSTRALIA	AS 1317	(1972)	Blended cements FA - portland fly ash FB - high early strength portland fly ash FC - low heat portland fly ash	15-40						<3.1	<5.0		
AUSTRIA	ÖNORM B 3319	(1981)	Cement additives										
CANADA	CAN/CSA-A23.5-M86	(1986)	Supplementary cementing materials										
DENMARK	DS 427 (proposed)	(1981)	Portland cement	5									
			Portland fly ash cement	10-35									
FRG*	DIN 1164(1)	(1978)	Portland, iron portland, blast furnace and trass cement					<5.0	<2.5	<3.5	<5.0	<0.1	<3.0
JAPAN	JIS-R 5210	(1979)	Portland cement	<5									
	JIS-R 5213	(1979)	Portland fly ash cement										
			A	5-10				<5.0		<3.0	<3.0		
			B	10-20									
			C	20-30									
SPAIN	RC-75			<20									
SWEDEN	B1 (ED.2)	(1982)	Cement regulations										
			Portland P	<5				<5.0		<4.0	<5.0	<0.1	
			Modified portland M	<35	$CaO+SiO_2+$			<5.0		<4.0	<5.0	<0.1	
			Blended cement B	35-80	$Al_2O_3>70\%$			-		<4.0	<5.0	<0.1	

USA	ASTM C150	(1981)	Portland cement		>20.0	<6.0	<6.0	<6.0	<2.5 or <3.5	<3.0
	ASTM C595	(1981)	Blended hydraulic cements	<15				<5.0	<4.0	<5.0
			PM - pozzolan modified	15-40				<5.0	<4.0	<5.0
			IP - portland-pozzolan		>70% if cement is to be sulphate resistant					

Table 4.10: Comparison of National Standards - Portland and Modified Cements (continued) (Cope and Dacey, 1984, supplemented)

COUNTRY	STANDARD	YEAR	TITLE	m^2kg^{-1} SPECIFIC SURFACE	OTHER PROPERTIES
AUSTRALIA	AS 1317	(1972)	Blended cements FA - portland fly ash FB - high early strength portland fly ash FC - low heat portland fly ash		Compressive strength (3 d, 7 d, 28 d) Soundness Constancy of volume Setting time
AUSTRIA	ÖNORM B 3319	(1981)	Cement additives		Compressive strength: 80% of test corps after 28 days in water Constancy of volume
CANADA	CAN/CSA-A23.5-M86	(1986)	Supplementary cementing materials		7 days accelerated pozzolanic activity index Activity index Compressive strength Soundness Increase of drying shrinkage
DENMARK	DS 427 (proposed)	(1981)	Portland cement Portland fly ash cement		
FRG*	DIN 1164(1)	(1978)	Portland, iron portland, blast furnace and trass cement	200-400	
JAPAN	JIS-R 5210	(1979)	Portland cement		
	JIS-R 5213	(1979)	Portland fly ash cement		Minimum compressive strength 3 d 7 d 28 d (MPa)
			A	>250	6.9 14.7 29.4
			B		5.9 11.8 25.5
			C		4.9 9.8 20.6
SPAIN	RC-75				

SWEDEN	B1 (ed.2)	(1982)	Cement regulations		Minimum compressive strength	1 d	3 d	7 d	28 d	91 d (MPa)
			Early strength cement			15	34	42	-	-
			Standard cement			-	16	26	42	-
			Low heat cement			-	-	16	29	42
					Constancy of volume					
					Setting time					
					Heat production					
USA	ASTM C150	(1981)	Portland cement	>280	Alkalis <0.6					
	ASTM C595	(1981)	Blended hydraulic cements							
			PM - pozzolan modified							
			IP - portland-pozzolan		>80% passing 45 μm					
					Pozzolanic acitivity test (compressive strength with added lime)					

* No standard for fly ash cement as such, but requirements are similar to those indicated for DIN 1164

Table 4.11: National Standards - Related Materials (Cope and Dacey, 1984, supplemented)

COUNTRY	STANDARD	YEAR	TITLE	COMMENT
AUSTRIA	ÖNORM B 3318	(1982)	Added slag for cement	
	ÖNORM B 3320	(1982)	Added fly ash for concrete production	See table 4.7
FRG	DIN 106		Bricks, sand-lime bricks	
	DIN 1045		Concrete additives	See table 4.7. Allows replacement of up to 20 % of bonding agent by fly ash, with minimum cement content of 240 kg/m^3 concrete.
	DIN 1168	(1975)	Building plasters	> 50 % $CaSO_4$. Particle size - > 98 % passing 200 µm (> 88 % for plaster of paris). Tests required for setting time and blending, compressive and tensile strengths.
	DIN 4226	(1980)	Additives for concrete - lightweight aggregate	SO_3 < 1 %, LOl < 5.0 %. Also specifications on size gradings.
	DIN 18180, 18181		Plasterboard	
	DIN 18163, 18169		Wall and ceiling boards	
UK	BS 3797	(1976)	Aggregate for concrete	SO_3 < 1 %, LOl < 4 %. Bulk density < 1200 kg m^{-3} for fine aggregate, < 960 kg m^{-3} for coarse (> 5 mm) aggregate. Size gradings covered.
USA	ASTM C311-85	(1985)	Sampling & testing fly ash or natural pozzolans for use as a mineral in portland cement concrete	

Though not specifically covered in tables 4.9 to 4.11, there are also standards in many countries specifying test procedures for the materials mentioned.

4.2 Biomass and Peat

Biomass as a renewable resource has become a target of renewed interest. In the case of energy production wood, wood residuals, straw and other agricultural residuals are included under the term biomass. Peat, having properties similar to those of biomass in many respects, but which is being produced during thousands of years and has also properties similar to those of coal, is considered as a fossil fuel or as a "semi-fossil" fuel. Biomass energy today accounts for approximately 15 % of the world's annual fuel supplies (Hall, 1982).

As the lignocellulosic materials contain little sulphur (as a rule less than 0.2 %, Nilsson and Timm, 1983) there are no serious problems with SO_2. Problems may occur from fuel NO_x (because of the low burning temperature there is no thermal NO_x), depending on combustion technology, as well as from polycyclic aromatic hydrocarbons (PAH) (Braun et al., 1986), aldehydes (Lipan et al., 1984) (Krapfenbauer, 1986), phenols (Nilsson and Timm, 1983) and other organic matter. This environmental and health impacts may be solved by an appropiate burner technology, efficient combustion and flue gas cleaning. Apart from conventional particulate filters, flue gas cleaning by condensation is being used. The process is similar to that used at municipal waste incineration, leaving a sludge to be disposed of and waste water. The amounts of sludge are very small.

The main by-product of combustion of biomass is ash. Modern biomass combustion plants are equipped with electrostatic precipitators or bag filters. The amount of bottom ash and fly ash, respectively, are dependent on the fuel ash content, the combustion process and the dust removal efficiency. The mineralogical ash content (dry weight) is in wood 0.1 to 1 %. Wood from fast-growing Salix and Populus (which are commonly used for short rotation energy forests; Siren, Sennerby-Forsse and Ledin, 1987) often have a higher ash content, up to 1.5 to 2 %. Bark may have ash contents as high as 4 to 5 %. The ash contents of straw are 3 to 10 % and of reeds 2 to 13 %. These values may be compared with peat ash contents of 0.5 to 15 %, with normal values for fuel peat around 2 to 5 %. Usual values for hard coal are 7 to 15 % and heavy fuel oil 0.01 to 0.1 %. The ash seperated in the combustion plant consists of mineral and soot formed by incomplete combustion. The amount of soot depends on the combustion technique used.

The composition of wood ashes differs partly from that of peat ashes (see tables 4.12 and 4.13). The contents of crystalline quarz, feldspars and ferric oxide are lower, whereas the contents of calcite or calcium oxide are higher. This is in accordance with the generally higher alkalinity of wood ashes than of peat ashes. Wood ash often contains 25 to 30 % calcium. In biomass ashes the contents of potassium sulfate, potassium carbonate and hydroxylapatite ($Ca_5OH(PO_4)_3$) are considerable.

Some data of chemical analyses from different bark ashes in comparison with coal ashes are given in table 4.12. Results of chemical analyses of test samples of biomass are collected in table 4.13.

Table 4.12: Ash Analysis of Wood Bark and Coal (Tillman, 1981)

Ash analysis (percent) by weight	Bark				Coal	
	Pine	Oak	Spruce	Redwood	Western	PA
SiO_2	39.0	11.1	32.0	14.3	30.7	49.7
Fe_2O_3	3.0	3.3	6.4	3.5	18.9	11.4
Ti_O^3	0.2	0.1	0.8	0.3	1.1	1.2
Al_2O_3	14.0	0.1	11.0	4.0	19.6	26.8
Mn_3O_4	Trace	Trace	1.5	0.1	-	
CaO	25.5	64.5	25.3	6.0	11.3	4.2
MgO	6.5	1.2	4.1	6.6	3.7	0.8
Na_2O	1.3	8.9	8.0	18.0	2.4	2.9
K_2O	6.0	0.2	2.4	10.6		
SO_3	0.3	2.0	2.1	7.4	12.4	2.5
Cl	Trace	Trace	Trace	18.4		

Table 4.13: Elemental Analysis of Test Samples of Biomass (Ossman and Gross, 1983)

	Elemental Analysis of Test Samples (in % Weight)									
	SiO_2	Fe	Mg	Ca	Zn	K	Na	S	P	total
1. Bean straw (I)	29.90	1.90	0.55	3.34	0.021	18.46	0.38	1.90	1.00	57.46
2. Safflower	20.47	0.84	3.68	7.75	0.0236	25.0	0.67	3.53	1.50	63.28
3. Rice bulls	94.60	0.018	0.01	0.018	0.002	2.0	0.1	0.90	0.20	98.0
4. Alfalfa	7.96	0.36	1.73	8.00	0.1	28.2	3.7	1.86	4.60	55.51
5. Cotton-gin trash	23.20	1.35	1.73	5.13	0.15	10.8	1.18	1.70	4.40	49.64
6. Barley straw	44.70	1.82	2.92	2.30	0.1	6.7	3.92	0.72	5.00	68.18
7. Corn stalks	50.70	2.20	1.86	2.79	0.74	8.5	0.39	4.44	4.40	76.02
8. Rice straw	75.20	6.27	0.38	0.52	0.0	9.9	0.21	0.60	3.87	90.95
9. Bean straw (II)	32.70	2.75	2.20	4.50	0.12	21.0	0.61	0.91	3.20	67.48
10. Wood chips	8.30	7.00	3.75	13.30	0.155	9.8	0.98	3.60	3.00	49.88
11. Corn fodder	55.30	1.68	2.50	0.75	0.07	7.96	0.55	1.39	1.30	71.00
12. Paper pellets	57.20	3.00	0.50	0.11	0.25	1.54	3.78	1.00	1.90	69.88
13. Corn stalks	63.30	3.30	2.88	0.40	0.0	6.95	0.32	2.90	0.90	89.05
14. Almond shell	22.60	2.64	1.50	8.77	0.04	11.74	3.77	3.20	2.40	59.66
15. Corn robs	40.30	2.84	1.50	0.90	0.176	16.97	0.88	3.50	3.00	67.08
16. Manzanita chips	5.97	2.00	2.98	17.50	0.2	9.1	2.04	2.70	3.58	46.07
17. Tree pruning	9.95	1.36	0.00	14.20	0.05	10.6	1.10	7.90	5.22	55.38
18. Walnut shell	13.60	1.74	0.20	5.00	0.36	17.86	0.80	3.40	2.00	46.95
19. Olive pits	10.50	1.54	3.10	18.50	0.09	2.6	5.68	6.90	3.30	51.21
20. Almond shells	18.60	2.68	1.20	11.44	0.188	12.2	4.36	7.00	3.40	61.06
21. Corn stalks	71.70	4.96	1.65	0.33	0.0165	8.5	0.25	0.90	0.29	88.59
22. Cotton stalks	33.00	2.80	3.70	2.55	0.05	17.7	1.08	2.65	2.13	66.66
23. Rice straw mix	75.00	0.33	1.53	0.76	0.0	13.1	0.4	0.40	0.48	92.00
24. Wheat and corn	71.70	2.33	5.05	0.68	0.0156	12.2	0.4	1.20	0.48	94.055
25. Rice straw	78.30	0.13	1.25	0.50	0.0	10.78	0.32	0.68	0.31	92.27
26. Rice straw	78.60	0.03	1.25	0.63	0.0	12.0	0.33	0.74	0.40	93.97

Ashes from biomass and peat combustion also contain varying amounts of trace elements and organic substances. The variation in heavy metal content is greater within the same type of fuel as between fuels. Wood ash as well as peat ashes contain more manganese than coal ash does, and wood ash contains less mercury than do coal and peat ashes. Table 4.14 gives a comparison of leaching tests with different ashes.

Table 4.14: Comparison of Heavy Metals in Leachates from Wood, Peat and Coal Ashes (Swedish leaching procedure: see Appendix I) (Nilsson and Timm, 1983)

Ash	pH	Cd	Cr µg/l	Cu (ppb)	Pb
Wood					
Fly	13.0-13.8	20 - 30	80 - 7000	20 - 90	1300 - 2100
Bottom	12.8-13.3	< 0,5 - 1	100 - 400	< 10	< 20 - 3500
Peat					
Fly	7.8-12.9	< 0.05 - 4	< 50 - 200	< 10 - 20	< 20 - 200
Bottom	8.2-10.7	< 0.5	< 50	< 10 - 20	< 20 - 40
Coal					
Fly	9.2-13.0	< 0.5 - 150	< 50 - 3000	< 5 - 20	< 5 - 90
Bottom	9.1.-10.9	0.5 - 2	< 50	< 10	< 5

Based on laboratory leaching tests the following conclusions may be drawn concerning the leaching of heavy metals from deposits of biomass and peat ashes (Timm, 1989):

- The content of heavy metals in leachate varies a lot. It is for most metals less than 1 mg/l. Exceptions are e.g. chromium, zinc and lead from wood ash and selenium and strontium from peat ash, which may be higher. The combustion of painted or impregnated wood may give rise to high contents of e.g. cadmium (18 mg/l has been analyzed) and chromium (2200 mg/l).

- Most heavy metal concentrations are 10 - 100 times higher in fly ash than in bottom ash. Also, fly ashes are more soluble than bottom ashes.

- The contents of heavy metals in leachates from wood and peat ashes are of the same order of magnitude as in leachate from household waste deposits. Only chromium and lead, and possibly other metals which are soluble in alkaline solutions, have higher concentrations in leachate from wood ash.

- A dilution of the leachate of some hundred to thousand times is needed to obtain lowest known effect levels for aquatic organisms.

- A comparison of the heavy metal concentrations in leachate from ash with WHO standard values for drinking water shows that a dilution by 10 - 100 times is necessary if the standard values for individual metals are not to be exceeded.

It must be emphasized that the conclusions are based on laboratory experiments. There are practically no field data on this type of residual products.

There is limited experience of the utilization of wood and peat ashes. Only very few peat ashes and no biomass ashes are suitable for use in construction. From a chemical point of view peat ashes, which have a relatively low content of aluminium oxide and high contents of silicon oxide and ferric oxide, would be possible to use in the cement and concrete industry. However, most ashes have too high content of unburnt carbon and also are dark coloured, and they will give frost sensitive concrete.

Wood and peat ashes contain relatively large amounts of potassium and phosphorus and have acid neutralizing capacity. Consequently, the application of ash should have a positive effect on growth in soils where those substances are deficient. This is probably particularly applicable to potassium and phosphorus in peat soil. On the other hand, the nitrogen content of ash is very low. Ash also has a pH-increasing effect. There is no significant difference between bottom ash and fly ash as regards the contents of potassium, calcium and magnesium. However, there are indications that part of the peat ash content of phosphorus is in a form which is less available for the plants (Carlson, 1983; Nilsson and Timm, 1983).

In Finland and Sweden biomass and peat ash used in forestry have been shown to result in a growth increase. The problems when applying ash in forestry are the spreading of dust and the leaching of toxic metals. The dust problem may be solved by agglomorating the ash before application. To avoid negative effects of heavy metals accumulation in the soil and in biota or effects of leaching to ground water, the amount of ash applied must be limited and only ashes with low concentrations of heavy metals be used. Field experiments are being conducted in Sweden in order to evaluate effects of ash application in forestry on biomass production and on the environment.

In some countries the ongoing acidification of forest soils is resulting in an increasing problem of nutrient shortage due to the leaching of important microsubstances.

There is a growing awareness of the importance of supplementing micronutrients to prevent severe long term effects on the production of biomass. These micronutrients may be supplied by recycling biomass ashes to forest soils.

Also, with the growing concern over the climatic effects from the usage of fossil fuels, biomass fuels will become increasingly important in future energy systems. This will leave us with ashes which have to be disposed of if they cannot be utilized. In Sweden, e.g. an energy scenario with maximum amounts of biomass will result in quantities of biomass ashes of the same order of magnitude as coal ashes today.

The application of ash to agricultural land has been shown to result in an increased uptake of heavy metals in grain and vegetables. This means that a widespread use of ashes as fertilizers in agriculture may increase the amount of e.g. cadmium in grain significantly and might thereby pose a risk to the public health. In Sweden, the application of ashes on land used for food production is not recommended (Swedish Environmental Protection Board, 1987a).

The content of trace elements, and important plant growing factors such as phosphorus and potassium, make use of ash as a fertilizer feasible. The use of a certain ash for this kind of utilization has to be examined for possible negative effects, for example the content of heavy metals, alkalinity and leachability.

Peat ashes are very similar to coal ashes. In a peat powder power plant fly ash is approximately 85 to 90 % of the total ash amount. In roast firing about half the amount of ashes is bottom ash. The chemical composition of peat fly ash and bottom ashes is shown in table 4.15. The major components of the ashes are silicate, aluminium, iron and calcium. The content of trace metals in the fly ash fraction are usually higher than in the bottom ash fraction, because many metals are vaporized during combustion (Statens energiverk, 1985). The most evident difference is that aluminium silicates in peat ashes are in the form of naturally occuring feldspar instead of mullite on coal ashes and that calcite dominates over calcium oxide. These differences are probably due to lower combustion temperatures in peat combustion plants.

Table 4.15: Chemical Composition of Peat Ashes from Different Burner Systems in Comparison with Coal Ashes (Statens energiverk, 1985)

Element mg/kg	Fluidized Bed		Grate		Pulverized Combustion		Coal Combustion	
	fly ash	bed ash	fly ash	bottom ash	fly ash	bottom ash	fly ash	bottom ash
unburnt	2-16	0.1-0.3	2-14	2-37	6-22	-	0.9-35	0.7-18
CaO	10-17	0.7-3	6-22	12-19	6-10	14	0-31	0-20
SiO_2	44-51	74-96	21-51	29-47	32-43	64	20-65	10-60
Al_2O_3	6-9	0.8-12	3-14	5-13	14-29	26	11-41	10-36
Fe_2O_3	10-21	0.7-3	6-23	11-20	14-36	9	3-40	3-40
MgO	1-2	0.1-0.9	1-5	1-8	1-4	0.8	0-10	0-10
TiO_2	0.2-0.3	0.04-0.3	0.1-0.8	0.2-0.5	0.3-0.4	0.1	0-2	0-2
P_2O_5	1-3	0.09-0.2	1-3	1-3	1-11	0.7	0-1	0-1
K_2O	0.9-2	0.2-4	0.7-3	0.6-2	2-7	7	0-5	0-3
SO_3	0.6-4	0.1	1-7	0.2-0.5	0.4-4	0.001	0-7	0-1
MnO	0.1-0.2	0.01-0.06	1-0.7	0.2-06	0.1-0.3	0.2	-	-
Na_2O	0.4-0.8	0.1-3	0.2-0.9	0.3-1.3	1-3	4	0-5	0-5
BaO	0.1	-	0.07-0.1	-	0.1-0.6	0.1	-	-
As	37-116	2	47-436	4-5	45-97	3	2-1700	1-250
B	7-21	-	7-9	-	-	<3	5-3000	42-300
Be	2-3	6	1-12	<1-17	-	-	1-1000	0.4-11
Cd	4-4	<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	5-1500	3-380
Cr	80-122	50-80	70-113	120-200	43-200	26-200	3-7400	3-270
Cu	60-106	30	90-190	50-180	68-160	15-25	30-3000	0.01-720
Hg	0.5-2	-	0.7-2	0.5	0.3-0.4	0.001	<0.01-80	<0.01-2
Mn	-	-	-	-	-	-	25-4400	57-1300
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	3-1800	1-250
Se	<10-21	<10	<10-26	<10	<	<3	0.7-<500	0.08-10
Sr	412	-	599	-	520-1300	1000	40-9600	170-1800
U	<10-41	<10	<10-70	<10-50	4-36	3	0.8-100	4-15
V	60-70	10-30	40-100	40-80	18-590	28-50	20-1200	<24-300
Zn	220-469	60-160	230-2600	60-370	48-540	20-22	14-13000	<8-1800
Sb	<50	<50	<50	<50	3-14	-	-	-
Tl	<100	<100	<100	<100	0.9-2	-	-	-
Th	20-53	<10	10-57	<10-30	11-18	-	-	-

The peat fly ash can be used in the building industry, if the quality standards are met. The Swedish quality standard for peat and coal fly ash is presented in table 4.10.

Peat ashes from powdered peat combustion are being used in the cement and concrete industry in Finland.

Some studies have been conducted in Sweden and Finland concerning the use of peat ash in forest liming. According to preliminary results liming can have a positive effect. However, the long term effects of forest liming are still to be studied. The use of peat ash in agricultural production is not recommended because it can result in an increased metal uptake (Andersson and Persson, 1988; Nordic Minister Council, 1986).

If the utilization of fly ash is not possible the fly ash has to be disposed on a landfill. The bottom ash is usually disposed in a landfill. The fly ash is mixed with water before disposal in order to reduce dust problems. Because fly ash from peat combustion has pozzolanic properties, moistened fly ash hardens when stored. The compression strength is usually 500 - 1000 kPa, but compression strengths up to 3000 kPa have been measured (Statens energiverk, 1985).

The leachate from peat fly ash is initially alkaline (pH 10 - 12). The leachate will probably remain alkaline or neutral for a very long time due to the high buffer capacity of peat fly ash. The major components of the leachate are salts (sodium, potassium, calcium, cloride, sulphate). The leachate also contains a number of trace elements (e.g. molybdenum, selenium, zinc). On a landfill a leachate with elevated trace metal content will be produced for a very long time.

The peat ash contains some radioactivity. According to a Swedish study the radioactivity of peat ash is not detrimental to the environment. In Sweden, there are restrictions concerning the radioctivity of fly ash, when used in building industry.

4.3 Heavy Oil Fractions

The amount of oil ashes produced in a power plant are about one thousandth per unit of energy produced compared to the amount produced in a coal power plant. On the other hand, there is a growing concern about the environmental effects of the oil ashes, which are acidic, with high concentrations of heavy metals, mainly vanadium and nickel, and with a very high leaching rate.

Ash is separated from the combustion chamber and from the dust collecting system. Oil ashes are very different from coal ashes, both with respect to chemical composition and physical character. The content of unburnt may be high. In a Swedish study of six ashes from heavy oil combustion, the amount of unburnt varied between 23 and 94 % (Lundgren and Elander, 1987b) (see table 4.16).

The inorganic part of the ashes mainly contains oxidation products of iron (Fe), silicon (Si), sodium (Na), aluminium (Al), calcium (Ca), and magnesium (Mg). The variation is considerable, which has been shown in an American investigation (see table 4.16 and 4.17).

Table 4.16: Trace Element Concentrations in Fly Ashes from Heavy Oil Combustion Compared to Coal Fly Ashes (Lundgren and Elander, 1987b)

Element	ppm of dry weight		
	Oil Ash Literature Revue 1983	Oil Ash 5 Swedish Ashes	Coal Ash Literature Revue 1983
As	10 - 10000	30 - 300	2 - 1700
Cr	10 - 10000	500 - 4000	4 - 7000
Cu	10 - 100000	200 - 2000	30 - 3000
Mo	10 - 10000	40 - 300	3 - 500
Ni	10 - 100000	500 - 80000	2 - 800
Pb	10 - 10000	200 - 2500	3 - 2000
V	10 - 100000	6000 - 60000	20 - 1200
Zn	100 - 100000	200 - 6000	10 - 13000

Also, the concentrations of heavy metals varies a lot, depending on both differences in oil quality and combustion and flue gas cleaning system. In the table below concentrations from a literature revue 1983 as well as results from some Swedish investigations are given. The variations in content are very big (Table 4.16). The contents of vanadium (0.6 - 5.9 %) and nickel (0.5 - 7.5 %) were especially high, but also, the contents of chromium (0.05 - 0.4 %) and zinc (0.02 - 0.6 %) were high. The trace element contents in oil ashes were generally higher than in ashes of other fossil fuels. The high contents of these metals, especially the vanadium, make a metal recovery possible, which is done in one Austrian plant.

Ashes from other fossil fuels have pozzolanic characteristics. This is not to be expected from oil ashes due to their chemical composition and high contents of unburnt. Compacted ashes have a hydrological conductivity of 10^{-6} to 10^{-7} (Lundgren and Elander, 1987b).

Table 4.17: Chemical Composition of Oil Ash, Main Minerological Components (Mezey et al., 1976)

Compound	% of dry weight ash
Al_2O_3	0.5 - 12.1
CaO	1.1 - 33.2
Fe_2O_3	0.3 - 29.0
Na_2O	3.0 - 46.5
NiO	0.1 - 17.9
Si_2O	0.9 - 11.7
SO_3	0.2 - 59.6
V_2O_5	0.1 - 64.9

Lundgren and Elander (1987b) showed that the leaching rate for oil ashes is high, leading to very high concentrations of nickel and vanadium in the leachate as it is shown in table 4.19. Even the concentrations of elements like arsenic, cobalt, copper and zinc were 2 to 3 orders of magnitude higher than in leachates from coal, peat and biomass ashes.

Stabilizing the oil ashes by mixing them with cement (40 - 60 % dry weight), lime (35 - 45 %) or cement and coal fly ash and water gave residual products with ten times lower permeability, higher strength (100 - 300 kPa) and lower leaching rates (Table 4.18).

The heavy metal concentrations in leachates from stabilized oil ash were of the same order of magnitude as in leachates from coal ashes.

Table 4.18: Concentrations of Some Heavy Metals in Leachates from Oil Ashes as Compared to Maximum Concentrations in Leachates from Coal Ashes. Data from Batch Leaching Tests with H_2SO_4-Solution (pH 4) (Lundgren and Elander, 1987b)

Element	Concentration, mg/l, in Leachate from Oil Ash	Coal Ash	Stabilized Oil Ash
Cd	< 0.05 - 4	0.02	< 0.005
Cr	< 0.05 - 63	0.2	0.01 - 0.05
Cu	< 0.05 - 110	0.1	0.01 - 0.02
Ni	< 0.2 - 2700	0.1	< 0.02 - 0.03
Pb	< 0.5 - 5	< 0.2	< 0.05 - 0.06
V	0.7 - 5800	-	0.4 - 4
Zn	0.06 - 160	-	< 0.002 - 0.003

5 BY-PRODUCTS AND WASTE FROM DESULPHURIZATION PROCESSES

Beside fuel treatment to lower sulphur content and technical means during combustion, treatment of flue gases prior to their release to the atmosphere is a way to reduce emissions of sulphur dioxide.

To subdivide the numerous different types of commercially applied FGD-processes into groups, several criteria are possible, for example according to the chemicals added to the flue gas. Among the chemical agents calcium compounds, i.e. lime and limestone, are those which are applied in most of the FGD-plants.

Another criteria which may be used is the procedure as a wet or a dry process. Using wet processes, SO_2 is chemically or physically removed by a washing liquid leading to a gaseous, liquid or solid but wet by-product, whereas in dry processes either an agent is added in pulverized solid form leading to a dry by-product, or a dry adsorption process (e.g. activated carbon) is applied producing a gaseous by-product. Spray drying processes generate a dry product though the additive is given as a slurry because the water content evaporates in the hot flue gas before the product is removed.

In total the most applied type for flue gas desulphurization is a wet process using calcium as reagent. The major types of used FGD-systems are listed in table 5.1.

Table 5.1: Main FGD-Systems in Use

Type of process	System	Sorbent	Major By-Product	Utilization	State of operation
Wet working	calcium	lime/limestone	gypsum	+	commcercial
			$CaSO_3/CaSO_4$	-	commercial
	fly ash	lime/fly ash	$CaSO_3/CaSO_4$/fly ash	-	commercial
	dual-alkali	primary: sodium hydroxide secondary: lime/ limestone	$CaSO_3/CaSO_4$	-	commercial
	sea-water	primary: sea-water secondary: lime	waste sea-water	-	commercial
	Wellman-Lord	sodium sulphite	SO_2, H_2SO_4, S	+	commercial
	magnesium	magnesium oxide	SO_2, MgO	+	commercial
	Ammonia scrubbing	ammonia	$(NH_4)_2SO_4$	+	commercial
	Linde	$C_{10}H_{22}O_5$1)	SO_2, H_2SO_4, S	+	commercial
	ISPRA-MARK 13A	Bromine2)	H_2SO_4, H_2	+	pilot plant
Spray drying	FLÄKT	lime	$CaSO_3/CaSO_4$/fly ash	-	commercial
	Rockwell	sodium carbonate	Na_2SO_3/Na_2SO_4/fly ash	-	commercial
Dry working	Uhde/BFV	activated carbon	SO_2, H_2SO_4, S	+	commercial
	DAS/CDAS3)	limestone/slacked lime	$CaSO_3/CaSO_4$/fly ash	-	commercial
	PFI4)	slacked lime	$CaSO_3/CaSO_4$/fly ash	-	commerical
	Electron beam	ammonia	$(NH_4)_2SO_4$	+	pilot plant

1) tetra-ethylene-glycol-dimethyl-ether
2) used as a catalyst
3) dry absorption system/conditioned dry absorption system
4) post furnace injection

The performance targets of flue gas cleaning vary considerably. Beside the kind of plant the FGD-units used and the legal SO_2 removals requirement vary from state to state. Moreover the kind and composition of the used fuel affect the performance targets.

Dacey and Cope (1986) examined the performance of FGD-systems for coal. They found as a conclusion that the "median availability of systems shows improvements to a level where the FGD unit matches the acceptable availability of boilers operation (means better than 85 %). The achievement of this satifactory level of operational reliability and performance has come about by a gradual process of system development across a range of systems, rather than from deployment of new types of FGD units with dramatically improved characteristics." They recommend that the performance of the best currently operating conventional systems (which means with no simultaneous NO_x removal) should be perfectly adequate to reduce capital or operating costs significantly.

Table 5.2 gives an outlook on estimated amounts of by-products of FGD-processes for the year 2000.

Table 5.2: Projected Amounts for the Year 2000 for By-Products from Flue Gas Desulphurization Processes in Member Countries (data provided by member countries, all values given in metric tons)

Country	Actual Amount	Year	Amount 2000	Remarks
AUSTRIA	61.000	1989	140.000	gypsum
	38.000	1989	85.000	sludge from dry or spray dry processes
	16.000	1989	16.000	sodium compounds
	12.000	1989	8.000	sulphuric acid
CANADA	none	1987	1.570.000	approx. 90 % utilization as commercial gypsum is expected
FEDERAL REPUBLIC OF GERMANY	3.000.000	1989	3.500.000	gypsum
	500.000	1989	500.000	sludge from dry or spray dry processes
	30.000	1989	40.000	sulphuric acid
	40.000	1989	40.000	sulphur dioxid
	60.000	1989	80.000	sulphur
	4.000	1989	4.000	ammonium sulphate
FINLAND			100.000 - 200.000	gypsum
			max. 15.000	sulphur
	30.000	1988	300.000 - 500.000	FGD from wet-dry process
	10.000	1988	200.000 - 300.000	by-product from LIFAC-process
ITALY	none	1988	3.000.000	gypsum
MALTA	none	1988	no data available	
NETHERLANDS	190.000	1989	340.000	gypsum
SWEDEN	80.000	1988	200.000	FGD-product
			50.000	gypsum
UNITED KINGDOM	none	1988	1.000.000 - 2.000.000	gypsum
UNITED STATES OF AMERICA	14.000.000	1985	45.000.000	sludge from lime/limestone scrubbers

5.1 Wet Processes

5.1.1 Survey of Processes

On the following pages a survey of the most common and applied wet FGD systems will be given. A detailed analysis and survey is given by the IEA Coal Research FGD-Handbook (Klingspore and Cope, 1987).

Lime/Limestone Scrubbing - Sludge

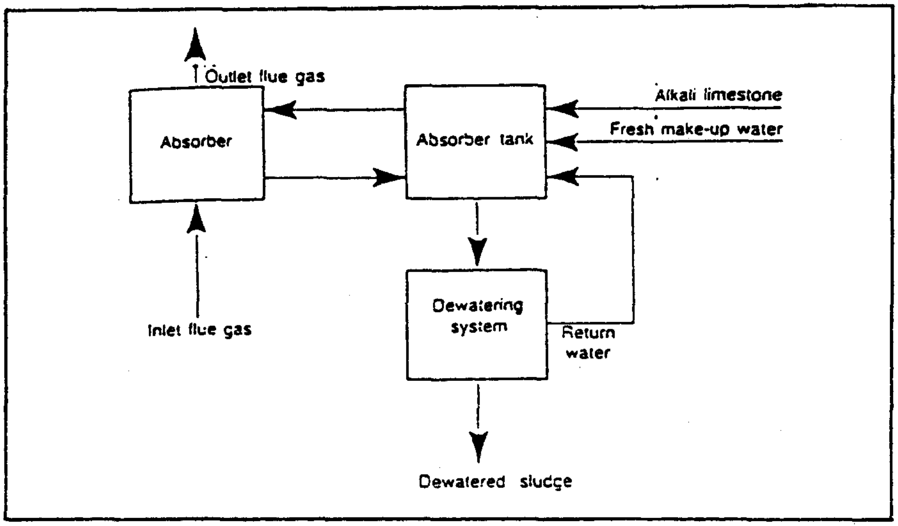


Figure 5.1: Block Diagram of Lime/Limestone - Sludge Procedure (Klingspore and Cope, 1987)

Systems to be treated: flue gas of hard coal, brown coal and oil
Scale of operation: commercial
Reacting agent: $CaO/CaCO_3$
By-product: sludge (not usable without further treatment)
Waste water: is to be treated

Short description of the process: The flue gas is scrubbed with a slurry of water and limestone or slaked lime in a washing tower (absorber). By absorbing SO_2 a mixture of solid particles is formed containing calcium sulphite, calcium sulphate, unreacted sorbent and a certain amount of fly ash. After separation in a dewatering system a sludge remains which has to be deposited.

Lime/Limestone Scrubbing - Gypsum

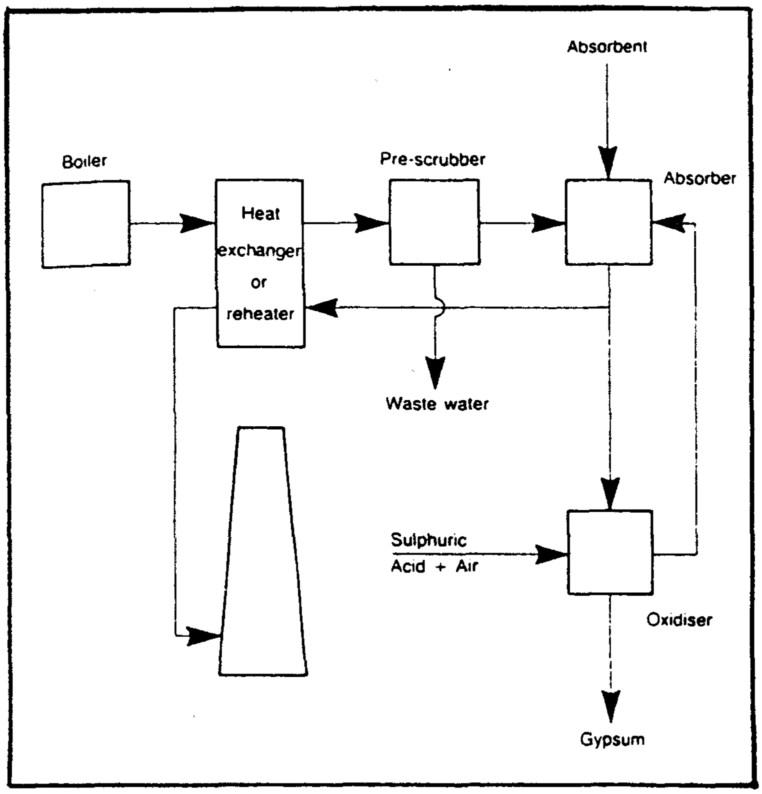


Figure 5.2: Block Diagram of Lime/Limestone - Gypsum Procedure (Klingspore and Cope, 1987)

Name of procedure: Lime/Limestone Scrubbing with enforced oxidation

Systems to be treated: flue gas of hard coal, brown coal and oil

Scale of operation: commercial

Reacting agent: $CaO/CaCO_3$

By-product: gypsum (solid, usable)

Waste water: has to be treated

Short description of the process: The flue gas is led into a prescrubber where it is cooled down and HCl, HF and fly ash are washed out. Down-stream in the mainscrubber SO_2 is scrubbed out with a slurry of lime or limestone, followed by an oxidizing stage in which the content of calcium sulphite is oxidized to calcium sulphate by air with the help of some sulphuric acid. The solid gypsum is then separated by a filter press or a centrifuge.

Sodium Carbonate Scrubbing

Systems to be treated: flue gas of hard coal, brown coal and oil
Scale of operation: commercial
Reacting agent: Na_2CO_3
By-product: Na_2SO_3/Na_2SO_4 (not usable sludge without treatment)
Waste water: is to be treated

Short description of the process: This scrubbing system, similar to the lime/limestone scrubbing process, is based on sodium carbonate as sorbent. Sodium compounds have a better sorbing effect in comparison to calcium compounds. The process operates similar to a conventional lime/limestone scrubbing and generates sodium sulphite and sodium sulphate for disposal.

Magnesia Based Scrubbing

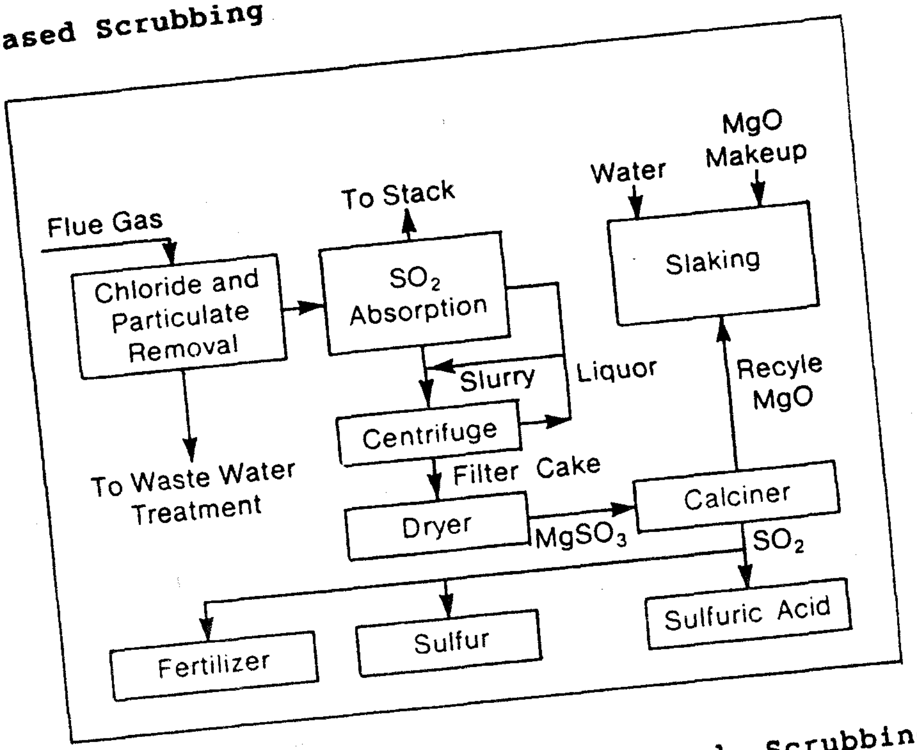


Figure 5.3: Block Diagram of Magnesia Based Scrubbing and MgO-System Regeneration (United Engineers Constructors, no year).

Systems to be treated: flue gas of hard coal, brown coal and oil
Scale of operation: commercial
Reacting agent: $Mg(OH)_2$
By-products: sulphur, SO_2, H_2SO_4 and MgO (usable)
Waste water: is to be treated

Short description of the process: The magnesia-scrubbing process uses hydrated magnesia oxide for sorption of SO_2. The flue gas, after being led through a prescrubber to remove halogene compounds and particles is brought into contact in the absorber with a slurry of magnesium hydroxide forming mainly magnesium sulphate and some magnesium sulphite. These solid by-products are separated from the washing liquor and after drying transported to the regeneration unit. By thermal treatment magnesium oxide and a SO_2 rich gas are generated. The magnesium oxide is reused to prepare new scrubbing slurry. The SO_2 can be processed to produce liquid SO_2, sulphuric acid or elemental sulphur.

Wellman-Lord Scrubbing

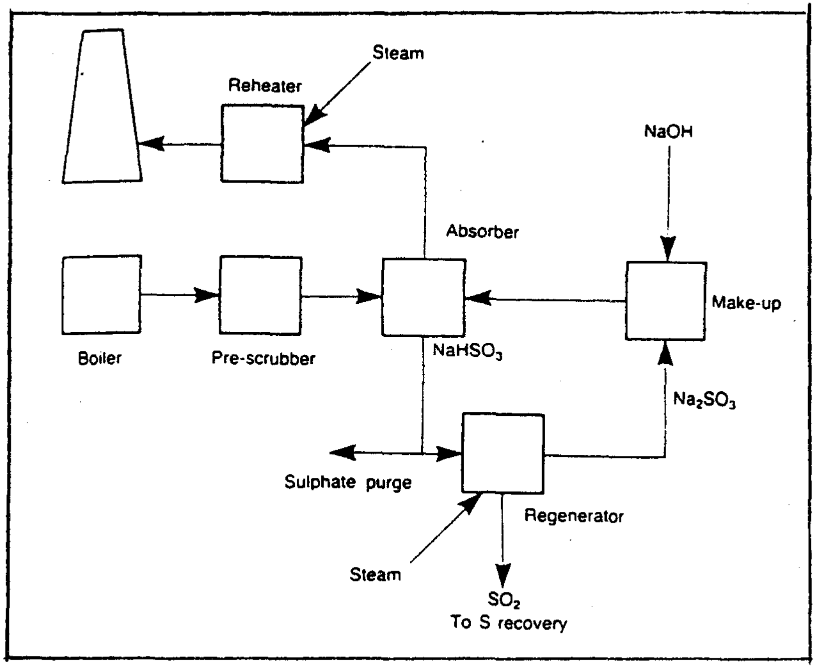


Figure 5.4: Block Diagram of Wellman-Lord Process (Klingspore and Cope, 1987)

Systems to be treated: flue gas of hard coal, brown coal and oil
Scale of operation: commercial
Reacting agent: $NaSO_3$
By-product: SO_2, H_2SO_4, S and Na_2SO_4 (usable, in different phases)
Waste water: has to be treated

Short description of the process: The Wellman-Lord process uses a solution of sodium sulphite to absorb the SO_2. The flue gas after beeing prescrubbed is led to the absorption tower where the SO_2 reacts with the sorbent forming sodium bisulphite and a small amount of sodium sulphite. The spent washing liquor is then led to the regeneration unit while a small side stream of this liquor is transferred to a crystallization section where the sodium sulphate is selectively separated by forming solid crystals. In the regenerater a thermal decomposition of the spent washing liquor generates sodium sulphite which is recycled to the absorption section, and SO_2 which can be used for producing liquid SO_2, sulphuric acid or elemental sulphur.

Scrubbing by Condensation

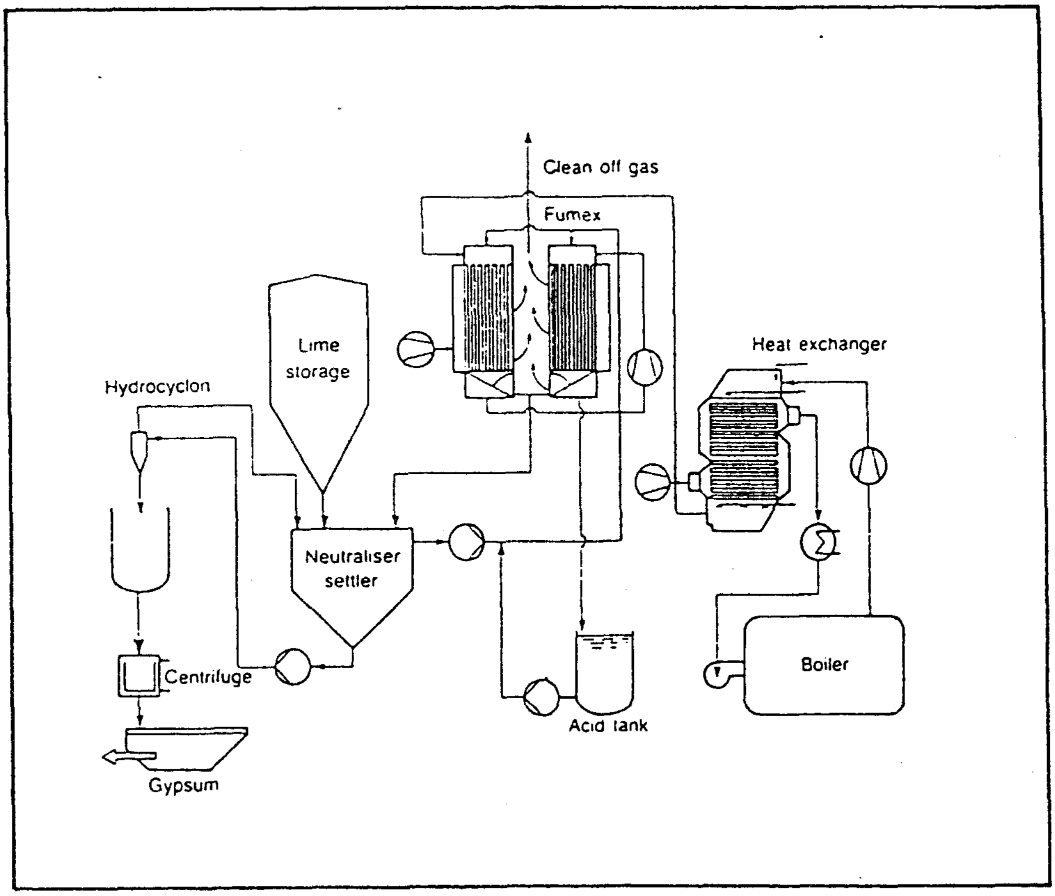


Figure 5.5: Flow Sheet Condensation Procedure (Klingspore and Cope, 1987)

Name of procedure: Condensation/Alkali Scrubber
Systems to be treated: flue gas of coal and oil
Scale of operation: commercial
Reacting agent: $NaOH/Ca(OH)_2$
By-product: $Na_2SO_3/CaSO_4$ (not usable solids and liquids)
Waste water: is to be treated

Remarks: In the so called FUMEX process the flue gas is cooled down in a condensing heat exchanger to 20 °C to 30 °C. In a downstream falling film scrubber the flue gas reacts with the alkaline scrubbing liquor. When lime is used as sorbent calcium sulphate is formed and separated in a centrifuge.

Sea-Water Scrubbing

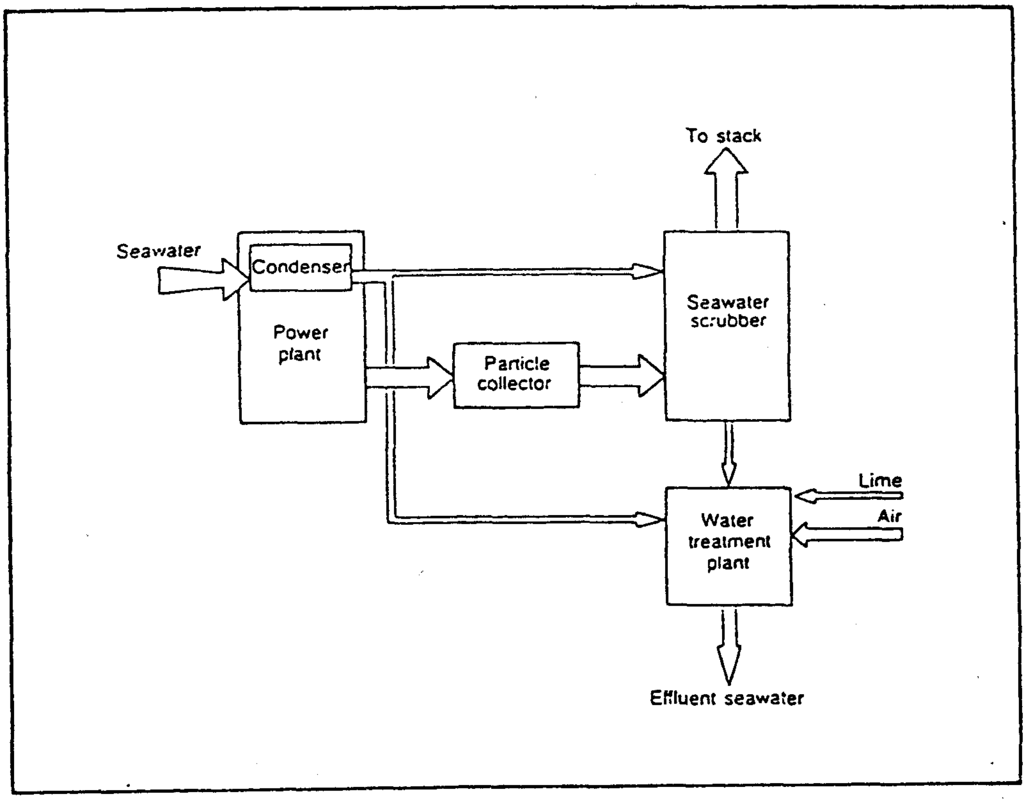


Figure 5.6: Flow Sheet of Sea-Water Procedure (Klingspore and Cope, 1987)

Systems to be treated: flue gas of coals and oil
Scale of operation: commercial
Reacting agent: alkaline sea-water
By-product: dilute $CaSO_4$-solution (not usable)
Waste water: is to be treated, goes back to sea

Remarks: The sea-water process uses the natural alkalinity of sea-water to scrub the SO_2 out of the flue gas. The flue gas is pretreated in a particle collector and then led to the scrubber. The spent scrubbing water before being discharged to the sea is pH adjusted by addition of lime.

5.1.2 Sludge

Using a lime/limestone slurry as washing liquor the sorption of SO_2 generates a sludge. Most of the lime/limestone FGD-plants installed in the USA are operated as sludge producing processes. Physical properties of such a by-product are given in table 5.3. This sludge contains mainly calcium sulphite, calcium sulphate and unreacted particles of the sorbent (see table 5.4) as well as fly ash. Such a mixture of more or less high content of sulphite with sulphate occurs when the washing tower does not have sufficient oxidation capacitiy that transforms all sulphite to sulphate.

Such a sludge cannot be utilized as by-product because of its high content of sulphite and also the content of unreacted sorbent. Therefore, in most of the plants the sludge is pumped or transported to a nearby sludge lagoon or pond. After sedimentation of the solid particles of the sludge, the water can be reused for preparation of the washing slurry.

Beside the disadvantage of a not usable by-product another disadvantage is the lower separating speed of the particles of the sludge mixture on comparison of gypsum particles in gypsum process with enforced oxidation. This means longer separating times and/or bigger sedimentation areas.

Table 5.4 shows the results of chemical analyses of major constituents of sludges, table 5.5 those of sludge liquors. Concentrations of trace elements of both, sludges as well as liquors are given in table 5.6.

Table 5.3: Representative Ranges of Values for the Physical Characteristics of FGD Sludge in the U.S.A. (Buhl and Perlsweig, 1988)

Characteristics	Wet	Dry
Particle Size (mm)	.001-.05	.002-.074
Density (g/cm^3)	0.9-1.7	Variable
Optimum Moisture Content (%)	16-43	0
Permeability (cm/sec)	10^{-6}-10^{-4}	10^{-7}-10^{-6}
Unconfined Compressive Strength (psi)	0-1600	41-2250

Table 5.4: Concentration of Major Chemical Constituents of Wet-FGD Sludge Solids by Scrubber System and Source of Coal*) (Buhl and Perlsweig, 1988)

Alkaline Lime	Direct	Lime	Direct	Limestone	Dual-Alkali		Fly Ash
	East	West	East	West	East	West	West
Calcium Sulphate ($CaSO_4$)	15-19	17-95	5-23	85	15-68	82	20
$CaSO_3 \cdot 1/2\ H_2O$	13-69	2-11	17-50	8	13-68	1	15
Calcium Sulphite ($CaSO_3$)	1-22	0- 3	15-74	6	8-10	11	--
Sodium Sulphate ($Na_2SO_4 \cdot 7H_2O$)	--	--	--	--	4- 7	4	--
Fly Ash	16-60	3-59	1-45	3	0- 7	8	65

*) Source of coal is categorized by Eastern producing regions (Northern Appalachia, Central Appalachia, Southern Appalachia, Midwest, Central West and Gulf; i.e., Bureau of Mine Districts # 1 - 15, 24) and Western producing regions (Eastern Northern Great Plains, Western Northern Great Plains, Rockies, Southwest and Northwest; i.e., BOM Districts # 16 - 23).

Table 5.5: Concentration of Major Chemical Constituents of Wet-FGD Sludge Liquors by Scrubber System and Source of Coal*) (Percent of Total) (Buhl and Perlsweig, 1988)

	Direct Lime	Direct Limestone		Dual-Alkali
Constituent**)	East	East	West	East
pH (units)	8-9.4	5.5-8.4	6.6-6.8	12.1
Total Dissolved Solids	2800-10260	5400	3300-14000	155700
Chloride	1050-4900	1000	620-4200	4900-5600
Potassium	11-28	24	8-28	320-380
Sodium	36-137	12	370-2250	53600-55300
Calcium	660-2520	1600	390-770	7-12
Magnesium	24-420	53	3-9	0.1
Sulphate	800-4500	2500	1360-4000	80000-84000
Sulphite	0.9-2.7	160	1-3900	-

*) Source of coal is categorized by Eastern producing regions (Northern Appalachia, Central Appalachia, Southern Appalachia, Midwest, Central West and Gulf; i.e., BOM Districts # 1 - 15, 24) and Western producing regions (Eastern Northern Great Plains, Western Northern Great Plains, Rockies, Southwest, and Northwest; i.e., BOM Districts # 16 - 23).

**) All constituent concentrations, unless noted, in milligrams per liter.

Table 5.6: Concentration of Trace Elements Found in Wet FGD Sludges (Solids and Liquors) (Buhl and Perlsweig, 1988)

	Sludge Solids*)		Sludge Liquors**)	
	Low	High	Low	High
Arsenic	0,8	52,0	0,0004	0,1
Boron	42,0	530,0	2,1	76,0
Cadmium	0,1	25,0	0,002	0,1
Chromium	1,6	180,0	0,0002	0,3
Copper	6,0	340,0	0,0045	0,5
Fluoride	266,0	1017,0	0,2	63,0
Mercury	0,01	6,0	0,00006	0,1
Lead	0,2	290,0	0,005	0,5
Selenium	2,0	60,0	0,003	1,9

*) Sludge solid concentrations in milligrams per kilogram

**) Sludge liquor concentrations in milligrams per liter

5.1.3 Gypsum

As already described in chapter 5.1.1, gypsum ($CaSO_4.2\ H_2O$) is a product of a wet FGD with lime or limestone as additive if in the scrubber or after the scrubber the content of $CaSO_3$ is oxidized to $CaSO_4$. This type of FGD is the most applied process in Europe. In comparison to natural gypsum the FGD-gypsum most times has a chemical composition more constant than that of the natural one. However, before being utilized, the FGD-gypsum has to be conditioned. Methods of conditioning vary and may include up to three steps:

1. Washing only in those cases in which a possible content of Cl is too high for the utilization of the gypsum (for standards see table 5.9). In many plants a prescrubber situated before the main scrubber, washes out the halogen content of the flue gas, thus avoiding a significant content of chloride in the produced gypsum.
2. Drying at about 90 degrees C (removal of surface water, crystal water remains).
3. Agglomeration to solid particles.

Thus a material is produced which can be utilized in the same way as natural or synthetic gypsum. The quality of such FGD gypsum is in most cases similar or better to that of natural gypsum, see the comparisons in table 5.7 and 5.8.

Table 5.7: Components of Natural and FGD Gypsum in Per Cent (VGB, 1986)

	Gypsum	
	Natural	**FGD**
Moisture	1	7 - 10
$CaSO_4.2H_2O$	78 - 95	98 - 99
Cl	< 0,001	< 0,01
Na_2O	0,02	< 0,01
MgO (soluble in water)	-	0,1
Fe	-	< 0,05
F (soluble in water)	-	< 0,05
SO_2	-	< 0,05
CO_2	-	1,0
K_2O (soluble in water)	-	0,5
pH-value	6 - 7	5 - 8
inerts	5 - 20	-

Table 5.8: Concentrations of Trace Elements in FGD Gypsum and Natural Gypsum (Gutberlet, 1983)

	FGD-gypsum					Natural-gypsum	
	A	B	C	D	E	F	G
As (mg/kg)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Pb	6	4	6	3	3	4	4
Cd	< 0,2	< 0,2	< 0,2	< 0,2	< 0,2	< 0,2	< 0,2
Hg	< 0,5	< 0,5	1,1	< 0,5	< 0,5	< 0,5	< 0,5
Se	< 0,5	2,8	11	2,6	< 0,5	< 0,5	< 0,5
Ti	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Zn	7	13	10	10	7	12	6

A - E: Gypsum from different plants with FGD-system
F - G: Natural ocurring gypsum

A material and mass balance for a limestone scrubbing process is given in figure 5.7. It shows a flue gas volume of 1.000.000 Nm^3/h containing 2.000 mg SO_2/m^3 will generate about 5.500 kg/h gypsum.

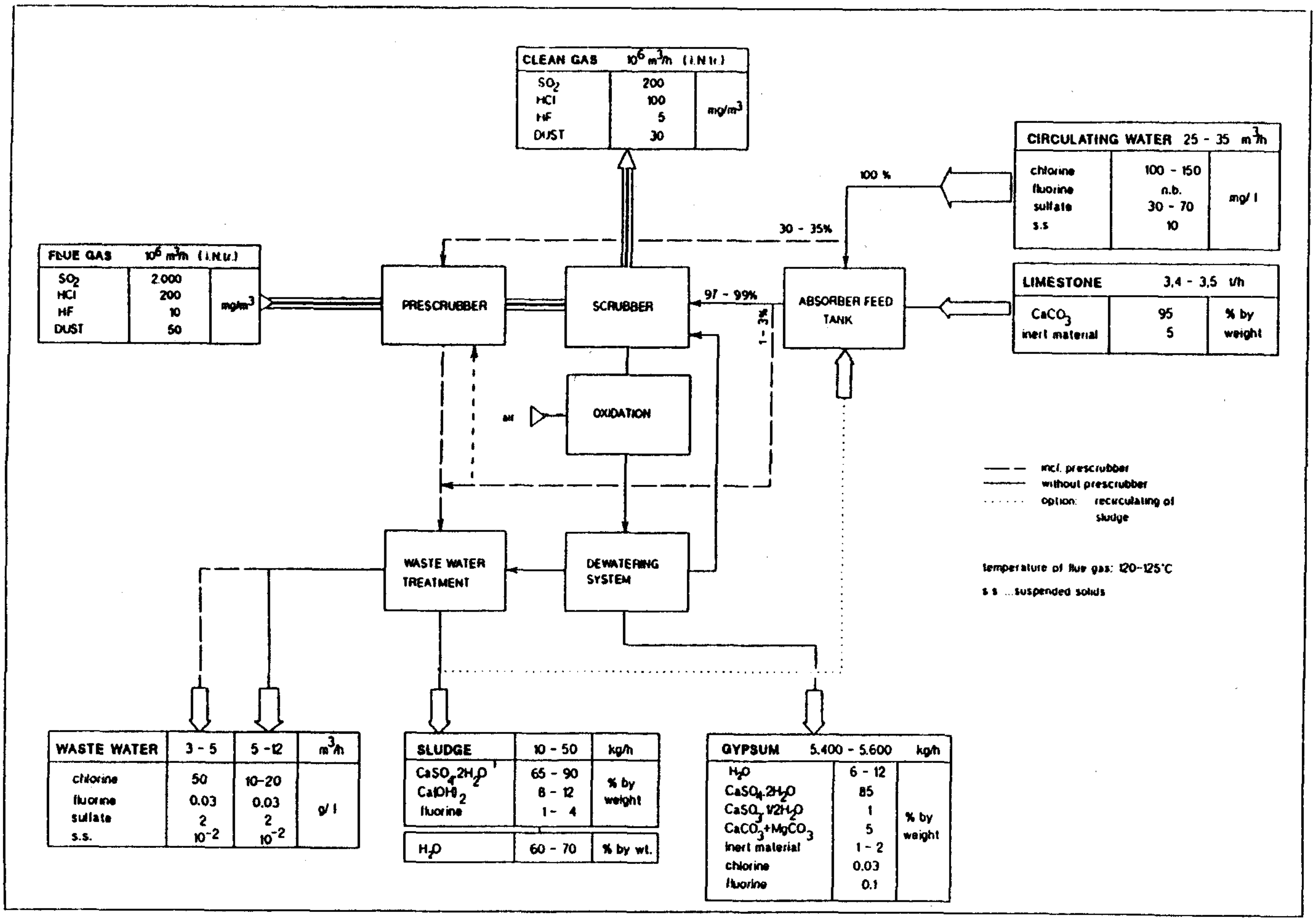


Figure 5.7: Material Balance for Limestone Scrubbing Process (Rentz, 1988)

As radioactivity of FGD gypsum is lower or equal to natural gypsum a possible use is in the field of building/construction. Possible uses are shown in figure 5.8.

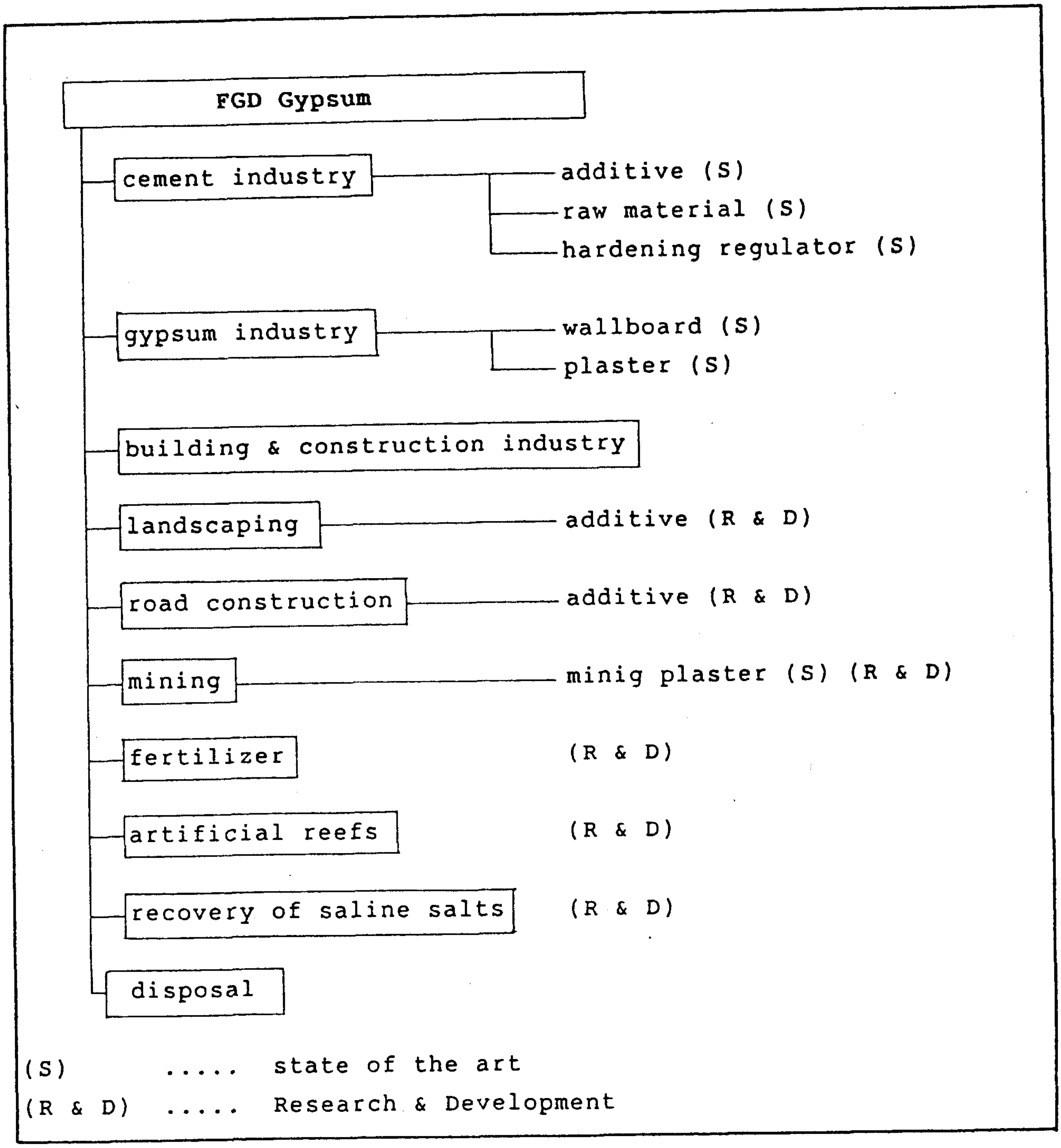


Figure 5.8: Possible Utilization of Gypsum
(Arbeitsgruppe "Kraftwerksreststoffe", 1988)

5.1.3.1 Standards and Specifications

In several countries there are official or industrial standards for gypsum. The following table 5.9 gives some information about standards required for commercially used gypsum in the United States, Japan, Austria, Federal Republic of Germany and the United Kingdom.

Table 5.9: Commercial-Grade Gypsum Specification in the United States of America, Japan, Austria, FRG and UK (Ellison and Hammer, 1988; Praxmarer et al., 1988; Arbeitsgruppe "Kraftwerksreststoffe", 1988; Kyte, 1989)

Parameter	National Gypsum Co	Georgia Pacific Corp.	US Gypsum Co	Japan	Austria	FRG	UK
Gypsum content, min. %	94	90	95	95	> 95	≥ 95*	95 (dry basis)
Calcium sulphite, max. %	0.5	-	2.0	0.25	0.25	0.25	-
Total soluble salts, max. ppm	-	-	600	1000	-	-	$MgO+K_2O+Na_2O$ 1000
Sodium content, max. ppm	250	200	75	-	600	600	-
Chloride content, max. ppm	400	200	120	-	1000	100	100
Magnesium content, max. ppm	250	-	50	-	1000 MgO	1000	-
Free water, max. %	1	10	10	10	8	10	10
pH	6 - 8	3 - 9	6.5 - 8	6.5 - 8	5 - 9	5 - 8	-
Inerts max. %	3.0	-	1	-	-	-	-
Colour	-	-	-	-	white	white (white level > 80 %)	-
Odour	-	-	-	-	neutral	neutral	-
Toxic components	-	-	-	-	-	none	-
Fe_2O_3 max.%	-	-	-	-	-	-	0.4
Total SiO_2 max.%	-	-	-	-	-	-	1.5
Respirable SiO_2 max.%	-	-	-	-	-	-	1 %

*) Inert impurities act in FGC-gypsum in exactly the same way as in natural gypsum. A reduction in the level of purity up to about 80 % is possible. Beside the points in the table some more impurities are regulated.

5.1.4 Sodium Compounds

The most common FGD process using sodium compounds as reagents is the Wellman Lord process. The Wellman Lord process using a regenerable washing liquor containing sodium sulphite generates finally divided sulphur or sulphuric acid, which are marketable products.

The Wellman Lord process is applied in several plants in Japan and the USA, one plant in Austria and in two plants in the FRG.
The sodium scrubbing process's major environmental drawback is that it produces a liquid effluent which is contaminated with about 5 % of dissolved sodium salts, mostly sodium sulphate. Although not particularly toxic, it is unlikely that such an effluent would be permitted as an uncontrolled discharge in most ECE countries. On-site treatment involving sulphite oxidation and pH neutralization, discharge into an evaporation pond or into an existing foul sewer for treatment are the possible treatment alternatives and each requires the existence of some site facilities and, for evaporation, favourable climatic conditions. It is unlikely that a sodium FGD unit could, by itself, carry the cost of building a dedicated treatment plant. It is this factor rather than preferred process or cost advantages which has caused a number of plants to discontinue the use of sodium scrubbing and to adopt other techniques (Prior and Holcomb, 1984). In Sardinia a pilot plant is operated to test this process.

For investigation and research in Denmark two district-heating plants have been supplied with FGD using NaOH as reagent (International Energy Agency/OECD, 1987).

5.1.5 Magnesia Compounds

The magnesia process as wet FGD is applied either as a regenerative process or a process leading to $MgSO_4$ which can be utilized in the magnesia industry. A survey on potential end products in connection with the magnesia process is given by figure 5.9.

It can be seen that the application of the magnesia process for FGD in the pulp industry is advisable because the $MgSO_3$ generated thereby can be utilized within the process of pulp production (Herzog et al., 1983).

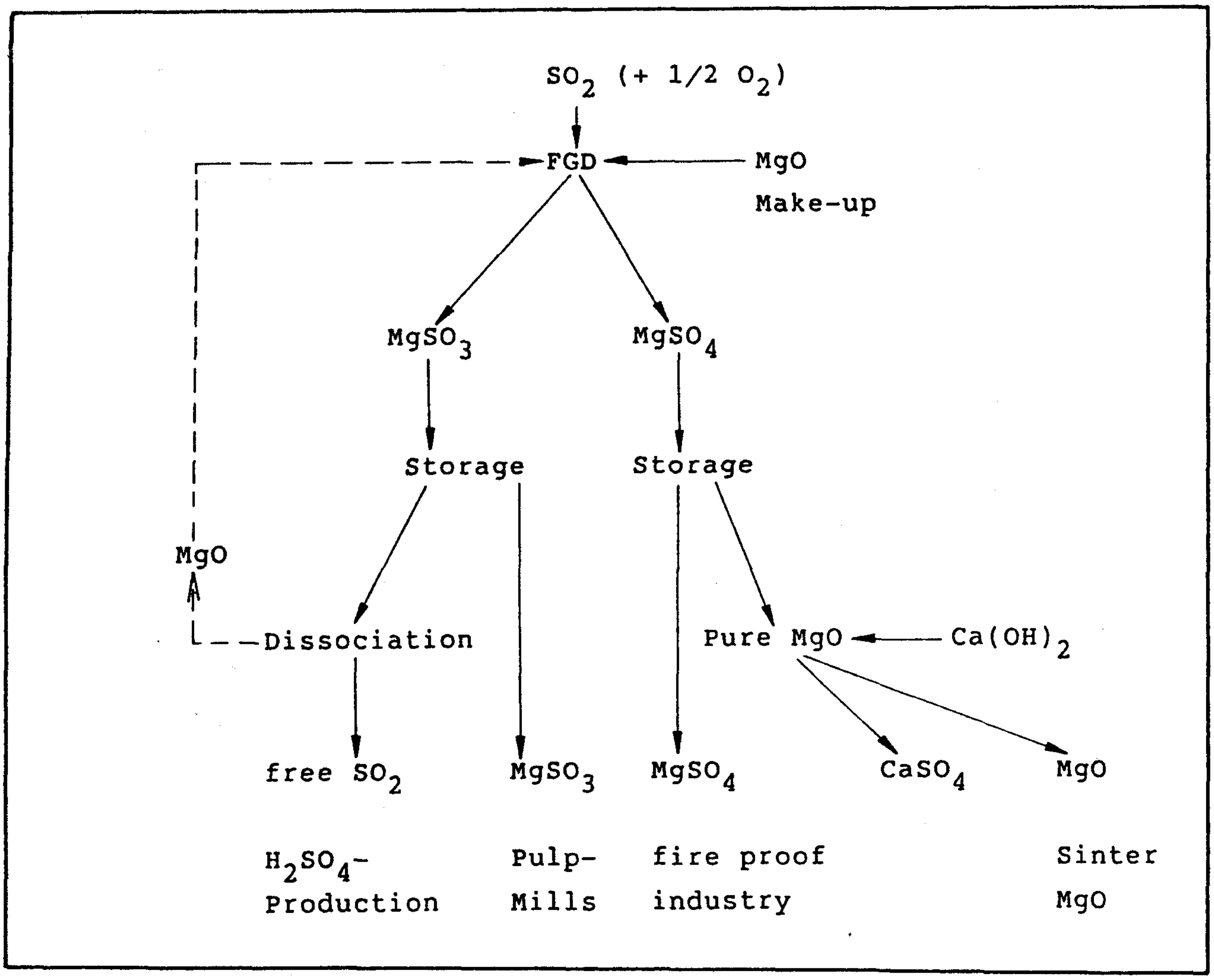


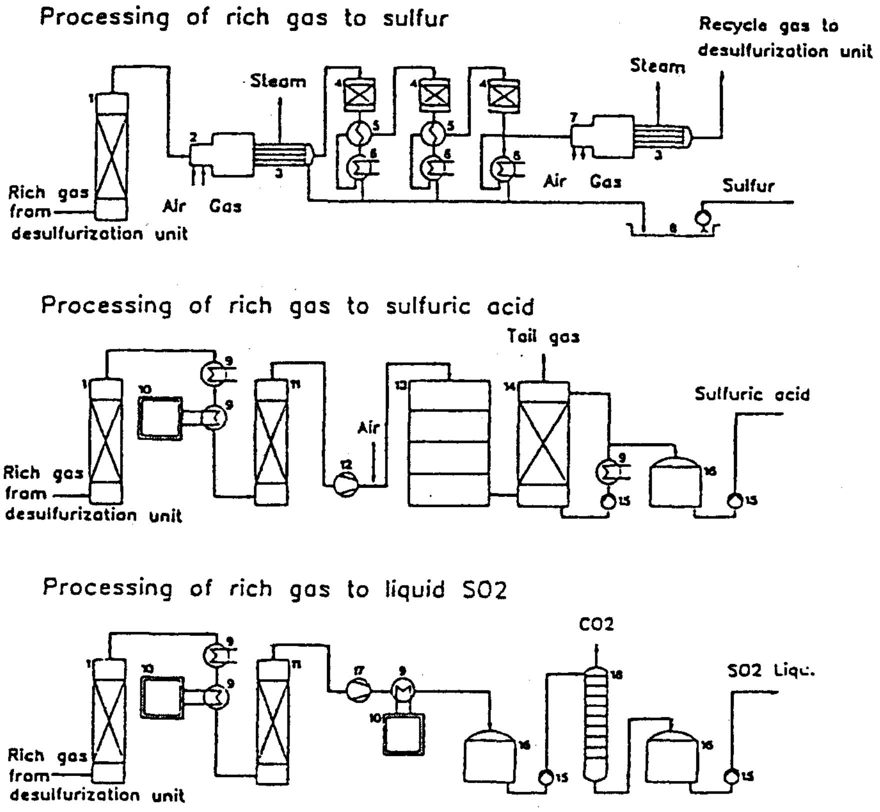
Figure 5.9: Possible End Products of Wet FGD with Magnesia (Loquenz, 1986)

5.1.6 Sulphur, Sulphur Dioxide, Sulphuric Acid

As described above, the regenerative types of sodium and magnesia processes lead to a SO_2-rich gas. This SO_2 rich gas can be used directly or it can be processed to elemental sulphur (e.g. by the so called Claus process) or sulphuric acid. A flow sheet of the three possibilities of processing SO_2-rich gas to products is given in figure 5.10. Sulphur is imported in most of the ECE member countries (Fike, 1989b). Therefore both sulphur and sulphuric acid are appropriate for utilization.

In the United Kingdom there are considerable restrictions on the utilization of sulphuric acid. H_2SO_4 is a bulk chemical which is produced on site as required and which is often needed in several different qualities. In addition the market is usually fragmented with many sites requiring only relatively small quantities of acid. In larger chemical plants the sulphuric acid production is closely integrated into the energy balance of the whole chemical complex and such plants would find it extremely difficult to accept a certain limit of their market requirements. Thus, in the current situation, these considerations make it unlikely that there would be a market for more than about two acid producing FGD plants within the U.K. (Fleet, 1989). Table 5.10 gives an estimation for the use of FGD-by-products in U.K.

The newly developed ISPRA MARK 13A system, now installed as a pilot plant in an oil refinery at Sardinia, Italy, generates H_2SO_4 and hydrogene as by-products by catalytic effects of bromide. Sulphuric acid and pure hydrogene are salable products (Jung, 1989).



1. Adsorber
2. Reduction burner
3. Waste heat boiler
4. Claus reactor, 3 stages
5. Heat exchanger
6. Condenser
7. Final combustion
8. Sulphur pit
9. Cooler
10. Refrigeration unit
11. Rich-gas dryer
12. Blower
13. Catalytic H_2SO_4 reactor
14. Adsorption tower
15. Pump
16. Storage tank
17. Compressor
18. CO_2 stripping column

Figure 5.10: Possibilites to Process SO_2 Rich Gas Yielding Sulphur, Sulphuric Acid or Liquid SO_2 (Richter, Knoblauch and Jüntgen, 1987)

Table 5.10: Annual Production of FGD By-Product from a British 2000 MW Power Plant (76 % utilisation, 2 % (wt) sulphur in coal, 90 % SO_2 removal) (Kyte and Halstead, 1989)

By-product	Regenerative System in t	Limestone Scrubbing in t	U.K. Market in %
Sulphur	75.000	-	-
Sulphuric Acid	280.000	-	10 - 12
Gypsum	-	500.000	15 - 20
Filter Cake	15.000	40.000	-
$CaCl_2$	25.000	25.000	-
$NaSO_4$	30.000	-	25

5.1.7 Ammonia Compounds

The Ammonia scrubbing process is a wet FGD process which leads to ammoniasulphate as an end-product. It is aimed to utilize this by-product as fertilizer.

A chemical analysis of the product according to its main components or heavy metal concentrations respectively is given in table 5.11.

Table 5.11: Example of the Composition and Concentration of Trace Elements of the Product Caused by Ammonia Scrubbing Process (Landesanstalt für Landwirtschaftliche Chemie, 1980)

Main components	Trace elements		
20,9 % ammonium nitrogen (N)	F	171	mg/kg
68,4 % SO4	As	31	mg/kg
1,9 % Cl	Se	12	mg/kg
	Cr	16	mg/kg
	Ni	18	mg/kg
	Cu	21	mg/kg
	Zn	93	mg/kg
	Cd	1,5	mg/kg
	Hg	0,11	mg/kg
	Pb	91	mg/kg

It can be seen that the low concentrations of heavy metals would not pose problems for utilization as fertilizers.

A material balance of the process is given in figure 5.11. It can be seen by comparing the three options shown in figure 5.11 that this process is suitable especially for flue gases with a relatively high content of SO_2.

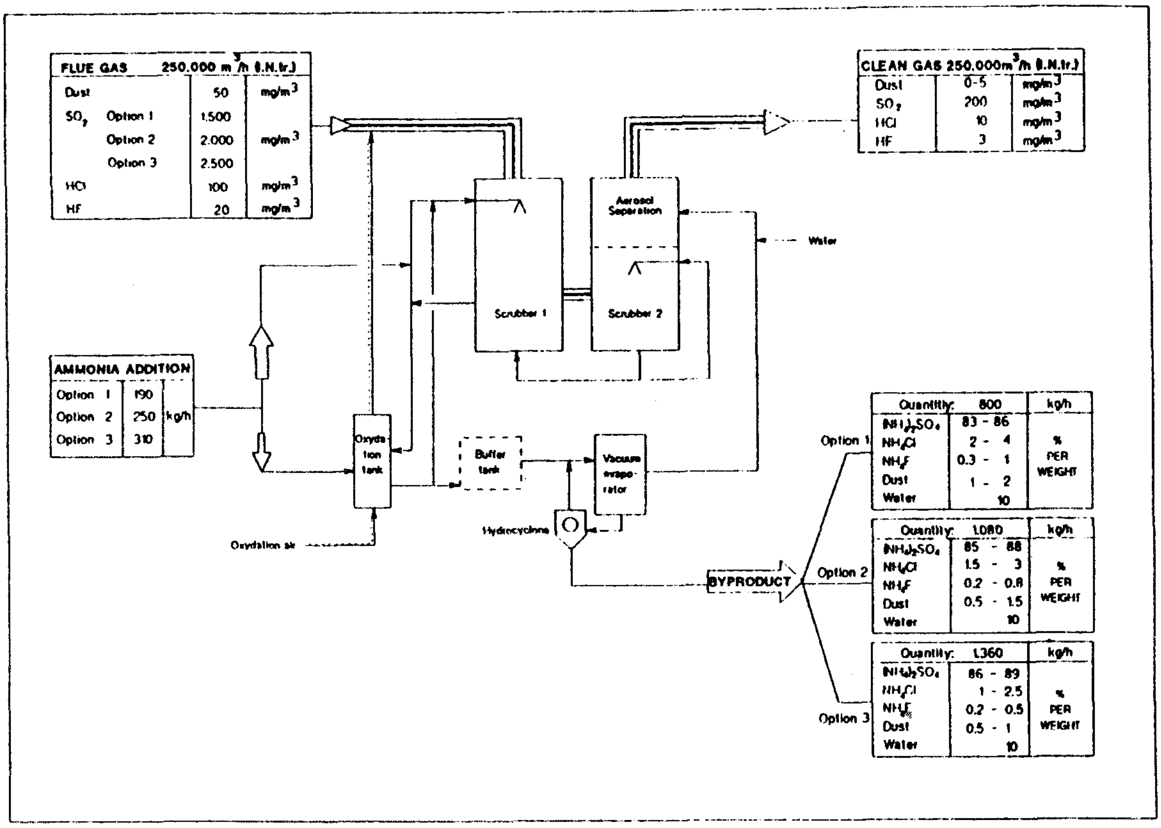


Figure 5.11: Material Balance of Ammonia Scrubbing Process (Arbeitsgruppe "Kraftwerksreststoffe", 1988.)

5.1.8 Waste Water

Waste water may arise as a consequence of wet flue gas desulphurization processes. If there is chloride in the flue gas the wet processes will produce considerable amounts of waste waters. In order to reduce the amount of waste water and to improve utilization of washing liquid later on is circulated and fed back to scrubbing process after separation of FGD product.

Thus contaminants being introduced to the FGD unit tend to accumulate in circulating water. Therefore a portion of circulating water periodically has to be drawn off to avoid disturbing effects both on performance of FGD process and on the quality of the FGD product probably caused by high amounts of impurities present in the washing liquor.

Thus to a certain extent the quantity of waste water occuring is determined by quality standards imposed to FGD-end product.

For predominantly applied lime/limestone scrubbing processes the most relevant parameter to quantity of waste water is the concentration of chlorides in washing liquid, chloride compounds being particulary undesired in gypsum.

Quality and composition of FGD-waste water is seriously influenced by

- composition of flue gas:
  besides SO_2, hydrochloride, hydrofluoride and some residual amounts of fly ash are introduced to FGD unit by flue gas.
- quantity and quality of fly ash separated in FGD unit
- leachability of metals present in fly ash under environmental conditions of FGD plant
- quality of used sorbent
- quality of water used to prepare washing liquid
- performance feature of the FGD plant.

Some data typical for composition of waste water occuring at limestone scrubbing processes are listed in table 5.12.

Table 5.12: Composition of Waste Water of a Limestone Scrubbing Process before Waste Water Treatment (Arbeitsgruppe "Kraftwerksreststoffe", 1988)

	Unit	Separate Prescrubber	Integrated Prescrubber	Without Prescrubber
pH		1	5 - 6	4 - 5
Sediment	ml/l	< 500	n.a.	< 50
Filtration residue	g/l	n.a.	10	5 - 40
COD	mg/l	50 - 150	150 - 200	50 - 150
Cl	g/l	15 - 20	20 - 200	20
F	mg/l	350 - 450	40 - 60	3 - 10
SiO_2	mg/l	350 - 450	n.a.	150 - 250
SO_4	g/l	6 - 7.5	3 - 4	1.2 - 2
Ca	g/l	25 - 3	30 - 5	2 - 4
Mg	mg/l	250 - 300	500 - 2000	500 - 1000
Fe	mg/l	10 - 20	80 - 120	40 - 100
Al	mg/l	5 - 10	80 - 120	130 - 180
Cd	µg/l	5 - 50	< 1500	10 - 100
Cr	µg/l	60 - 180	< 50000	40 - 1500
Cu	µg/l	200 - 1000	< 6000	200 - 600
Hg	µg/l	100 - 350	< 1000	70 - 150
Ni	µg/l	140 - 300	< 20000	500 - 8500
Pb	µg/l	300 - 500	< 5000	200 - 1000
Zn	µg/l	650 - 4500	< 20000	100 - 3000

n.a. ...... not analyzed

Main demands to be met by plants suitable to refine FGD-waste water are:

- regulation of pH to neutral or alkaline range
- removal of metals dissolved in waste water
- separation of high solids content.

Treatment with alkali, a widely accepted measure in waste water refinement, has proven to be also suitable from FGD waste water.

By alkalization of waste water in order to rise pH simultaneously numerous metals dissolved are precipitated by formation of hardly soluble metalhydroxides.

Because of different pH-optima for precipitation of these hydroxides it is advantageous to perform neutralization gradually in a two step procedure. Further precipitation of heavy metals can be achieved by sulphide addition. For waste water of high acidity the application of a two stage neutralization seems to be definitely necessary to enable sufficient precipitation of hydroxides.

After the neutralization/precipitation stage, solids are separated by sedimentation in sludge separators. The time needed for sedimentation of precipitated metalhydroxides can be accelerated by the addition of a flocculation aid (i.e. iron compounds, polyelectrolytes or slugde).

Dependent on the original composition of waste water and efficency of separation desired it might be necessary to install more than one separator.

Sludge drawn off from separators is concentrated and dewatered in order to get it suitable for discharge.

To promote utilization of any kind of by products recently, potential possibilities for reuse of sludges have been investigated.

Figure 5.12 shows a simplified flow sheet of a waste water treatment plant.

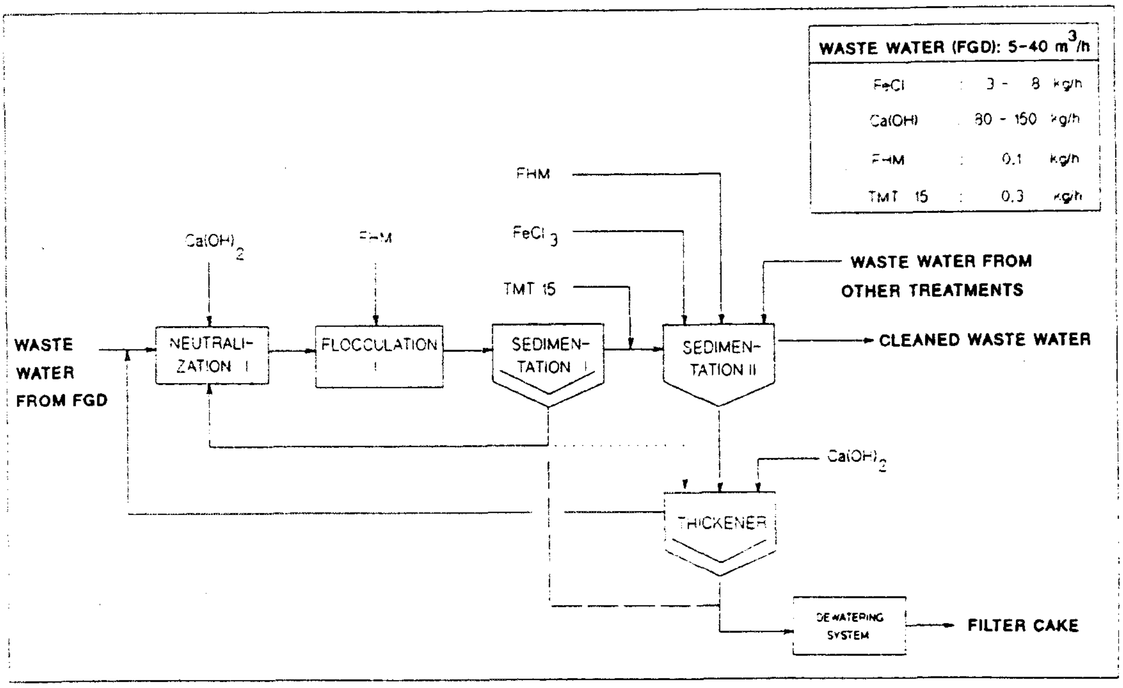


Figure 5.12: FGD-Waste Water Treatment Plant
(Arbeitsgruppe "Kraftwerksreststoffe", 1988)

Table 5.13 shows comparison of composition of FGD waste water of a limestone scrubbing plant before and after waste water treatment.

Table 5.13: Composition of FGD-Water Before and After Waste Water Treatment Plant (Burgmann, 1986, adapted). Two Types of Lime had been Used in the Scrubbing Process.

		Before Treatment		After Treatment	
	Unit	95 % CaO	83 % CaO	95 % CaO	83 % CaO
pH		4.0 - 4.5	4.0 - 5.0	9.0 - 9.8	9.0 - 9.5
Sediment	ml/l	15 - 35	250 - 550	< 0.1	< 0.1
Filtration residue	g/l	0.4 - 2.0	9 - 13	2 - 10	2 - 10
Cl	g/l	- 7	- 5.5	5 - 8	5 - 6
SO_4	g/l	1.2 - 1.4	1.5	1.1 - 1.3	1.4
F	mg/l	100 - 130	100	10 - 20	10 - 20
Fe	mg/l	40 - 70	280 - 560	< 0.1	< 0.1
Al	mg/l	130 - 180	800	0.1 - 0.4	0.3
Mn	mg/l	20 - 40	70 - 80	< 0.1	0.3
Ca	g/l	2 - 4	2 - 3	3 - 4	2 - 3
Mg	g/l	0.5 - 0.9	0.2	0.04 - 0.08	0.06
SiO_2 solved	mg/l	150 - 200	190 - 250	10 - 20	10 - 20
COD	mg/l	50 - 100	80 - 100	50 - 100	80 - 100
Cd	µg/l	10 - 20	15	< 0,5 - 2	< 0,5 - 2
Cr	µg/l	400 - 500	1100	10 - 20	10
Cu	µg/l	200 - 600	1400	< 10	10
Hg	µg/l	70 - 100	35	25 - 35	15
Ni	µg/l	100 - 300	700	< 20 - 40	20
Pb	µg/l	100 - 250	600	< 10	< 10
Zn	µg/l	1000 - 2000	2600	< 40	< 40

Figure 5.13 shows the degree of separation for some metals achievable by treatment process described in Burgmann, 1986. The reduction capacity depends on the kind of metal and is between 60 and 97 %.

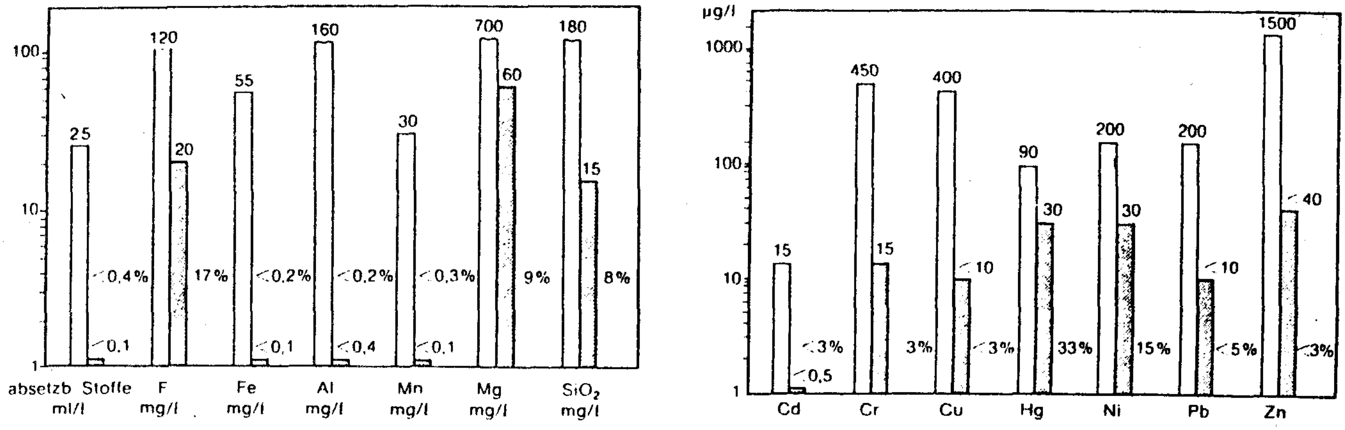


Figure 5.13: Degree of Separation for Some Metals (Burgmann, 1986) Percent values give the remaining part

Table 5.14 gives values of trace element concentration for heavy metals in the remaining filter cake of the waste water treatment plant. Burgmann (1986) stated that in comparison to sludges from other waste water treatment plants the filter cake does not contain hazardous amounts of heavy metals.

Table 5.14: Concentration of Trace Elements in Filter Cake from Waste Water Treatment (Burgmann, 1986)

Element	Concentration in mg/kg Using 95 % CaO	Using 83 % CaO
As	20	20
Ba	300	300
Cd	5	3
Cr	100	100
Ni	100	100
Pb	40	60
Hg	10	5
Se	150	50
Sr	80	400
Zn	200	300

Another possibility for treatment of waste water is spray drying, yielding a dry powdered end product which might be deposed.

Environmental concerns with dissolved solids and metals in FGD waste waters can be virtually eliminated by "zero discharge" of process waste waters, i.e. operating an FGD system with a "closed process water loop" (Finlay and Ross, 1988). This is of course readily achievable with "dry" FGD systems (see chapter 5.3). It is also relatively easily achievable with some "wet" FGD systems such as alkaline fly ash and dual-alkali FGD systems, where water balances indicate that "waste water" is evaporated in the flue gas or occluded in the solid waste from the system. However, some wet limestone FGD systems may present a challenge to achieve closed loop, especially for forced oxidation sulphate systems (rather than natural oxidation sulphite systems), and commercial FGD gypsum systems (which may require washing for chloride removal to produce gypsum suitable for construction wall board).

Studies were conducted in Canada to investigate the feasibility of closed loop for the common wet limestone FGD systems. FGD systems considered include natural oxidation, forced oxidation without blowdown, and forced oxidation with blowdown treatment (for dry and wet stacking of waste, or production of commercial gypsum). Blowdown may be required to control the level of chlorides in the system. For the commercial gypsum option, blowdown from a prescrubber or from the gypsum dewatering stage were both considered. Blowdown treatment options considered included reverse osmosis, electrodialysis, freezing and vapour compression evaporation.

An example for a closed loop wet FGD system is shown in figure 5.14.

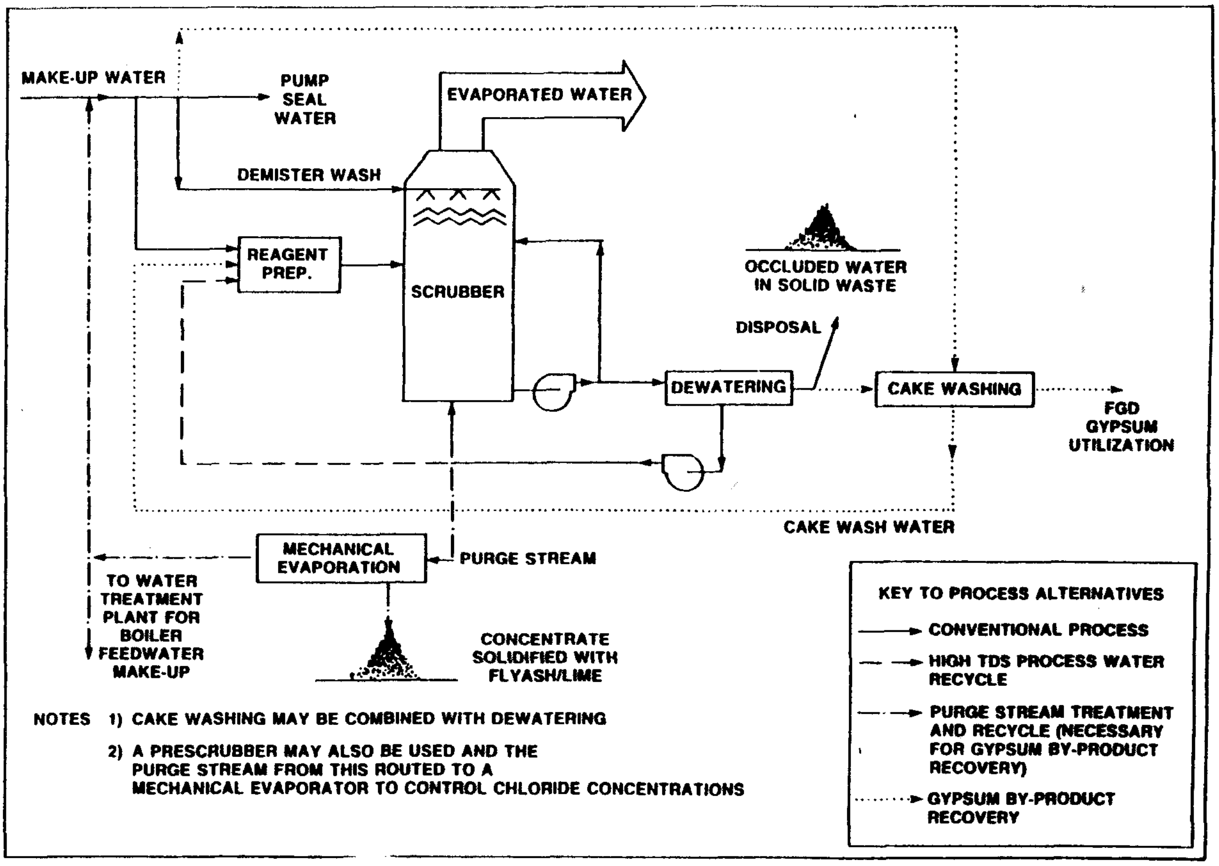


Figure 5.14: Closed Loop "Wet" FGD-System
(Finlay and Ross, 1988)

Major conclusions from the studies include the following (Finlay and Ross, 1988):

i) Closed-loop FGD system operation is technically feasible.

ii) The lowest cost option for achieving a closed loop depends on factors such as FGD system selection, chloride levels of coal, choice of solid or thin alloy cladding construction for corrosion control, prescrubber or cake wash blowdown treatment, etc.

5.2 Spray Drying

5.2.1 Survey of Processes

During spray drying absorption an aqueous suspension of the absorbent with a high content of solids is injected into the hot flue gas in a spray dry unit, a dry powdery product is generated, the so-called SDA-product (spray-dry-absorption). This type of FGD-process is commercially applied till now with calcium compounds as reagents, although application with sodium or magnesia compounds would be a conceivable variant.

A typical scheme of a spray drying absorption plant is shown in figure 5.15.

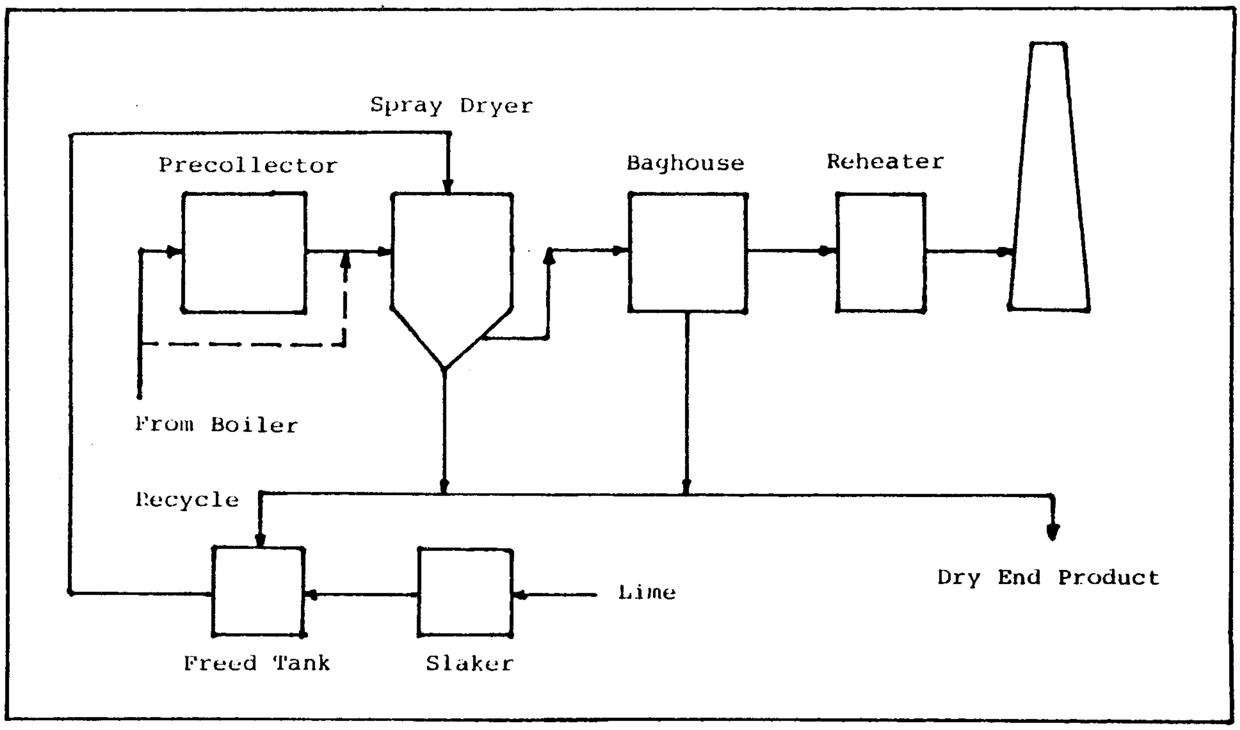


Figure 5.15: Flow Sheet of FGD with a Spray Drying Absorption Process (Klingspore and Cope, 1987, adapted)

Spray drying processes based on sodium carbonates are very similar to those using calcium compounds. The advantage of better SO_2-sorption efficiency is combined with the disadvantage of a more soluble by-product which can not be used. Spray drying processes on base of sodium compounds are commercially available for hard coal and brown coal systems.

It can be seen from figure 5.16 that three different types according to alternative fly ash precollection steps are applicable. The first one works with an almost total fly ash precollection, the second with a partial fly ash precollection and the third without fly ash precollection. Corresponding to this the composition of the spray dryer product is either an almost clean FGD-product or a mixture between fly ash and FGD-product.

It can be seen that all the spray drying absorption (SDA) products contain a considerable amount of calcium sulphite, partly calcium sulphate and a significant part of unreacted calcium hydroxide.

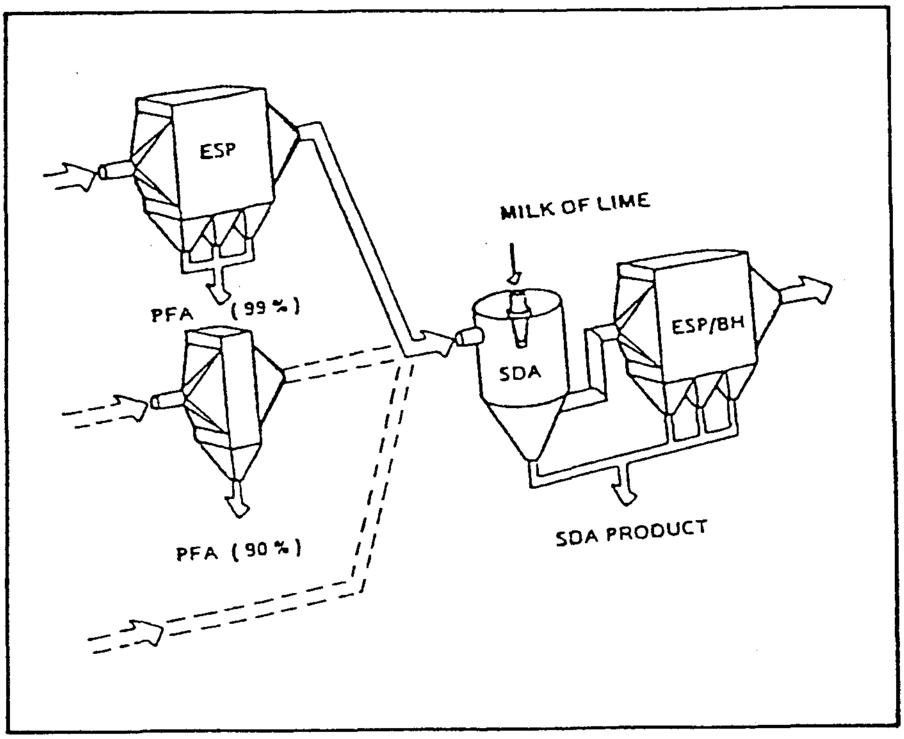


Figure 5.16: **Flow Sheet of FGD with a Spray Drying Absorption Process. Possibilities for Fly Ash Removal (Jons, Russel and Aahman, 1987)**

PFA ... Pre collected fly ash
ESP ... Electrostatic precipitator
BH ... Baghouse dust collector
SDA ... Spray dry absorber

5.2.2 Calcium Compounds

The chemical composition of the FGD-product caused by a spray drying process with calcium compounds as reagent is listed in the tables 5.15 to 5.17. The difference in the data of the tables is caused by the different content of fly ash and by different processes. Table 5.15 shows the composition without fly ash, table 5.16 that with a fly ash content of 10 - 30 % and table 5.17 that with one of 28 - 52 %.

Table 5.15: Chemical Composition of the FGD-Product from Drypac Spray Absorption Process (Mosch, 1986)

	% by weight
$CaSO_3 \cdot 1/2\ H_2O$	60 - 70
$CaSO_4 \cdot 2\ H_2O$	8 - 12
$CaCl_2 \cdot 4\ H_2O$	7 - 11*)
CaF_2	< 1
$Ca(OH)_2$	6 - 17
$CaCO_3$	1 - 4
Inert material	1 - 8
Humidity	1 - 2
degree of SO_2-reduction	85 - 95 %
S-content of coal	0.8 - 1.2 %
Cl-content of coal	0.15 %
Size of product	
Particulates	5 - 50 10^{-6} m

*) equivalent to 2.7 to 4.3 % chloride

Table 5.16: Chemical Composition of Spray Drying Absorption Product Including 10 - 30 % Fly Ash (Jons, Russel and Aahman, 1987)

Fly Ash	10 - 30 %
Calcium sulphite	40 - 60 %
Calcium sulphate	3 - 20 %
Calcium carbonate	1 - 8 %
Calcium hydroxide	3 - 15 %
Calcium chloride	0 - 8 %
Inerts	3 - 10 %

Table 5.17: Chemical Composition of Spray Drying Absorption Product Including 28 - 52 % Fly Ash (Neumann, 1989a)

Fly Ash	28 - 52 %
$CaSO_3 \cdot 1/2\ H_2O$	25 - 36 %
$CaSO_4 \cdot 2\ H_2O$	5 - 7 %
$Ca(OH)_2$	2 - 6 %
Humidity	0.5 - 1 %
$CaCl_2$	2 - 6 %*)

*) depends on the chlorine content of the coal

A more detailed analysis of SDA-product (with about one third fly ash) is given in the table 5.18. The used fuel was Polish hard coal.

Table 5.19 shows contents of trace elements of SDA-products compared to those of the fly ashes and the lime added from two plants.

Table 5.18: Composition of a SDA Product Including about 20 % Fly Ash (Neumann, 1989a)

SiO_2	9.40 %
Al_2O_3	5.46 %
Fe_2O_3	2.78 %
MnO	0.07 %
TiO_2	0.29 %
CaO	22.08 %
MgO	2.24 %
SO_3	37.01 %
K_2O	0.36 %

Table 5.19: Trace Elements in Fly Ash, the Added Lime and the Resulting SDA-Product (Neumann, 1989a; Jons, Russel and Aahman, 1987)

Element	Unit	Lime	Fly Ash	SDA-Product	SDA-Product*)	Precollected Fly Ash*)
Na	%	< 0.02	0.54	0.12		
K	%	0.02	1.76	0.24		
Sr	ppm	308.0	773.0	377.0		
Ba	ppm	10.0	2379.0	483.0	620	1150
Al	ppm	0.23	11.75	2.74		
B	ppm	n.a.	n.a.	n.a.		
Ag	ppm	n.a.	n.a.	n.a.		
Be	ppm	< 0.1	11.3	2.3		
Cd	ppm	n.a.	n.a.	n.a.	< 10	< 10
Co	ppm	22.0	42.0	24.0		
Cr	ppm	13.0	157.0	41.0	85	180
Cu	ppm	9.0	153.0	46.0		
Fe	%	0.11	8.43	1.51		
Mn	%	0.001	0.138	0.030		
Ni	ppm	5.0	89.0	29.0		
Pb	ppm	18.0	52.0	101.0	45	105
Zn	ppm	7.0	249.0	92.0		
Hg	ppm	< 10.0	< 10.0	< 10.0	0.22	0.39
V	ppm				96	350
Cl	ppm				23000	1500
As	ppm				7	60
Se	ppm				< 3	< 3

n.a. ..... not analyzed

*) ..... Jons, Russel and Aahman, 1987

Table 5.20 presents a comparison of leaching-tests for pure fly ash with the SDA-product mixed with fly ash. Both samples were taken in the Austrian power station Dürnrohr (Neumann, 1989a, b).

Table 5.19: Leachate-Concentrations of a SDA-Product Mixed with Fly Ash (1 : 1) Compared with Pure Fly Ash Measured with DEV-S4 Method (Neumann, 1989a, b)

		Fly Ash 90 days	Fly Ash 180 days	SDA-Product 90 days	SDA-Product 180 days
Ca	mg/l	55	43	210	170
Mg	mg/l	< 0.02	< 0.01	< 0.02	< 0.01
Na	mg/l	60	50	80	100
K	mg/l	97	66	171	186
Cl	mg/l	8	41	540	126
SO_4	mg/l	102	76	69	59
NO_3			4.0		4.5
Sr	μg/l	665	-	2133	-
Ba	"	96	1	489	5
Al	"	9750	-	6740	-
B	"	597	< 10	< 150	< 10
P	"	207	-	37	-
Ag	"	12	-	3	-
Be	"	1000	-	400	-
Cd	"	< 1	0.5	< 1	0.2
Co	"	< 3	-	8	-
Cr	"	264	34	11	13
Cu	"	10	4	9	4
Fe	"	n.a.	-	n.a.	-
Mn	"	< 10	-	10	-
Ni	"	7	5	5	2
Pb	"	102	2	48	2
Zn	"	25	38	23	26
Hg	"	< 1	< 1	< 1	< 1
Li	"	0.55	-	1.49	-
As	"	-	3	-	0.2
electric conductivity mS/cm		1.28	-	2.32	-

n.a. ... not analyzed

Currently SDA-products are disposed of in most cases though there are extensive investigations about possible utilization.

The discussion which class of disposal site (see chapter 2.1) is necessary for disposing respectively the necessity of any sealings is not finished. Nowadays observations at landfill sites already being filled with SDA-products will help to find the right answer.

Permeability tests in a laboratory gave the results in figure 5.17 (SDA-product of power station Dürnrohr, about one third fly ash).

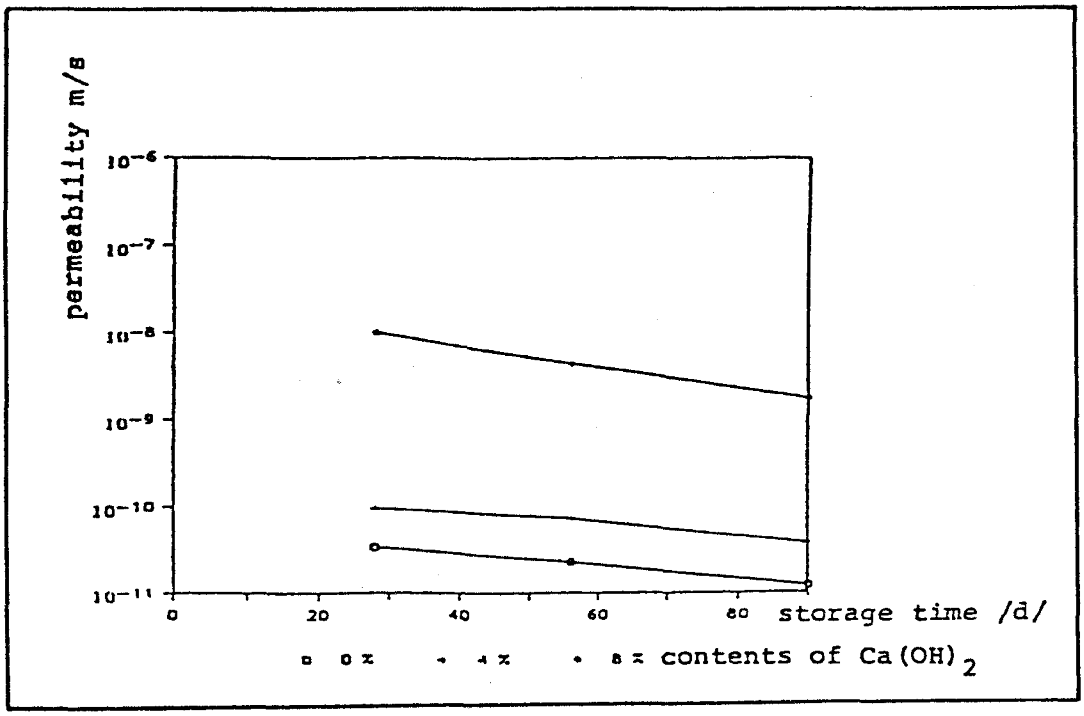


Figure 5.17: Results of Permeability Tests of SDA-Fly Ash Mixture Containing 0, 4 and 8 % $Ca(OH)_2$ in Laboratory (Neumann, 1989b)

The compression strength of mixture of fly ash and desulphurization waste depends on the water content, storage time and the degree of compaction. Figure 5.24 shows the compression strengths of some waste mixtures stored for different periods of time.

The water permeability of mixtures of fly ash and desulphurization waste are normally quite small, approximately 10^{-9} - 10^{-8} m/s. When cement is added, the water permeability is even smaller, approximately 10^{-11} - 10^{-9} m/s. The magnitude of water permeability depends on degree of compaction and storing time.

Figure 5.18 gives a qualitative picture of strength and permeability of PFA-SDA-cement mixtures.

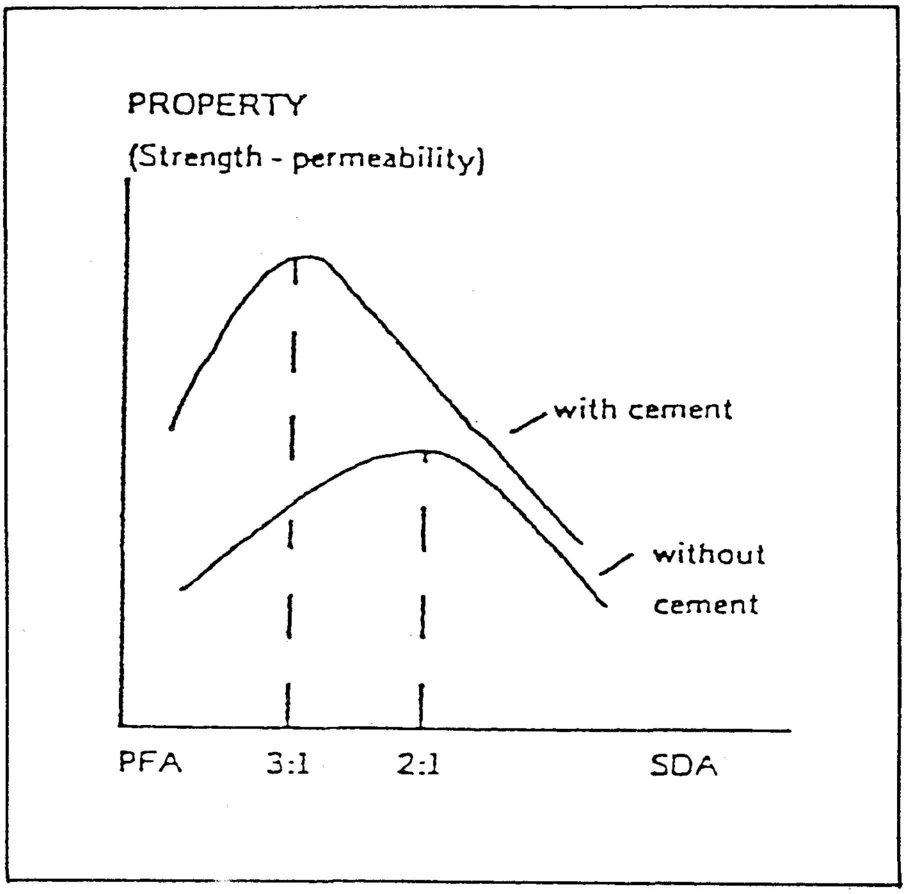


Figure 5.18: Schematic Drawing of Properties of Fly Ash/SDA/Cement Mixtures (Jons, Russel and Aahman, 1987)

Thermal oxidation (at about 750 degrees Celsius) of the SDA-product with air oxygen within a fluidized bed (see figure 5.19) leads to the following concentrations of the so produced technical anhydrite as given in table 5.21. A flow sheet of such an procedure is given in figure 5.20.

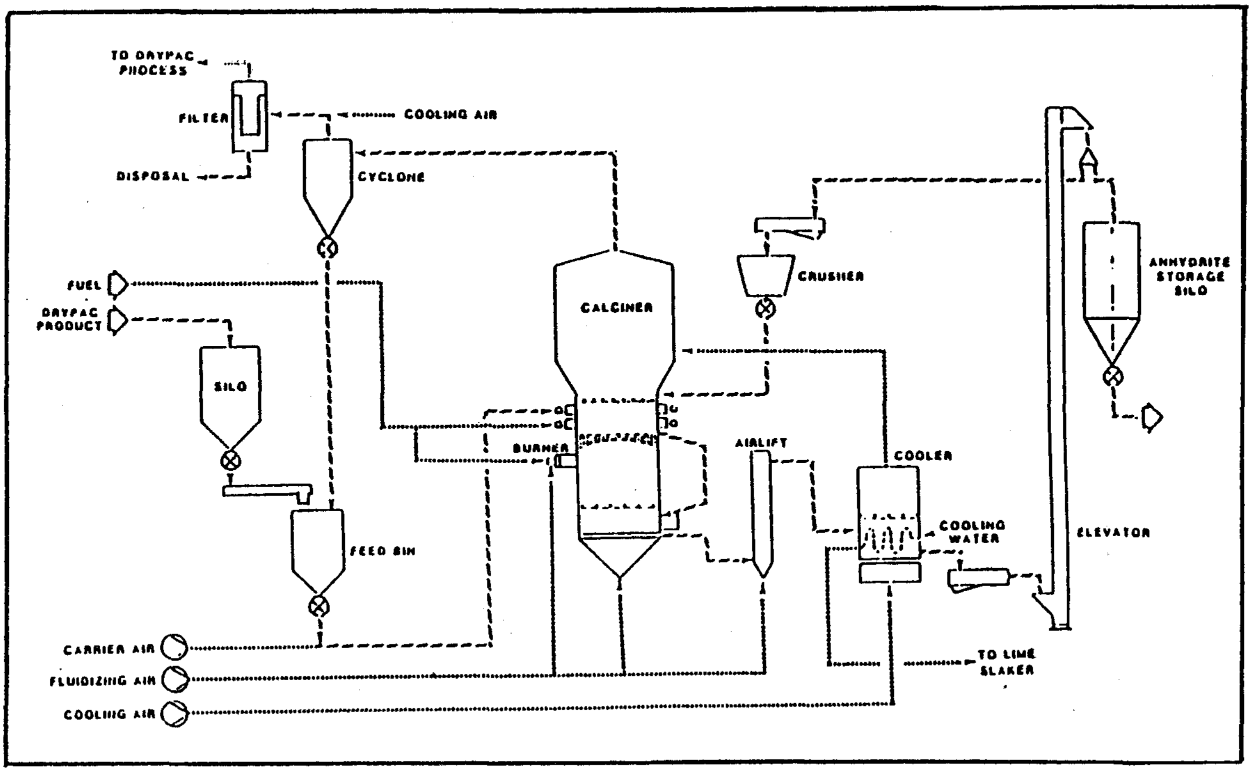


Figure 5.19: Generation of Technical Anhydrite by Oxidation of Calcium Sulphite - Containing FGD-By-Products (Bengtsson and Ahman, no year)

Table 5.21: Composition of Commerical Technical Anhydrite Produced by Thermal Oxidation of Drypac Spray Absorption Process from Raw Material According Table 5.15 without Dechlorination (Mosch, 1986)

	% by weight
$CaSO_4$	70 - 80
$CaSO_3$	2 - 3
CaS	0 - 0.2
$CaCl_2$	4 - 7*)
CaF_2	< 1
CaO	5 - 14
$CaCO_3$	1 - 4
Inerts	1 - 8
Humidity	0 - 1

*) according to 2.6 - 4.5 % chloride

Possibilities of utilization are investigated in the following fields (Dietl and Schmole, 1986; Jons, Russel and Aahman, 1987; Mosch, 1986; Neumann, 1989b; Neumann and Novak, 1988):

- cement replacement as precollected fly ash activator
- sulphur extraction by conversion to SO_2 rich gas
- filler applications as fine pale powder
- gypsum replacement after forced oxidation (as technical anhydrite)
- cement additive after forced oxidation
- sealing material for land-fills

In the following triangle diagram various applications with the mixture-ratio between precollected fly ash (PFA), cement (C) and SDA as parameters are shown in figure 5.20:

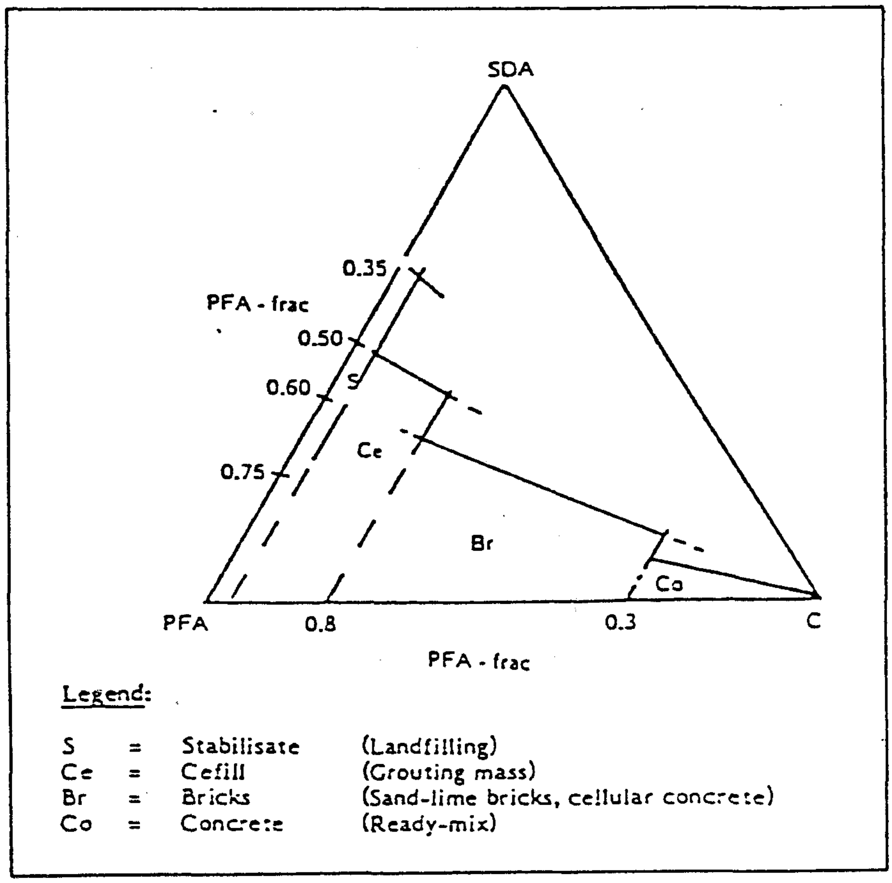


Figure 5.20: Various Applications of SDA - Precollected Fly Ash (PFA) - Cement (C) Mixtures (Jons, Russel and Aahman, 1987)

Possible applications in the building materials industry are uses as a component of cement, as a binding material or as a dry aggregate of concrete and gypsum boards and pastes. However, the market for the residue in the building industry is currently poor due to low material price.

The uses in soil engineering are road constructions, municipal engineering, fillings and overlays on landfills. The waste from the wet-dry method must be mixed with fly ash to achieve sufficient stability when used in soil construction. By mixing different proportions of fly ash, desulphurization product, cements and stabilizing additives, products (market name Cefyll) can be obtained with variable qualitites according to the type of application, for instance with a more or less fluid composition. Cefyll products have been used as a sealing material and in fillings.

The possibilities for utilization in soil engineering are restricted in the individual case by the quality (e.g. geotechnical properties) of the residue, by economic factors, such as transport cost and by environmental factors. The environmental hazard of the waste is determined by the leaching of pollutants from the waste to environment.

The results obtained in the Swedish leaching tests from SDA-products are presented in table 5.22. Leaching tests show that it is primarily chlorides that are easily soluble. The concentrations of heavy metals leached from the desulphurization waste are usually < 1 mg/l. The concentrations of most components are highest in first leachate and level off to low values as the leaching progresses.

Table 5.22: Maximum Concentration in Leachate from the Desulphurization Wastes (liquid/solid-ratio 1:1)

ELEMENT	FA mg/l	FGD 1 mg/l	FGD 2 mg/l	NIRO 1 mg/l	NIRO 2 mg/l	CEMENT mg/l	BETON K250 mg/l
Cl^-	21	12800	36900	440	485	56	6
SO_4^-	1020	430	168	1260	312	3060	17
As	0.07	0.057	< 0.15	< 0.030	< 0.15	< 0.22	< 0.03
Ba	0.38	1.1	1.6	0.19	0.75	0.48	1.6
Be	< 0.001	0.001	< 0.01	< 0.001	< 0.01	0.003	< 0.004
Pb	< 0.05	0.12	1.8	< 0.050	1.8	0.31	< 0.05
P	1.5	260	44	0.8	1.7	1.1	< 0.04
Fe	0.08	0.17	5.7	0.04	0.45	0.32	0.031
Cd	< 0.005	0.010	< 0.03	< 0.005	< 0.03	0.02	< 0.003
Ca	1300	7300	9900	1360	1034	990	470
K	110	540	503	70	89	4300	917
Co	< 0.003	0.009	< 0.02	< 0.003	0.03	0.06	< 0.003
Cu	0.16	0.78	< 0.03	0.16	< 0.03	0.20	0.057
Cr	0.36	0.073	< 0.04	0.10	0.25	2.9	0.012
Li	2.8	0.20	0.19	1.2	2.3	0.69	0.12
Mg	0.12	0.46	1015	0.16	0.83	0.69	< 0.04
Mn	0.002	0.013	7.5	0.003	0.02	0.05	0.004
Mo	1.1	0.025	0.02	1.3	0.28	0.11	< 0.004
Na	111	60	68	52	71	150	180
Ni	< 0.02	< 0.02	0.10	< 0.02	< 0.10	0.07	< 0.02
Sr	7.3	9.3	16	3.5	3.8	33	23
V	-	-	0.09	-	0.12	-	< 0.005
Zn	0.02	0.01	< 0.01	0.04	< 0.01	0.04	0.021

High strengths are achieved if the portion of fly ash is approximately twice that of the desulphurization waste (a 2:1 ratio). If cement is added, strength increases and permeability decreases further. When adding cement, the proportion of the desulphurization product should be reduced. The addition of 3 - 5 % cement produces an exceptionally impervious product suitable, for example, in covering environmentally hazardous waste.

Freeze-thaw tests have shown that mixtures of fly ash and desulphurization products are not frostresistant. However, a frost-resistant product appears obtainable by adding at least 10 % cement together with sand or an air pore agent.

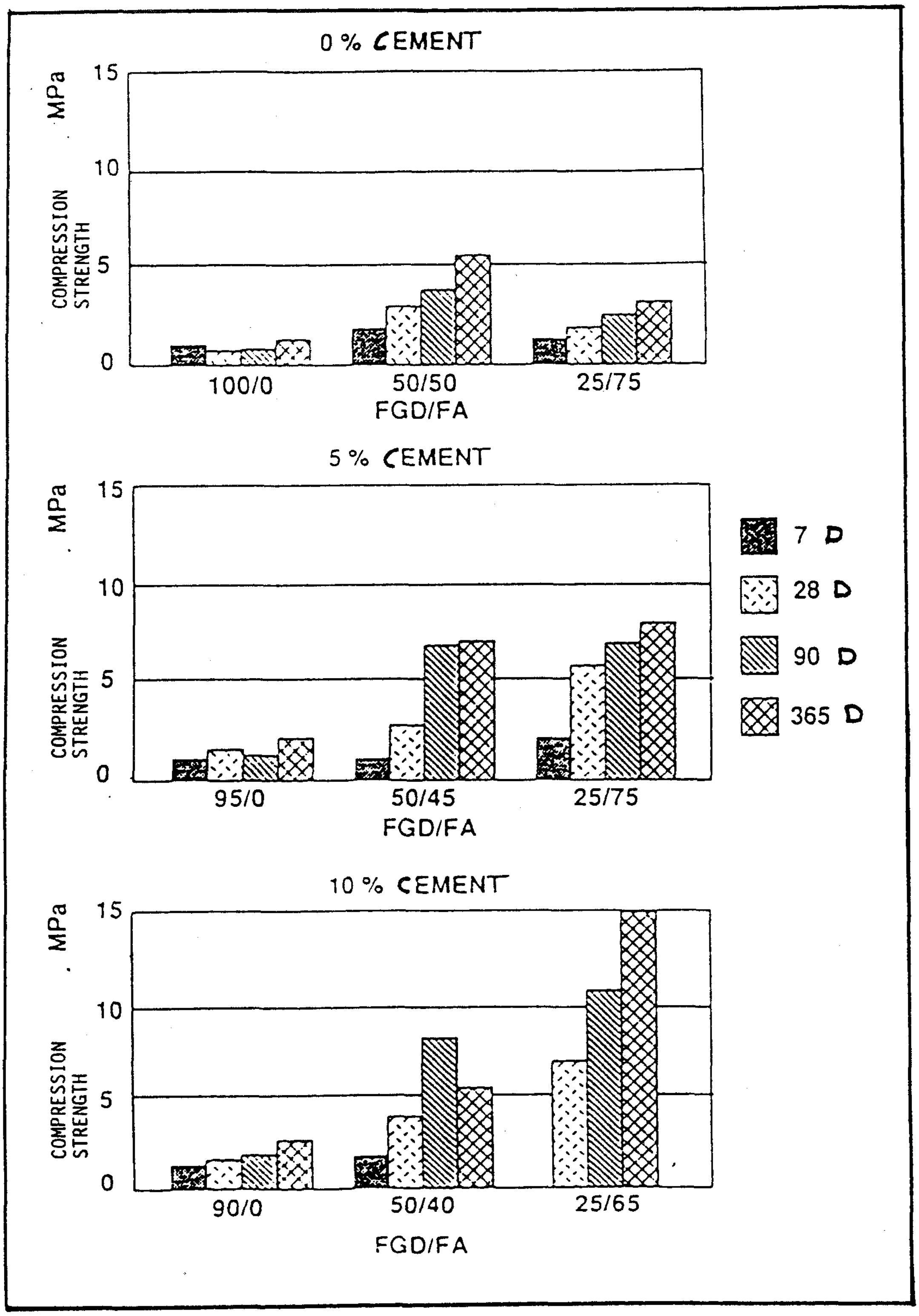


Figure 5.21: Compression Strengths of Mixtures of Fly Ash (FA), Desulphurization Waste of Wet Dry-Process (FGD) and Cement Stored for 7, 28, 90 and 365 Days (Stiftelsen Reforsk. Fou, 1986)

Table 5.23: Trace Metals in the SDA Waste from Wet-Dry Process

Element	FA mg/kg	FGD 1 mg/kg	FGD 2 mg/kg	NIRO 1 mg/kg	NIRO 2 mg/kg	CEMENT mg/kg
As	59	25	-	119	-	< 10
Ba	1617	102	43	1198	950	162
Pb	103	130	15	143	81	77
Cd	0.6	0.3	0.2	0.5	0.5	0.2
Co	54	< 10	2	53	36	< 10
Cu	191	88	19	149	98	121
Cr	157	88	9	139	100	121
Hg	0.7	1.4	0.08	0.4	0.7	0.5
Mo	14	20	< 1	18	12	24
Ni	162	46	10	151	81	13
Se	1.0	0.6	1.8	1.4	2.3	< 0.25
Sr	839	221	150	1041	1220	877
Sn	< 100	< 100	< 2	< 100	7	< 100
V	257	23	17	204	160	23
W	< 20	94	3	23	5	147
Zn	276	57	1	254	180	120

FA	....	coal fly ash
FGD 1	....	desulphurization waste from wet-dry process
FGD 2	....	desulphurization waste from wet-dry process
NIRO 1	....	desulphurization waste from wet-dry process, contains 82 % coal fly ash
NIRO 2	....	desulphurization waste from wet-dry process, contains 70 % coal fly ash

5.3 Dry Processes

As can be seen in figure 5.22, modification of the combustion process or addition of dry additives into the combustion chamber or secondary flue gas desulphurization with dry processes are dry processes for desulphurization.

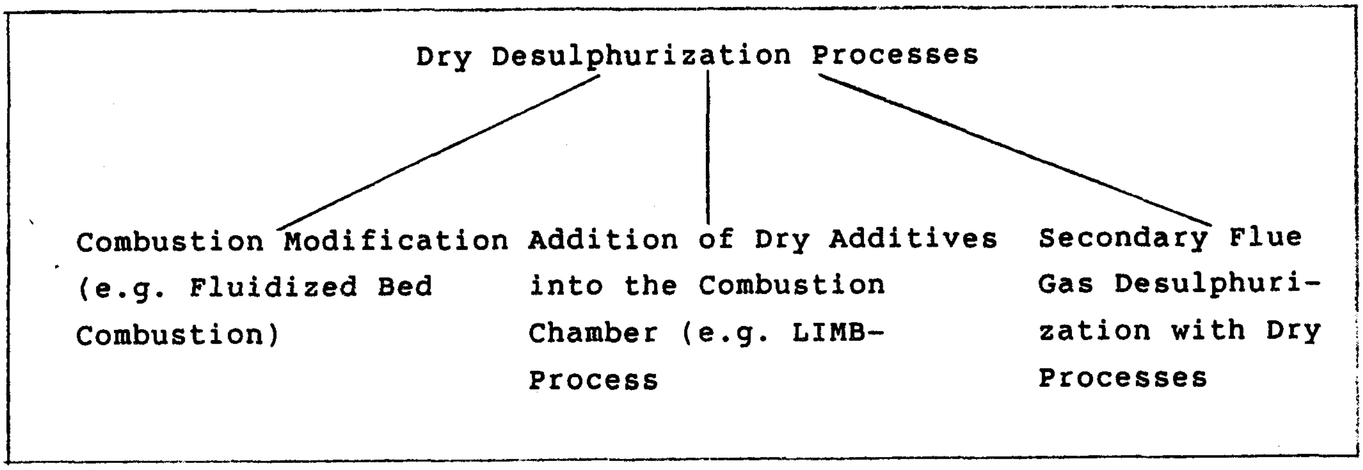


Figure 5.22: Survey of Dry Desulphurization Processes

Dry processes, i.e. processes working with the addition of a dry sorbent causing naturally dry products, are applied in different ways referring to the position of the sorbent addition.

5.3.1 Survey of Processes

Dry Additive

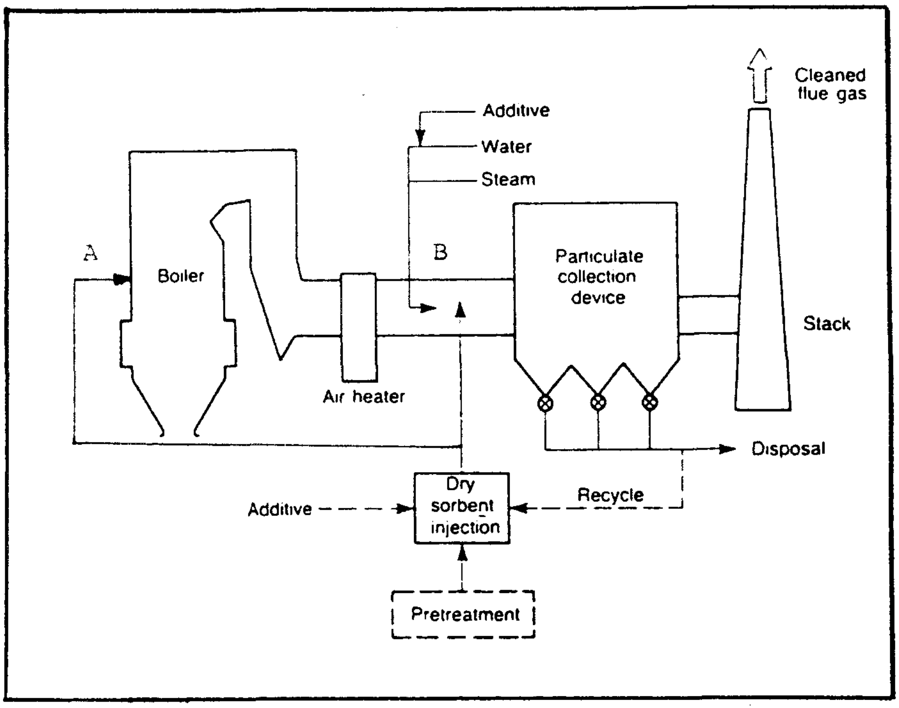


Figure 5.23: Block Diagram of Dry Additive Desulphurization (Klingspore and Cope, 1988; adapted)

Systems to be treated: flue gas of brown coal
Scale of operation: commercial
Reacting agent: $CaCO_3/CaO$
By-products: $CaSO_3/CaSO_4$, fly ash (solid, not usable)
No wastewater occurs.

Remarks: Dry additive processes can be operated in two ways:

Procedure A: Powdered limestone is injected into the boiler above the section of the burners. Calcination of the limestone in the boiler is followed by the sorption of SO_2 in the cooler part of the boiler and the ductwork downstream. The reaction product consists of calcium sulphite, calcium sulphate, unreacted sorbent and fly ash and is removed from the flue gas in a dust collector. Some of this dry by-product can be recycled for injection together with new sorbent. The rest has to be disposed.

Procedure B: The sorbent, most times lime, is injected after the furnace into the ductwork accompanied by water or steam injection for humidifying the flue gas to increase sorbent utilization and desulphurization.

Carbon Adsorption

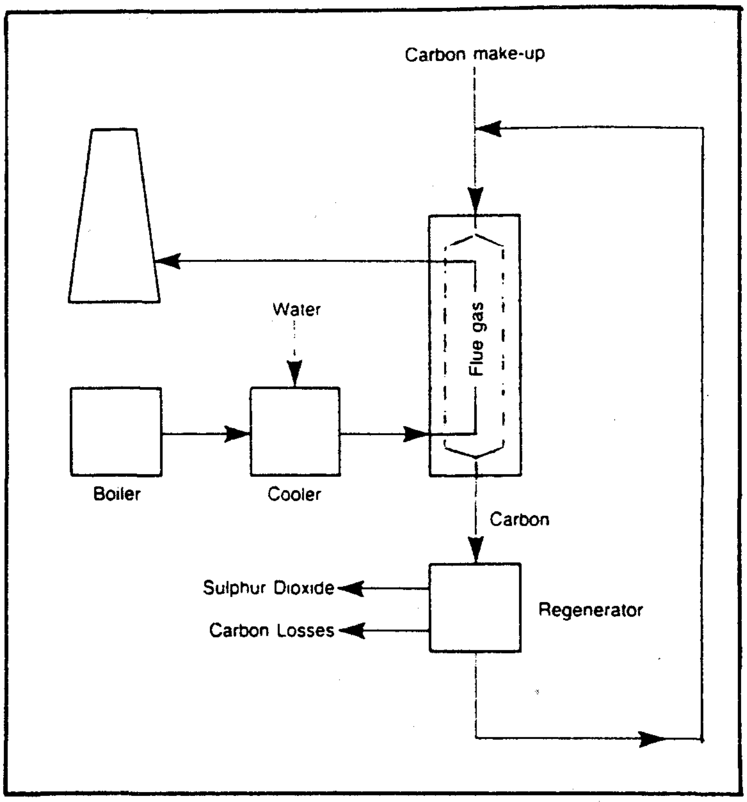


Figure 5.24: Block Diagram of Carbon Absorption Process (Klingspore and Cope, 1987; adapted)

Name of procedure: Carbon Adsorption
Systems to be treated: flue gas of hard coal
Scale of operation: commercial
Reacting agent: activated carbon
By-products: usable solid, liquid and gaseous
Waste water is to be treated.

Remarks: In the carbon adsorption process activated carbon is used to adsorb SO_2 out of the flue gas. At temperatures about 120 ^oC in the adsorption section the adsorbed SO_2 reacts with water vapour and oxygen to generate sulphuric acid. In a downstream regeneration section at temperatures of about 400 ^oC the sulphuric acid is decomposed to a SO_2-rich gas (about 30 % SO_2) and H_2O, under formation of CO_2 therefore causing a chemical carbon loss. After concentrating the SO_2 it can be used for producing liquid SO_2, sulphuric acid or elemental sulphur. The regenerated activated carbon after cooling down is recycled to the adsorption section.

LIFAC (Limestone Injection into the Furnace and Activation of Calcium Oxide)

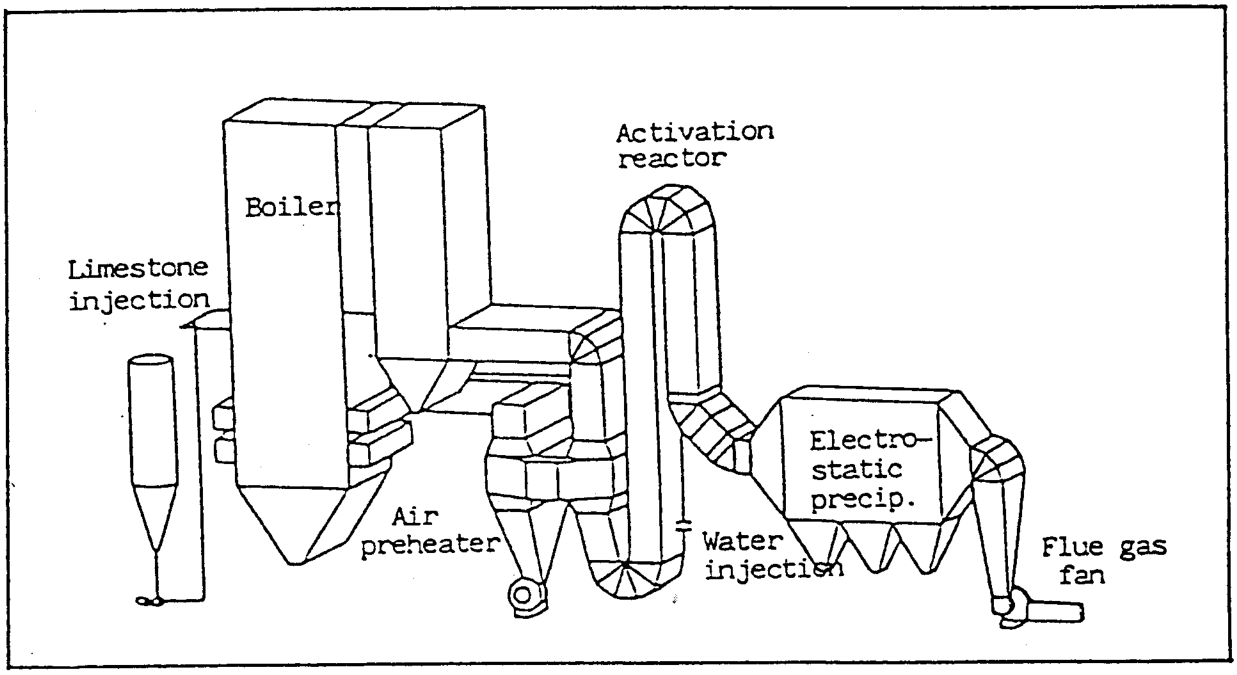


Figure 5.25: Block Diagram of LIFAC-Process (Kenakkala and Laine, 1987)

Systems to be treated: flue gas of brown coal and hard coal
Scale of operation: commercial

Remarks: The so-called LIFAC-process achieves improvement in performance of desulphurization of lime in furnace injection. In a separate reactor unreacted lime carried out of furnace with flue gas is activated by increasing flue gas humidity. The utilization of calcium can be significantly improved in a reactive environment caused by water injection.

The end product separated from flue gas is a dry powder consisting of fly ash, calcium sulphate, calcium sulphite and small amounts of calcium oxide and calcium hydroxide.

LIFAC-material can be utilized in landfilling and land construction with quite good success (Kenakkala and Laine, 1987).

Sodium Based Dry Desulphurization

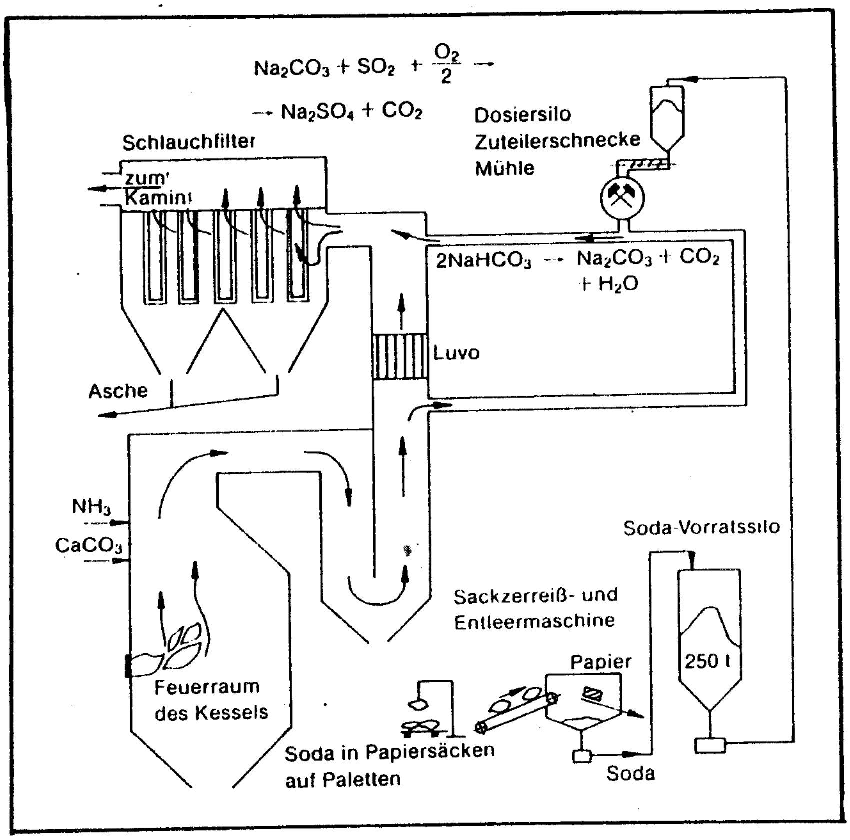


Figure 5.26: Block Diagram of a Sodium Based Dry Method (Schröfelbauer, Tauschitz and Maier, 1988)

Systems to be treated: flue gas of hard coal

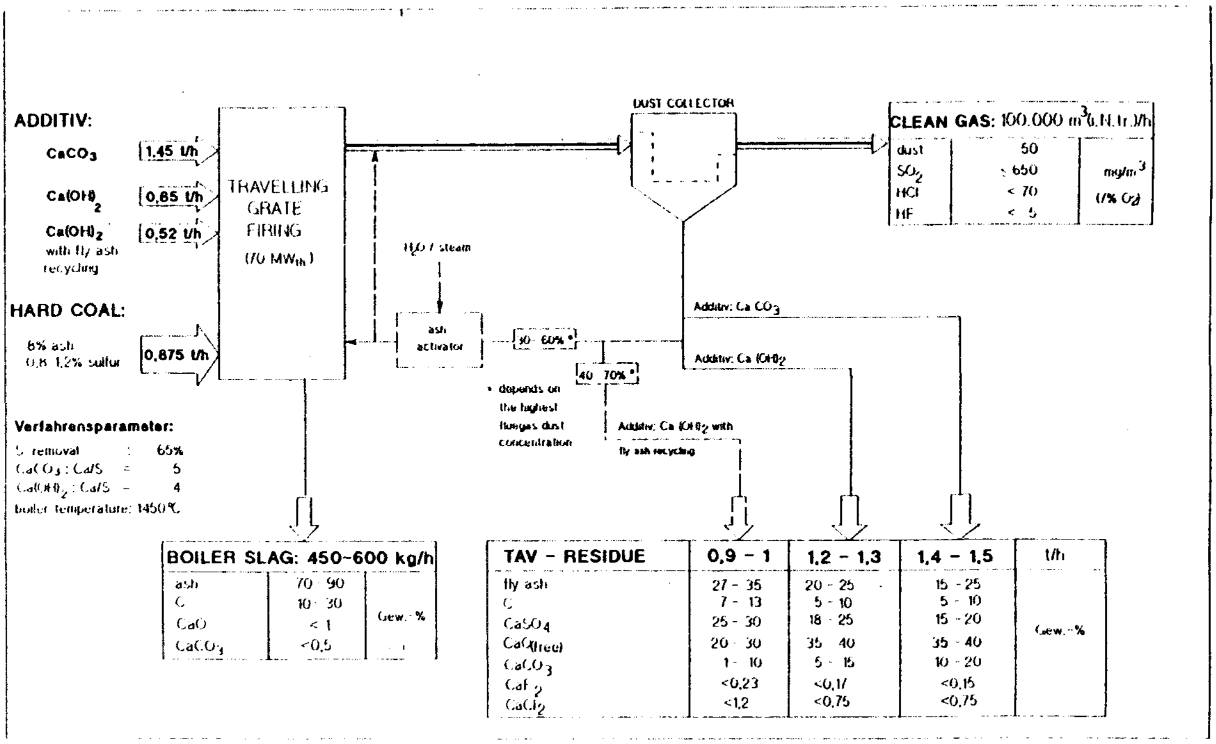
Scale of operation: commercial

By-products: not usable mixture of $NaSO_3$, $NaSO_4$

5.3.2 Products from Dry Additives

Addition of dry sorbents into the combustion chamber for reduction of the SO_2 emissions is applied first of all for retrofitting plants and for plants with a smaller capacity because of its smaller expense compared with secondary flue gas desulphurization. In most cases calcium compounds (lime, limestone) are added but also magnesia compounds or mixtures (dolomitic powder) are applied as the sorbent.

Figure 5.27 gives material balances for different additives and the resulting amounts and composition of the by-products.



CLEAN GAS: 100.000 m^3(i.N.tr.)/h		
dust	50	mg/m^3 (7% O_2)
SO_2	≤ 650	
HCl	< 70	
HF	< 5	

BOILER SLAG: 450-600 kg/h		
ash	70 - 90	Gew.-%
C	10 - 30	
CaO	< 1	
$CaCO_3$	<0,5	

TAV - RESIDUE	0,9 - 1	1,2 - 1,3	1,4 - 1,5	t/h
fly ash	27 - 35	20 - 25	15 - 25	Gew.-%
C	7 - 13	5 - 10	5 - 10	
$CaSO_4$	25 - 30	18 - 25	15 - 20	
$CaO_{(free)}$	20 - 30	35 - 40	35 - 40	
$CaCO_3$	1 - 10	5 - 15	10 - 20	
CaF_2	<0,23	<0,17	<0,15	
$CaCl_2$	<1,2	<0,75	<0,75	

Figure 5.27: Dry Additive Process - Generation of By-Products (Arbeitsgruppe "Kraftwerksreststoffe", 1988)

The following table 5.24 gives more detailed values from the Plants Timelkam No. 2 and Riedersbach No. 1. The values are compared for the composition of the ash before and after furnace limestone injection.

Table 5.24: Comparison of Ashes from two Austrian Plants with Furnace Limestone Injection (FLI) and Lignite as Fuel (Staudinger and Schröfelbauer, no year)

Constituent % wt	without FLI	with FLI
SiO_2	54.0 - 56.60	43.7 - 50.4
Al_2O	22.10 - 24.1	18.70 - 32.2
Fe_2O_3	4.37 - 6.88	4.18 - 5.29
TiO_2	0.66 - 0.82	0.69 - 0.81
CaO	4.74 - 8.95	12.5 - 20.4
MgO	2.31 - 2.53	2.16 - 2.30
Na_2O	0.27 - 0.78	0.23 - 0.63
K_2O	2.50 - 2.68	2.11 - 2.12
SO_3	0.77 - 0.88	1.82 - 3.96
Loss of ignition (815 °C)	1.07 - 1.84	1.63 - 2.59
Loss of ignition (1000 °C)	2.21 - 3.06	4.48 - 6.04
CO_2	0.13 - 0.34	0.79 - 3.41

Figure 5.28 gives possible fields for utilization of by-products from dry additive process.

DRY ADDITIVE PRODUCT

- Road Building (soil) (S)
- Land Construction (filling material) (S)
- Industrial Processes (neutralization of sludge) (S)
- As additive for concrete, aerated concrete and sand-lime bricks (R & D)

S ..... state of the art
R & D ..... Research and Development

Figure 5.28: Possible Uses for Dry Additive Product (Arbeitsgruppe "Kraftwerksreststoffe", 1988)

The chemical composition of the by-products of the LIFAC-Process applied to oil and coal firing is given in table 5.25. The contents of hazardous metals are higher in fly ash than in desulphurization wastes.

Table 5.25: Composition of LIFAC-End Products Arising from Combustion of Oil and U.S. Coal (Kenakkala and Laine, 1987)

Fuel	Oil POR 650	Coal from the U.S.A.
Sulphur content	2.5	1.5
Ash content	< 1	10 - 15 %
Reaction product	Ca/S 1.5 - 2	Ca/S 1.5 - 2
Fly ash	-	60 - 80 %
$CaSO_4$	15 - 20	8 - 15 %
$CaSO_3$	30 - 35	1 - 3 %
$Ca(OH)_2$	25 - 30	20 - 30 %
$CaCO_3$	15 - 20	1 - 7 %
Moisture	< 5	< 3 %

Table 5.26 gives a comparison of the chemical composition of fly ash, limestone and the LIFAC by-product.

Table 5.26: The Chemical Composition of Fly Ash, Limestone and End Product (Hämälä, 1987)

Chemical	Fly Ash	Limestone	LIFAC End Product
Silicates (CaO, SiO_2, Fe_2O_3, Al_2O_3)	90 %	< 3 %	55 %
$CaCO_3$	-	97 %	4 %
CaO, $Ca(OH)_2$	< 5 %	-	25 %
$CaSO_4$, $CaSO_3 \times H_2O$	< 5 %	-	15 %
Moisture, H_2O	< 1 %	< 1 %	< 1 %

The activated carbon process produces SO_2 rich gas by thermal activation. This can be treated as described in chapter 5.2.6.

In the Federal Republic of Germany a commercial FGD plant working with the activated carbon process has been in operation since August 1987 (power station Arzberg, two blocks with a total flue gas capacity of about 1.100.000 m^3/h, lignite as fuel, desulphurization rate of 95 %). A detailed description of this process is given in chapter 7.

6 BY-PRODUCTS AND WASTE FROM DeNO$_x$-PROCESSES

Strategies to limit emissions of NO$_x$ basically may be divided into:

- primary measures
- secondary measures

Primary measures, so called Combustion Modification (CM) tend to decrease the formation of NO$_x$ whereas secondary measures have to remove already generated NO$_x$ from flue gas.

Figure 6.1 gives a survey on various possibilities to control NO$_x$ emissions.

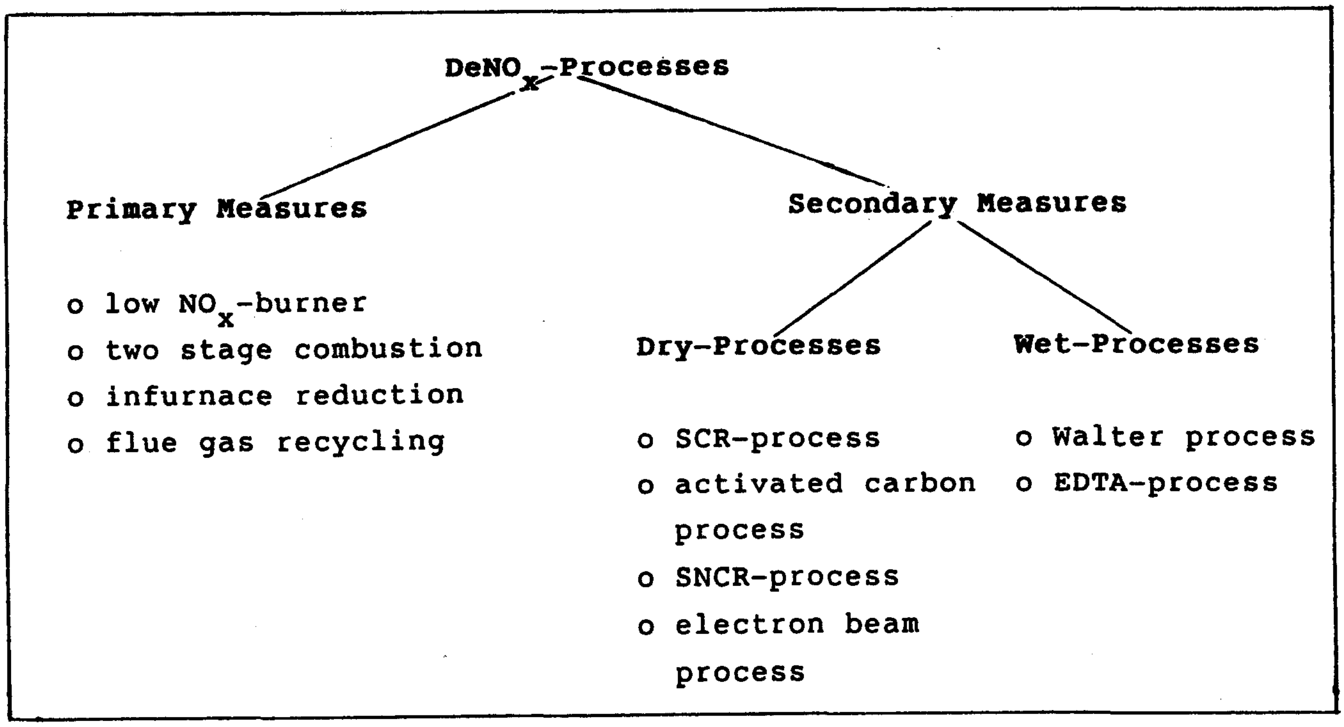


Figure 6.1: Survey on Important DeNO$_x$-Processes (Konieczny et al., 1988)

6.1 Primary Measures (Low NO_x-Combustion)

Primary NO_x-reduction technologies are available for all fossil fuels and most types of firing installations. Some reduction of NO_x-formation may be obtained by simple modification of combustion process such as operating at less excess air.

Higher reduction of NO_x-formation can be achieved by installation of low NO_x-burners or by application of two stage combustion.

However, low NOx-combustion systems might be attended with rather high amounts of unburnt carbon and the risk of incomplete combustion (CO in flue gas). This may effect thermal efficiency of the firing installation, the quality and therefore the possible utilization of the fly ash in cement industry.

Yet primary NO_x-reduction techniques are not able to meet the most stringent NO_x-emission limits either already being in operation or being expected in application in the near future.

6.2 Secondary Measures

In order to achieve highly efficient control of NO_x-emissions, definitely being necessary, a number of secondary measures to remove NO_x out of flue gas have been developed. But at present only few of them are available to full scale commercial application.

$DeNO_x$-processes currently commercially proven and offered are:

- selective catalytic reduction (SCR)

and to some extent

- selective non catalytic reduction (SNCR)
- activated carbon process (mostly for simultaneous removal of NO_x and SO_2)
- oxidation/adsorption and adsorption/reduction processes for simultaneous removal of NO_x and SO_2 (Chapter 7).

6.2.1 Selective Catalytic Reduction

Selective Catalytic Reduction (SCR) is the most applied process within the secondary measures for denoxing of flue gases. With the help of a catalyst containing metal oxides as catalytically active components nitrogen oxide and nitrogen dioxide can be chemically reduced with ammonia or another reducing agent. After injection of ammonia or an aqueous solution of ammonia or urea the flue gas is led into the catalytic reactor (see figure 6.2). In the reactor within a temperature range between 280 and 400 °C in the presence of oxygen the nitrogen oxides react with ammonia forming molecular nitrogen and water as reaction products. Both components are harmless by-products and are emitted with the cleaned gas to the atmosphere.

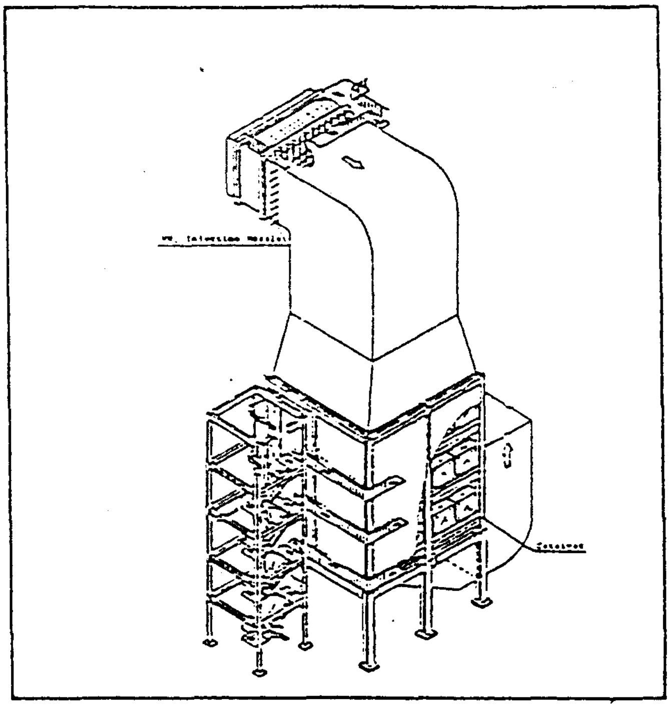


Figure 6.2: Functional Diagram of a SCR-Reactor

Figure 6.3 shows possible positions of a SCR-reactor in the downstream of a boiler.

In the case of coalfired facilities and the SCR-unit in the so-called highdust position - that means that no dust is collected before entering the SCR-reactor - the fly ash can absorb such a quantum of ammonia that utilization of this fly ash in the cement industry is impossible. If the SCR-unit is in a lowdust position - that means that the fly ash is collected before the flue gas gets in contact with ammonia, the ammoniafree uncontaminated fly ash can be utilized.

Choice of catalytic material is highly dependent on fuels used because of differences in flue gas composition (i.e. dust, SO_3, Alkali, ...).

Predominantly used materials for catalyzers are mixtures of titanium oxide as the main component and various amounts of ferrous oxide, vanadium oxide, molybdenum, tungsten, nickel, chromium, copper, cobalt. Recently ceolitic material has been tested on its catalytic performance feature.

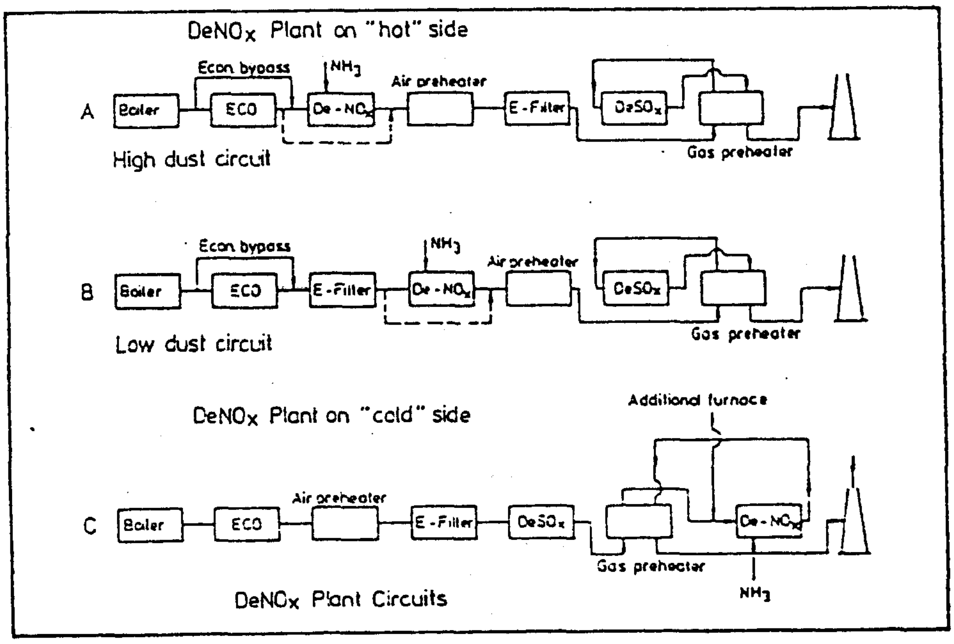


Figure 6.3: Possibilities for Application of SCR-Reactors (Necker, 1987)

SCR-units are commercially proven for all kind of fossil fuels except brown coal, where demonstration units are in operation.

Although reduction of NO_x does not generate by products by itself small amounts of unreacted NH_3 passing the SCR-reactor (NH_3 slippage) and SO_3 may produce troublesome by-products. Within the catalytic reactor some SO_2 present in flue gas, might be converted to SO_3 although catalyzers used are operating selectively on NO_x-reduction. By reaction of ammonia and SO_3 at temperatures below 300 °C hygroscopic and corrosive ammonium hydrogensulphate is formed. It is particulary undesired because of its tendency to precipitate on cooler areas of the plant forming a thin layer on surfaces. Although this layer can easily be washed off with water, it causes difficulties during continous operation of the plant. In waters ammonium compounds are exceptionally undesired because of their aquatic toxicity and high oxygen demand due to their bacterial decomposition. Therefore washing waters containing NH_4-compounds, have to be treated chemically or incinerated in the furnace.

To avoid problems incident to the formation of ammonium compounds both NH_3-slippage (see figure 6.5) and the conversion rate of SO_2/SO_3 have to be kept to a minimum.

Beside the used catalyst itself other residuals and waste water do not arise directly when NO_x is reduced using the SCR-process. In the case of the high dust system, however, the NH, slip can be too high, which may result in problems caused by scaling or plugging of the air preheater by ammonium hydrogen sulphate and excessive levels of NH_3 in the fly ash and in the waste water from the FGD-plant.

Many years of experience with using the SCR technology for the different types of furnaces (lignite-, oil-, coal-fired wet bottom and dry bottom boilers) are available. Approximately 80 % of the NH_3 slip is removed together with fly ash (see figure 6.4). When fly ash is recycled, NH_3 levels in excess of 100 ppm may result in odour problems, but even a considerably higher NH_3 content does not affect the constructional properties of fly ash.

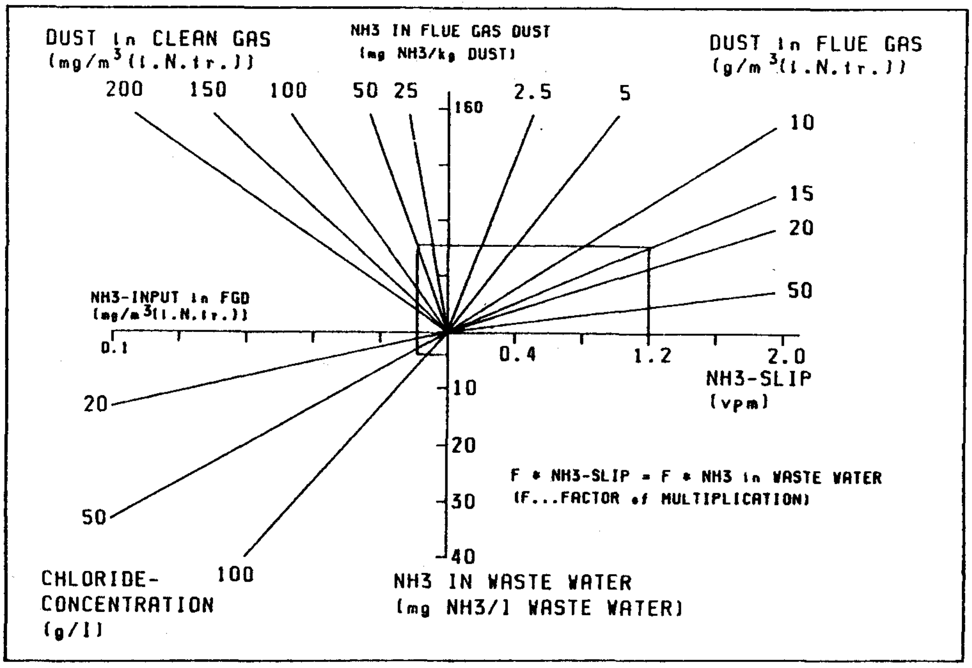


Figure 6.4: Remain of NH_3-slippage (Arbeitsgruppe "Kraftwerksreststoffe", 1988)

Nethertheless, in the Federal Republic of Germany and Austria, for example, SCR plants (high dust system) in coal-fired power plants are operated so that the NH_3, slip remains below 3 mg/m^3 in order to avoid odour problems (see figure 6.5). With an NH_3-slip as low as this, difficulties in the operation of the air preheater have not been observed, nor have excessive NH_3-levels in the FGD waste water been assured. Measurement of the NH_3-content of fly ash is a simple method which is suitable for determining the NH_3-slip and thus for monitoring the SCR-plant.

Used up catalytic material might be recycled by its producers or it has to be disposed of. Procedures were developed for recycling of metals like vanadium, molybdanium and platin, however they are not yet state of the art.

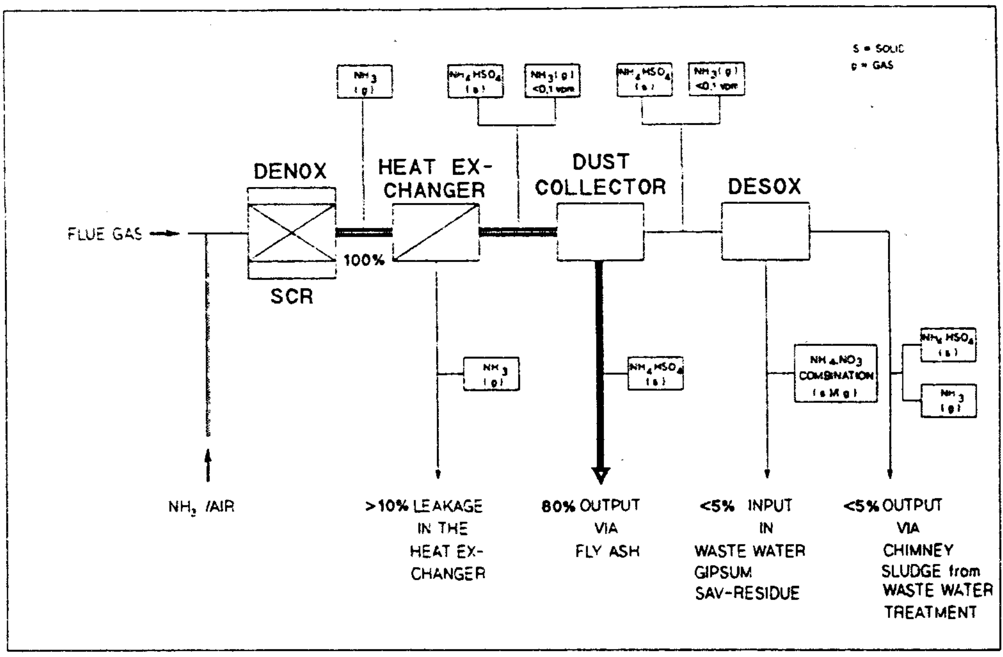


Figure 6.5: Introduction of Ammonia to Waste Water of FGD-Unit (Arbeitsgruppe "Kraftwerksreststoffe", 1988)

The main component of catalysts, TiO_2, can be returned to the supplier. Spent activated carbon or coke catalysts can be combusted. Zeolite and iron oxide/chromium oxide catalysts can be recycled for use in the ceramics or iron and steel industries.

6.2.2 Selective Non-Catalytic Reduction

Selective Non-Catalytic Reduction (SNCR) of the nitrogen oxides is possible within the temperature range of 900 to 1000 °C without the implementation of catalysts. Similar to the SCR process for reducing the nitrogen oxides ammonia or aqueous solutions of ammonia or urea can be used. To meet the requirements of a relatively high working temperature of this process it is necessary to inject the reducing agent within the boiler and in any case before dust collection as shown in figure 6.6. By this fly ash in the flue gas absorbs ammonia and this brings difficulties for any utilization of the fly ash.

Another disadvantage could be the fact that the NH_3/NO-molar ratio has to be higher in comparison to the SCR technique and this leads in some cases to a higher ammonia slip in the clean gas.

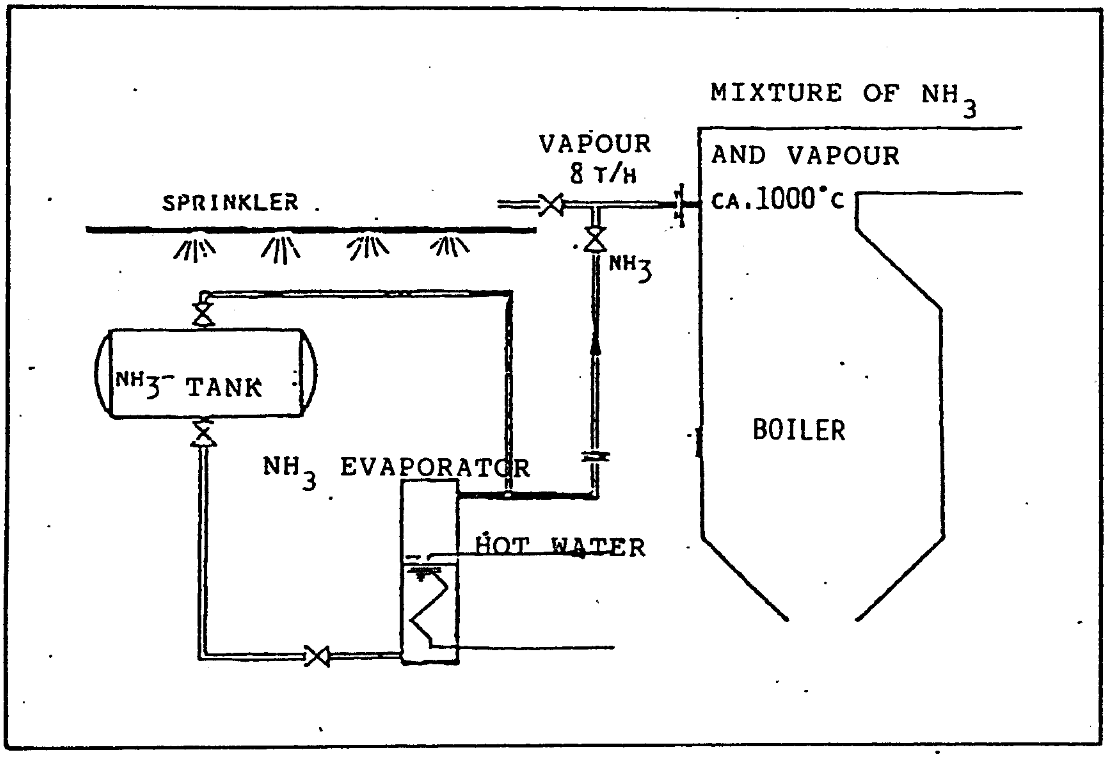


Figure 6.6: Flow Sheet of SNCR-Process Using NH_3 as Reducing Agent (Schröfelbauer, Tauschitz and Maier, 1988)

This type of $DeNO_x$-system is commercially available and in use for hard coal, brown coal and municipal waste. As a solid by-product, not usable in most cases, fly ash is retained as a waste.

7 BY-PRODUCTS AND WASTE FROM SIMULTANEOUS AND COMBINED SYSTEMS

Some processes offer the possibility to remove SO_2 as well as NO_x. Integrated procedures for simultaneous removal of SO_2 and NO_x work with the same agent for both $DeSO_x$ and $DeNO_x$ reaction while contact systems operate with a different agent for each of the two flue gas treatment processes. Most of them are in the state of development or in pilot size.

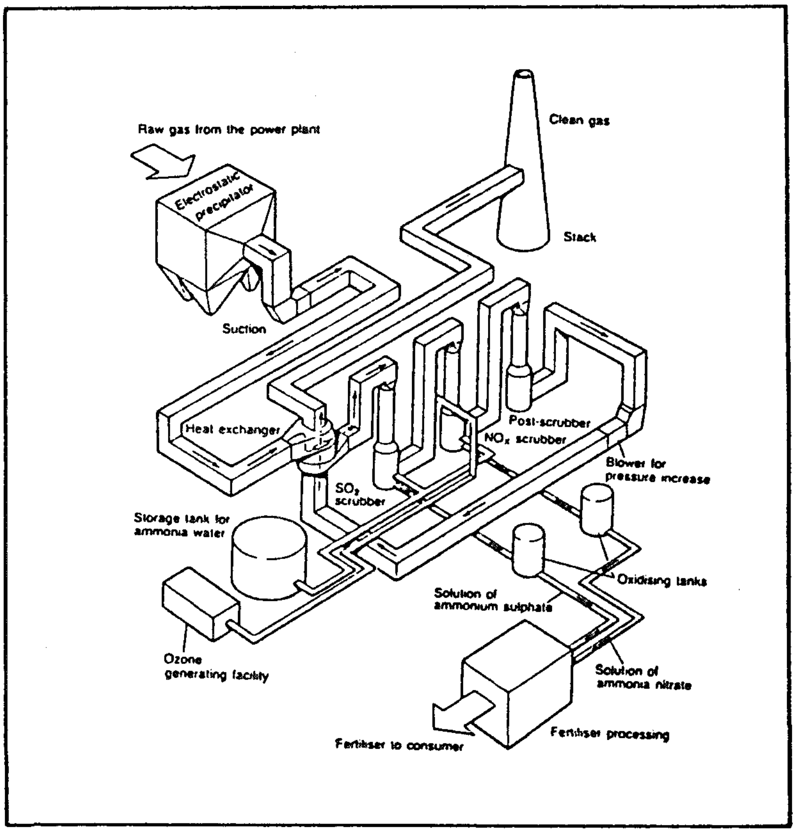


Figure 7.1: Block Diagram of the Ammonia-Ozone Process (Klingspore and Cope, 1987)

Process: Ammonia-Ozone Process
Systems to be treated: flue gas of hard coal
Scale of operation: demonstration
Reacting agent: ammonia (for $DeSO_x$), ozon (for $DeNO_x$)
By-Products: solid usable

Remarks: The Ammonia-Ozone Process is a wet working system for combined desulphurization and denitrification. Using ammonia as reacting agent, SO_2 is chemically bound as ammonia sulphate. In a second stage with the help of an oxidizing agent, i.e. ozone, NO_x is oxidized forming together with ammonia nitrate. Both compounds soluted in the washing liquid are then led to a spray tower. In the spray tower the water content of the washing liquor is evaporated by the heat of the incoming raw gas with the effect of cooling down the raw gas for the scrubbing operations and generating solid particles of ammonia sulphate and nitrate. These solid by-products can be used as fertilizer.

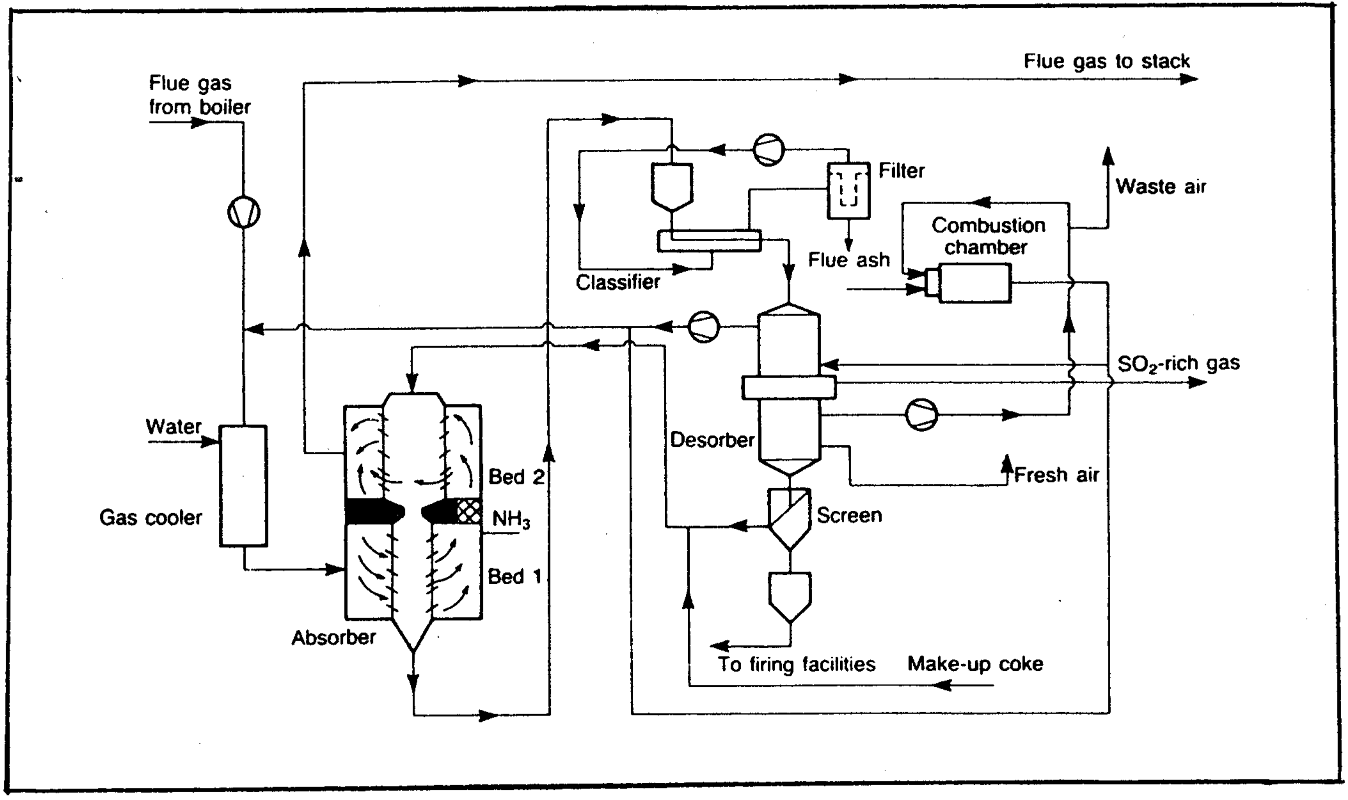


Figure 7.2: Block Diagram of the Activated Carbon Process (Richter, Knoblauch and Jüntgen, 1987)

Name: Activated Carbon Process
Systems to be treated: flue gas of hard coal
State of operation: commercial
Reacting agent: ammonia
By-products: usable solid and gaseous

Remarks: The Activated Carbon Process is a dry working procedure for combined desulphurization and denitrification. The process uses activated carbon to adsorb SO_2 by physical means and by injecting ammonia to convert NO_2 to nitrogen by catalytical means.

A moving bed of activated carbon is used. In a first stage the flue gas enters the absorption tower where at temperatures about 125 °C SO_2 is physically absorbed and reacts with water vapor and oxygen to form sulphuric acid. In a second stage together with injected ammonia the activated carbon reduces NO_x catalytically to nitrogen and water.

The activated carbon loaded with sulphuric acid is then led to the desorber where at temperatures about 400 °C a thermal destruction of the sulphuric acid to SO_2, CO_2 and water vapor takes place. The regenerated activated carbon after being coold down to absorption temperatures is used again in the absorber.

The SO_2-rich gas generated in the desorber contains about 30 % of SO_2 which can be used for producing liquified SO_2, sulphuric acid or elementary sulphur. The erosion losses of carbon generated by the movement of the activated carbon within the system can be burnt in the boiler.

8 BY-PRODUCTS AND WASTE FROM FLUIDIZED BED COMBUSTION

Fluidized Bed Combustion (FBC) has been recognized for its potential to provide an environmentally acceptable combustion system for a wide range of different fuels and is becoming an accepted technology. A still growing number of plants are operating with different fuels (Figure 8.1).

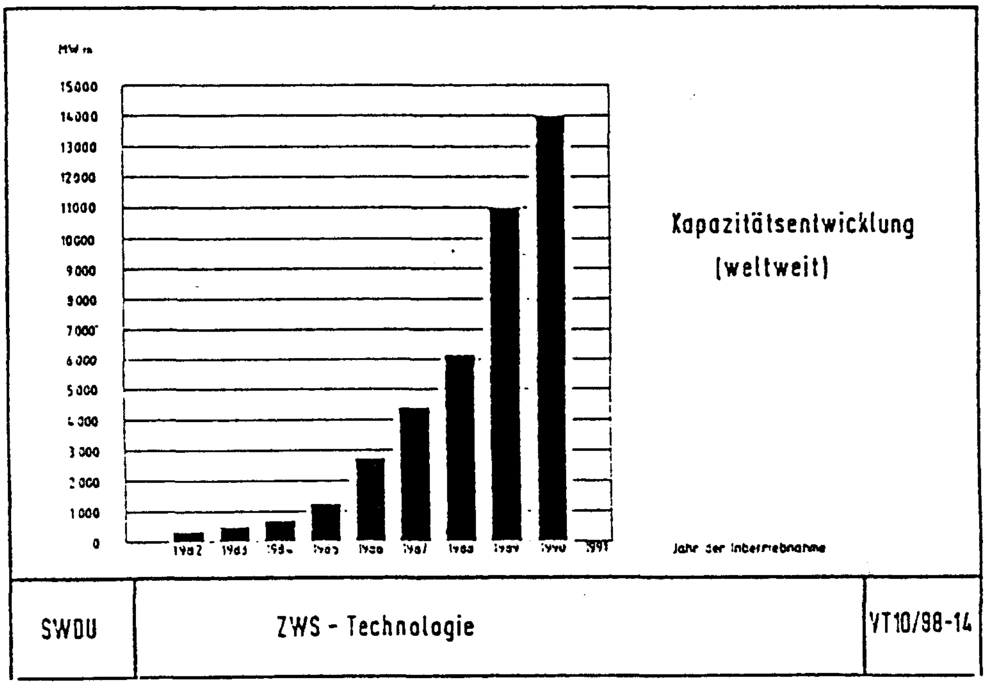


Figure 8.1: Prospected FBC Development of Capacity in the Whole World (Wein, 1988). The year means year of putting into operation.

Table 8.1 gives an overview over projected amounts of generated FB-by-products in the year 2000.

Table 8.1: Projected Amounts for the Year 2000 for By-Products from Fluidized Bed Combustion in Member Countries (data provided by member countries, all values are given in metric tons)

Country	Actual amount	Amount 2000	Remarks
AUSTRIA	55.000	90.000	total by-products
CANADA	16.000	205.000	total by-products
FEDERAL REPUBLIC OF GERMANY	500.000	1.000.000	total by-products
FINLAND	11.500	200.000 - 300.000	FBC ash incl. $CaSO_4$ and unreacted lime
ITALY	none	100.000	total by-products
MALTA	none	none	
NETHERLANDS	3.800	15.000	FBC ash
SWEDEN	60.000	140.000	FBC ash incl. $CaSO_4$ and unreacted lime
	20.000	50.000	FBC slag
UNITED KINGDOM	50.000	> 50.000	
UNITED STATES OF AMERICA	1.380.000	1.570.000	total by-products

8.1 Process Description

8.1.1 General Operating Principle of Fluidized Bed Combustion

A bed of granular inert material (SiO_2) is suspended by an upmoving stream of air. The generated turbulent mixture of gas and bed particles assumes properties similar to those of a fluid. Good heat and mass transfer, high heat capacity of bed material, good fuel mixing and long residence time provide conditions for a stable and highly efficient combustion process at rather low combustion temperature. Even low grade fuels being introduced into the fluidized bed will burn effectively.

Combustion of solid fuels in fluidized beds operates with relatively low temperatures of about 800 to 850 °C. That means that formation of NO_x is low in comparison to conventional combustion systems with grates or burners for pulverized coal. Therefore no separate denoxing system is needed if NO_x-requirements are not overly stringent.

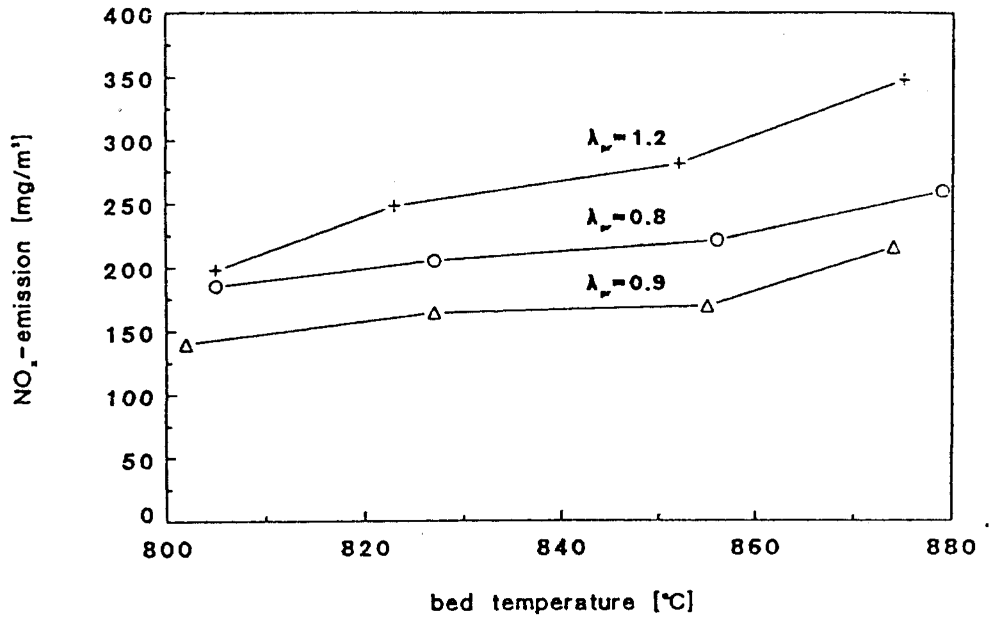


Figure 8.2: Influence of Bed Temperature on the NO_x-Emission at Different Primary Air Ratios, $_{tot}$ = 1.2, R/C = 1.5, Ca/S = 1.5, Polish Coal, Duwa 95 Limestone (Bramer et al., 1988)

For desulphurization it is possible to add pulverized limestone to the inorganic bed material of the fluidized bed. The limestone or dolomite is calcined and together with SO_2 it forms a mixture of calcium sulphite and calcium sulphate. The mixture of solid calcium compounds is then deflected in a downstream dust collector. Because of the fact that this solid product consists of fly ash, calcium sulphite and calcium sulphate, the utilization of this by-product is not yet state of the art.

8.1.2 Survey of Processes

Five main kinds of fluidized bed processes had been developed for combustion systems. Fluidized bed systems are applied as well for gasification processes. The following pictures give an overview over typical working principal.

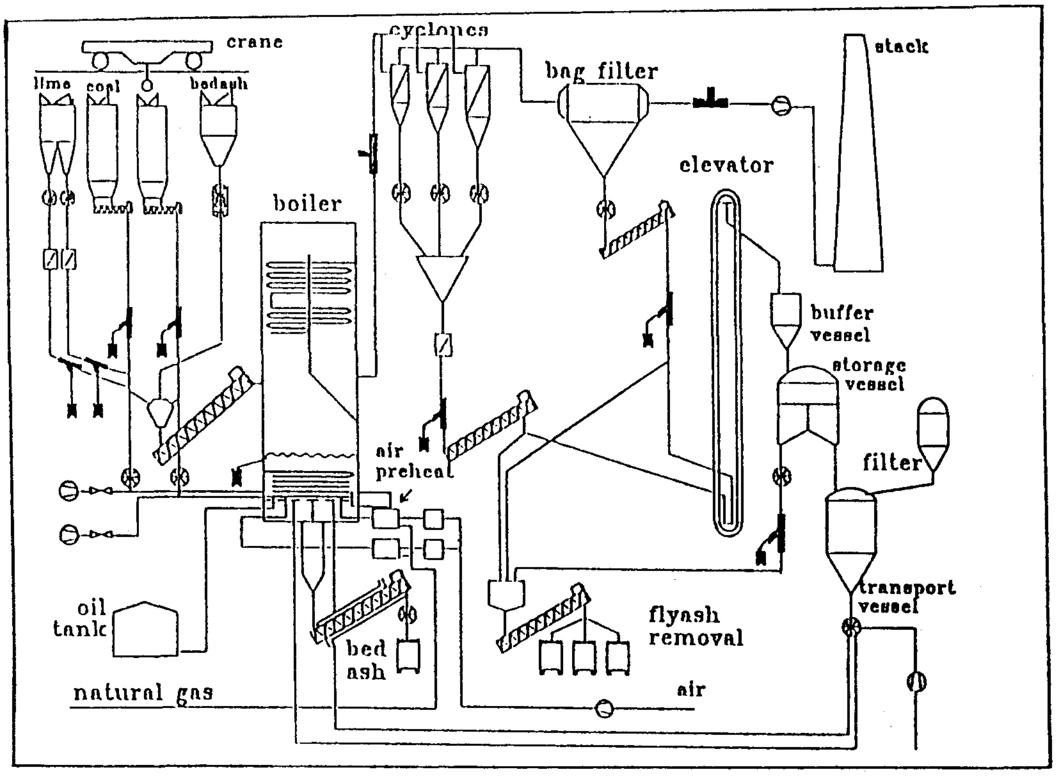


Figure 8.3: AFBC Flow Chart (Mulder and Gerritsen, 1987)

The Atmospheric Fluidized Bed Combustion (AFBC) is used commercially for coal, municipal waste and biomass. With $CaCO_3$ as an additive the process can be used for desulphurization. Waste water does not occur.

AFBC-systems working at comparatively low velocities of fluidizing air are characterized by a fixed bed depth. Suspensions of bed material is done by upstreaming air. Because only few particles of bed material are carried along with flue gas there is no need to recycle bed material.

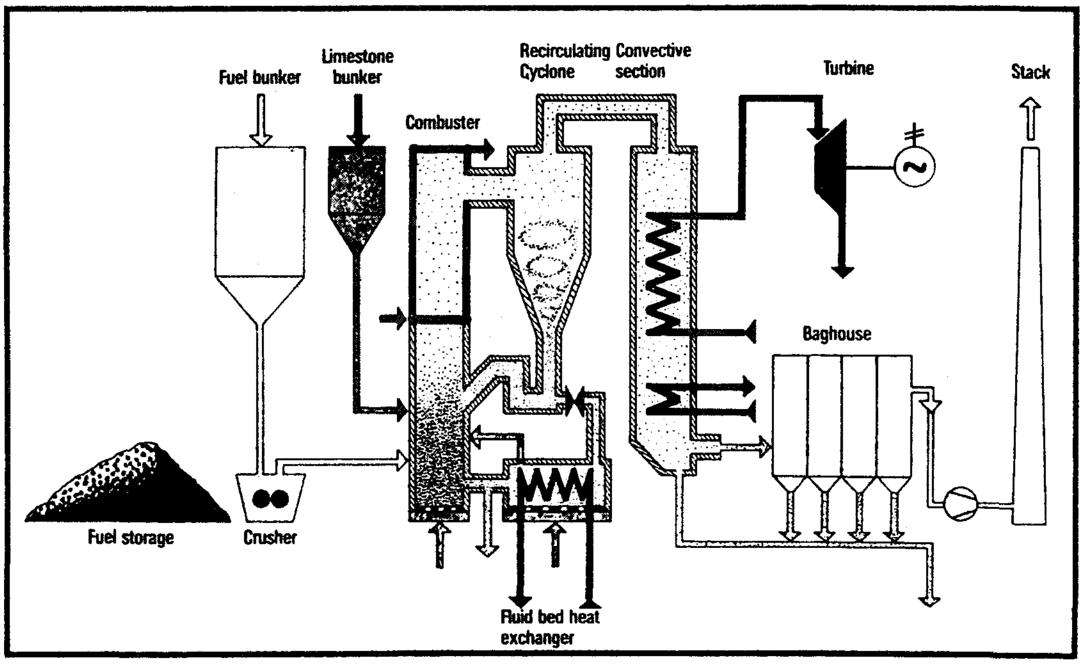


Figure 8.4: CFBC Flow Chart (Lurgi, 1984)

Circulating fluidized bed combustion (CFBC) is commercially used for brown coal and bituminous coal. $CaCO_3$ can be used as an additive for desulphurization. The solid by-products are not usable yet. Waste water does not occur.

CFBC operates at high velocity of fluidizing air and small particle size of bed material to ensure proper circulation of bed material and fuel which results in high concentration of bed material in flue gas.

Using a cyclone bed material is collected from the flue gas and reinjected to the combustion chamber. CFBC offers advantages referring to SO_2-reduction and utilization of sorbent and improved burning of low reactive fuel due to increased residence time and small particle size. Effective staging of combustion air in order to reduce NO_x-emissions may be arranged more easily.

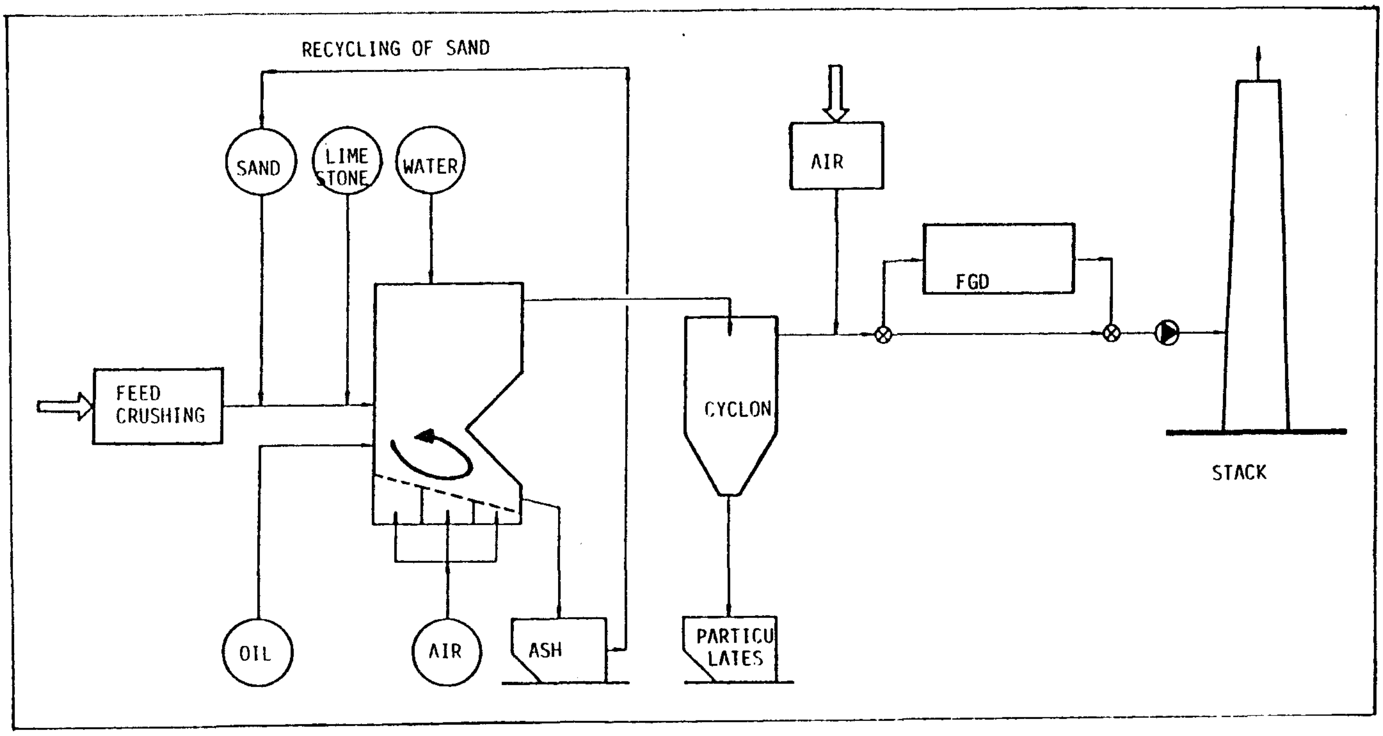


Figure 8.5: RFBC Flow Chart

Contrary to CFBC the rotating fluidized bed combustion (RFBC) works with an internal circulating system caused by different upstream air rates through the gridplate respectively air nozzles (see figure 8.5). RFBC is commercially applied for municipal waste mainly in Japan. $CaCO_3$ can be used as an additive for desulphurization. By-products are not usable yet. Waste water does not occur.

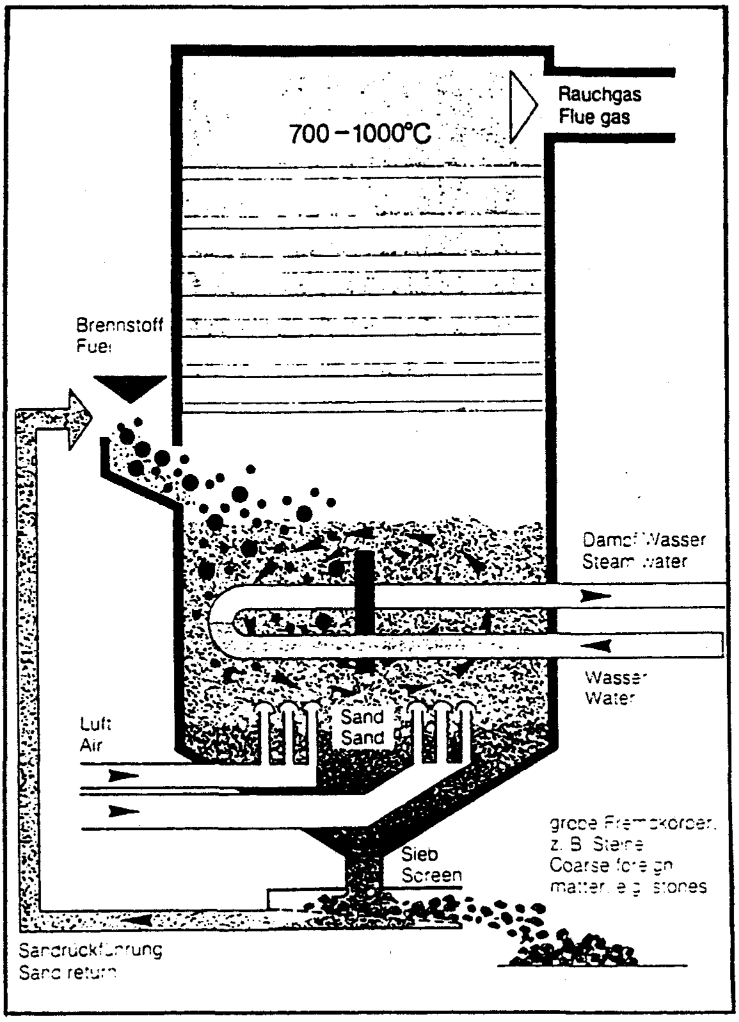


Figure 8.6: ICFBC Flow Chart (SGP, 1987)

Internal circulation fluidized bed combustion (ICFBC) works with a separating wall in the middle of the bed, dividing the bed in an upstream part and a downstream part according to the different air velocities in these two parts (see figure 8.6). ICFBC is applied for brown coal in a plant of demonstration size. Even "calcing" types of coal can be burnt in this equipment if they are fed directly. By-products are not utilized yet. Waste water does not occur.

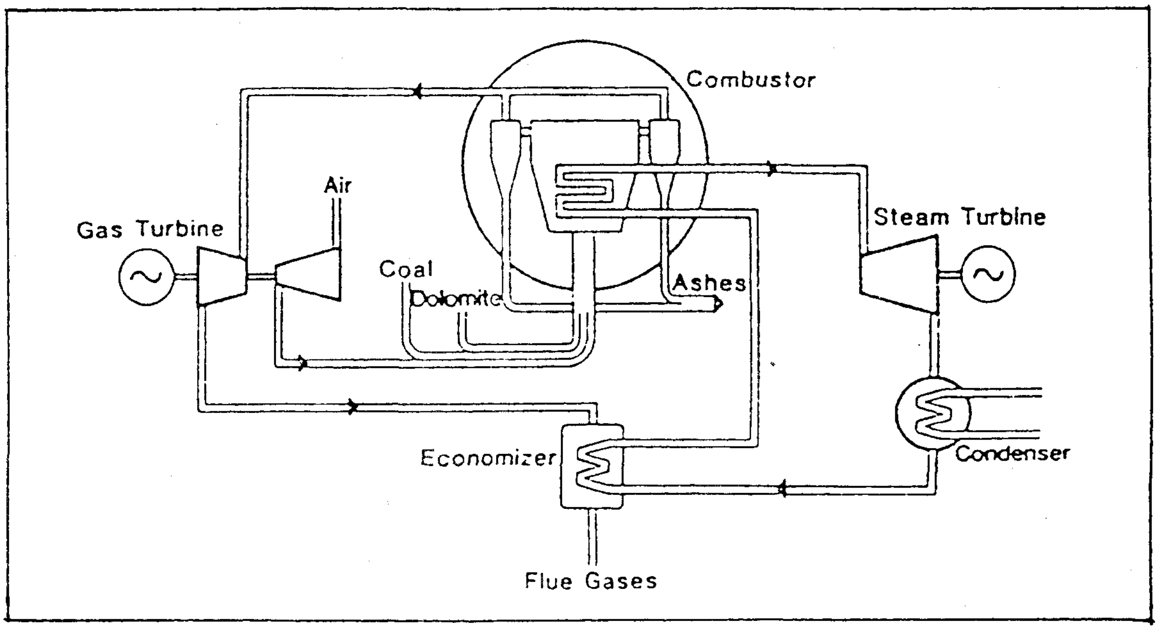


Figure 8.7: PFBG Flow Chart (Almqvist et al., 1986)

Pressurized fluidized bed combustion (PFBC) is in principle a bubbling fluidized bed combustion working however with elevated pressure up to 20 bar (see figure 8.7). Burning under pressure brings some advantages, like smaller units, expansion of flue gases through a gas turbine, lower NO_x formation, higher overall effiency (Anon, 1989). PFBC is applied for coal in plants of demonstration size in United Kingdom, Sweden and FRG.

8.2 By-Products

Given FBC's extremly good performance features concerning reduction of air pollution and its high flexibility referring to fuels an increase of application of FBC technology has to be supposed.

Nevertheless it should be emphasized that there is generated a considerable amount of ash as a by-product. Expected increase of firing systems operating on FBC-technology consequently will result in increasing quantities of ash either to be utilized or disposed.

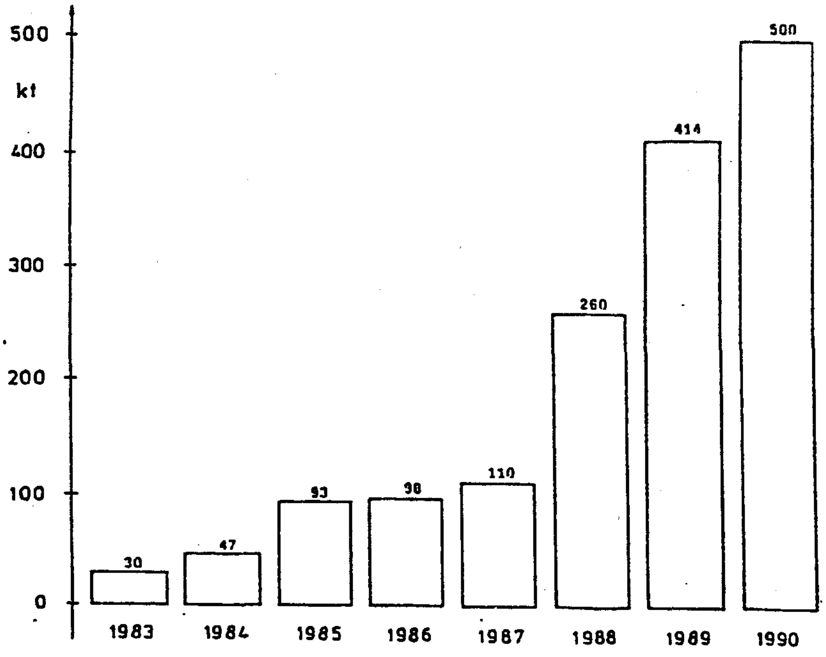


Figure 8.8: Quantities of FBC-Ash Generated in FRG (Huth, 1987)

Because of low combustion temperature chemical and physical properties of FBC-ash are quite different from those of ash generated by conventional firing.

AFBC-ash is due to low combustion temperatures scarcely slagged which results in increased leachability and reactivity. Additionally it might contain higher amounts of unburnt compounds and in consequence of limestone injection a lot of calcium compounds (CaO, $CaSO_4$). Besides composition of AFBC-ash depends on fuel used and technology applied. Even bed ash and fly ash should be considered separately.

Tables 8.2 to 8.5 give analyses from by-products from the FRG, table 8.6 and 8.7 a more detailed chemical characterization from AFBC by-product samples.

Table 8.2: Composition of Ash Generated by Combustion of Hard Coal in an AFBC-Reactor (Huth, 1987)

	Bed Ash	Bed Ash	Change over Plate	Cycla	Filter
SiO_2	32.2	20.5	21.1	21.7	36.2
Fe_2O_3	3.2	2.2	3.1	3.4	4.8
Al_2O_3	14.2	8.7	11.5	13.3	22.6
CaO_{total}	28.4	44.3	15.1	7.5	7.0
MgO	1.3	1.3	1.0	0.91	1.2
Na_2O	0.47	0.27	0.44	0.51	0.78
K_2O	2.17	1.57	1.81	1.72	2.08
SO_3	10.2	12.9	5.5	3.0	3.9
C	5.3	0.31	36.4	43.4	17.4
CaO_{free}	19.1	26.4	9.4	3.9	0.17
CO_2	0.8	4.5	0.8	0.74	0.15

Table 8.3: Chemical Composition of Ash Generated by Combustion of Hard Coal in Three Different AFBC-Reactors (Huth, 1987)

	Bed Ash	Bed Ash	Bed Ash	Fly Ash	Total Ash
SiO_2	15.5	13.2	14.1	25.7	37.0
Fe_2O_3	1.8	3.4	3.0	8.7	10.3
Al_2O_3	2.4	3.3	4.4	11.7	13.2
CaO_{total}	41.8	47.8	46.8	23.8	17.2
MgO	0.97	1.18	1.07	1.77	1.73
Na_2O	0.24	0.08	0.12	0.24	0.73
K_2O	0.42	0.49	0.58	1.9	3.14
SO_3	10.1	20.9	17.9	8.9	3.7
CO_2	25.0	6.2	7.9	6.4	5.3
C	0.42	0.3	0.7	4.8	12.4
CaO_{free}	0.7	18.7	18.3	6.8	n.a.

n.a. ... not analyzed

Table 8.4: Chemical Composition of Ash Generated by Combustion of Hard Coal and Lignite in CFBC-Reactors (Huth, 1987)

	Brown Coal				Hard Coal
	Bed Ash	Filter Ash	Filter Ash	Filter Ash	Total Ash
SiO_2	79.7	16.5	11.5	7.0	35.03
Fe_2O_3	1.0	9.5	8.8	8.9	5.56
Al_2O_3	0.53	6.4	4.1	3.7	22.31
CaO_{total}	11.3	35.7	45.0	47.3	18.05
HgO	1.01	8.0	8.3	9.0	2.11
Ha_2O	0.15	0.12	0.12	0.15	0.7
K_2O	0.07	0.66	0.37	0.30	2.9
SO_3	1.28	10.6	11.8	10.7	12.54
CO_2	0.7	0.93	1.85	4.07	4·5
C	0.12	7.63	4.8	5.51	
CaO_{free}	0.31	3.17	16.2	20.2	5.0

Table 8.5: By-Products of a CFBC-Reactor (Hackl, 1986b)

Components	By-Products of CFBC (% dry matter)		
	bed		additive
		with Ca/S	with Ca/S 1.5 to 2.5
loss of ignition	2.40	5.88	4.13 - 4.38
CO_2	0.48	1.21	2.04 - 3.36
burnt C	1.92	4.47	2.09 - 1.02
S	0.78	1.82	2.31 - 3.08
$CaSO_2$	3.32	7.72	9.81 - 13.07
$CaCO_3$	1.09	2.75	4.64 - 7.64
CaO	9.13	7.37	10.85 - 12.55

Table 8.6: Chemical Characterization of AFBC Waste Samples (Lees et al., 1988) (mg/kg except where noted)

Chemical Parameter	AFBC Waste Streams			
	Spent Bed Material	Char	Fly Ash	Composite
Inorganic Elements (ICAPES)				
Aluminium	7200	19300	39800	16200.1
Antimony	13*)	17*)	23	18*)
Arsenic	< 12	< 12	< 120	< 12
Barium	57	90	190	50
Beryllium	0.2*)	< 0.2	< 0.2	< 0.2
Boron	< 10	34*)	131	< 10
Cadmium	3.7	1.3*)	< 4	4
Calcium	321900	219900	161700	279500
Chromium	9.7*)	46	84	76
Cobalt	5.2*)	5.3*)	< 1	6.1
Copper	11	14	29	12
Iron	16700	46200	66100	59900
Lead	18*)	< 16	< 16	19*)
Lithium	22	16	35	19
Magnesium	3730	2860	3090	3240
Manganese	87	140	110	160
Molybdenum	6	9.4	< 0.4	16
Nickel	80	16	33	81
Potassium	1300	3230	8020	3010
Selenium	39*)	61*)	< 160	62*)
Silicon	14800	37200	71200	28200
Silver	1.1*)	7.5	22	2
Sodium	990	180	1260	1070
Strontium	220	230	250	170
Thallium	< 18	< 18	< 18	< 18
Tin	< 24	< 24	< 24	< 24
Titanium	430	890	2360	870
Uranium	< 25	< 25	35*)	130
Vanadium	64	68	150	110
Zinc	62	190	290	69
Volatile Metals (AA))**				
Arsenic	4	11	44	7.5
Cadmium	1.2	0.6	1.1	0.4*)
Lead	4.8	1.1	9.0	4.3
Mercury	< 0.05	< 0.05	1.4	0.19
Selenium	< 0.4	< 0.7	< 0.7	< 0.4

*) Value is less than 5 times the detection limit.

**) Atomic absorption provides more accurate volatile metals analyses.

Table 8.7: Chemical Characterization of AFBC Waste Samples (Lees et al., 1988) (mg/kg except where noted)

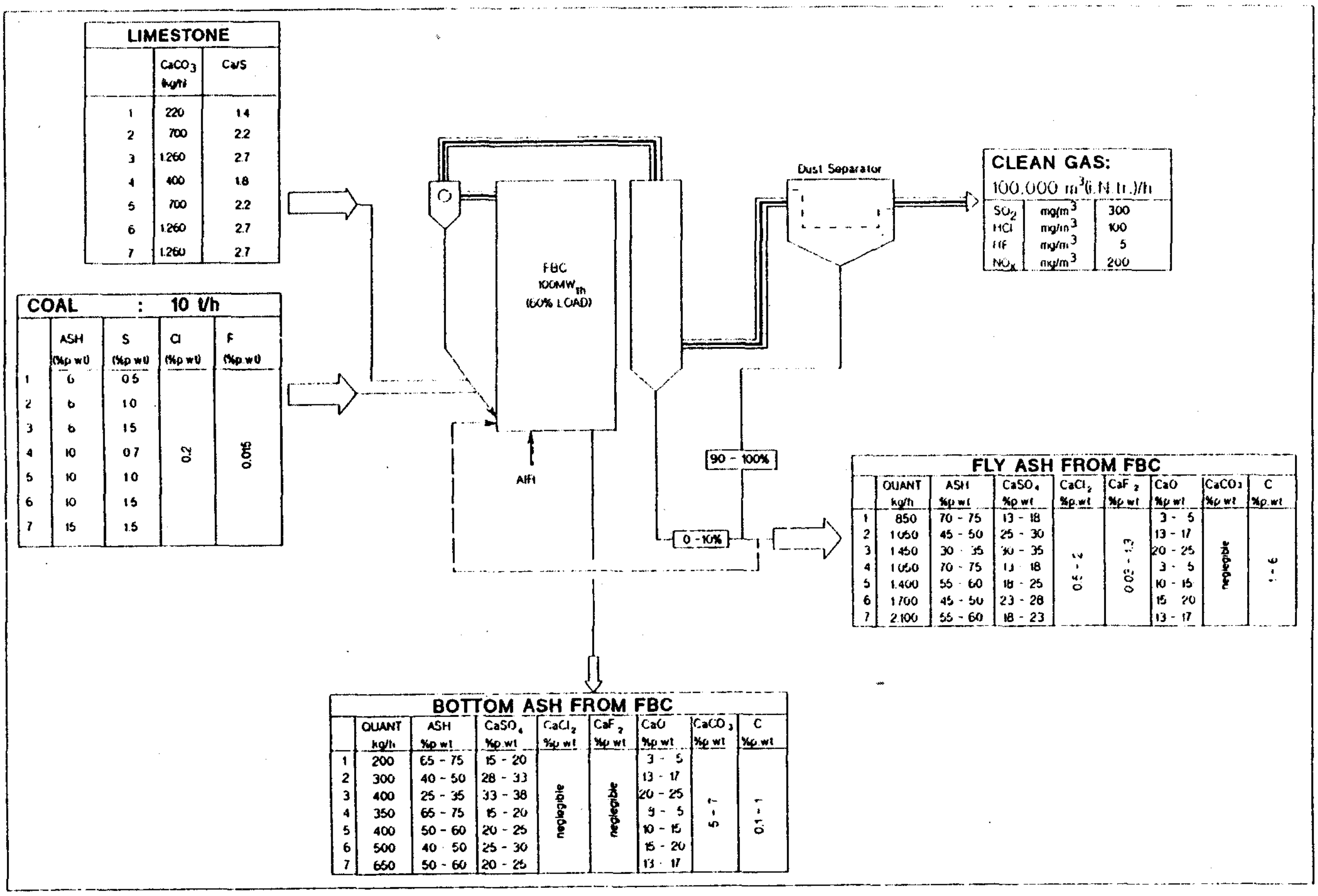
Chemical Parameter	AFBC Waste Streams			
	Spent Bed Material	Char	Fly Ash	Composite
Hydroxide (mg/g)	178.2	63.2	33	99.5
Acid Soluble Sulphur (mg/g as S)	26	80	69	48
Water Soluble Sulphate	63	164	168	76
Water Soluble Sulphite (SO_3)	4.8	10	11	11
Water Soluble Chloride	0.2*)	0.3*)	0.6	0.5*)
Water Soluble Carbonate	< 2.5	n.a.	n.a.	< 2.5
Water Soluble Fluoride	< 0.05	0.3	0.4	0.2
Radioactivity				
Grossalpha (pCi/g)	1.57 ± 8.45	5.1 ± 10	17 ± 12	0 ± 7.36
Grossbeta (pCi/g)	23.8 ± 10.8	28 ± 1	55 ± 11	19.8 ± 10.6
Ra-226 (pCi/g)	0.913 ± 0.080	1.83 ± 0.42	6.2 ± 0.5	1.71 ± 0.13
U-235 (pCi/g)	0.534 ± 0.144	0.026 ± 0.068	0.084 ± 0.088	0.153 ± 0.161
Organics GC & GC-MS As Necessary				
Acenaphthene	< 1	< 1	< 1	< 1
2,4-dimethylphenol	< 1	< 1	< 1	< 1
Fluoranthene	< 1	< 1	< 1	< 1
Naphthalene	< 1	< 1	< 1	< 1
Diethyl phthalate	< 1	< 1	< 1	< 1
Dimethyl phthalate	< 1	< 1	< 1	< 1
Benzo(a)pyrene	< 1	< 1	< 1	< 1
3,4-benzofluoroanthene	< 1	< 1	< 1	< 1
Chrysene	< 1	< 1	< 1	< 1
Acenaphthalene	< 1	< 1	< 1	< 1
1,12-benzoperylene	< 1	< 1	< 1	< 1
Fluorene	< 1	< 1	< 1	< 1
Phenanthrene	< 1	< 1	< 1	< 1
1,2,5,6-dibenzanthracene	< 1	< 1	< 1	< 1
Pyrene	< 1	< 1	< 1	< 1

n.a. ... not analyzed

*) Value is less than 5 times the detection limit.

**) Atomic absorption provides more accurate volatile metals analyses.

Figure 8.9 gives a material balance for a CFBC-system fed with hard coal as a fuel and limestone as an additive.



LIMESTONE	CaCO$_3$ (kg/h)	Ca/S
1	220	1.4
2	700	2.2
3	1.260	2.7
4	400	1.8
5	700	2.2
6	1.260	2.7
7	1.260	2.7

COAL : 10 t/h

	ASH (%p wt)	S (%p wt)	Cl (%p wt)	F (%p wt)
1	6	0.5	0.2	0.015
2	6	1.0		
3	6	1.5		
4	10	0.7		
5	10	1.0		
6	10	1.5		
7	15	1.5		

CLEAN GAS:
100.000 m^3(i.N.tr.)/h

SO_2	mg/m^3	300
HCl	mg/m^3	100
HF	mg/m^3	5
NO_x	mg/m^3	200

FLY ASH FROM FBC

	QUANT kg/h	ASH %p wt	CaSO$_4$ %p wt	CaCl$_2$ %p wt	CaF$_2$ %p wt	CaO %p wt	CaCO$_3$ %p wt	C %p wt
1	850	70 - 75	13 - 18	0.5 - 2	0.02 - 1.3	3 - 5	negligible	1 - 6
2	1.050	45 - 50	25 - 30			13 - 17		
3	1.450	30 - 35	30 - 35			20 - 25		
4	1.050	70 - 75	13 - 18			3 - 5		
5	1.400	55 - 60	18 - 25			10 - 15		
6	1.700	45 - 50	23 - 28			15 - 20		
7	2.100	55 - 60	18 - 23			13 - 17		

BOTTOM ASH FROM FBC

	QUANT kg/h	ASH %p wt	CaSO$_4$ %p wt	CaCl$_2$ %p wt	CaF$_2$ %p wt	CaO %p wt	CaCO$_3$ %p wt	C %p wt
1	200	65 - 75	15 - 20	negligible	negligible	3 - 5	5 - 7	0.1 - 1
2	300	40 - 50	28 - 33			13 - 17		
3	400	25 - 35	33 - 38			20 - 25		
4	350	65 - 75	15 - 20			3 - 5		
5	400	50 - 60	20 - 25			10 - 15		
6	500	40 - 50	25 - 30			15 - 20		
7	650	50 - 60	20 - 25			13 - 17		

Figure 8.9: FBC Combustion - By-Products (Arbeitsgruppe "Kraftwerksreststoffe", 1988)

8.2.1 Utilization

8.2.1.1 Atmospheric Fluidized Bed Combustion

Recent studies have been conducted to review the possible uses of by-products from AFBC (Gerritsen, 1988; Smith, 1989; Carr and Price, 1987; Lotze and Wargalla, 1985; Arbeitsgruppe Kraftwerksreststoffe", 1988).

Figure 8.10 shows possibilities for the utilization of AFBC by-products.

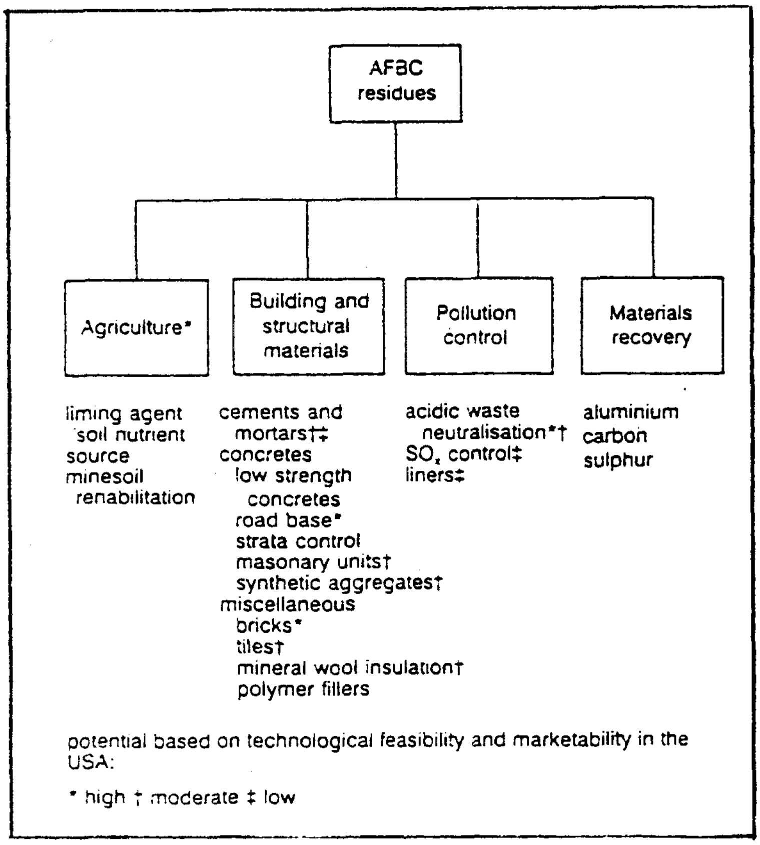


Figure 8.10: Possible Utilization of By-Products from AFBC By-Products (Smith, 1990)

The high content of SO_4-compounds (Table 8.8) and unburnt carbon (up to 56 weight percent on dry basis for AFCB-ash) sets some limitation to its use as cement additive or component of concrete or mortar. Best results were achieved in preparing liner material and mortar used in mining (Carr and Price, 1987).

Table 8.8: Average Composition and Specific Physical Properties of AFBC Residues (Gerritsen, 1988)

Property	AFBC Fly Ash	AFBC Bed Ash	
Carbon (organic)	11 - 13	0 - 0.2	%
Silica	28 - 32	36 - 44	%
Aluminium oxide	13 - 16	12 - 16	%
Iron oxide	6 - 8	4 - 6	%
Calcium oxide	12 - 15	15 - 25	%
Calcium sulphate	12 - 15	12 - 18	%
Other	5 - 10	4 - 8	%
Absolute density	2350 - 2450	2700 - 2900	kg/m^3
Bulk density (compacted)	1050 - 1150	1350 - 1450	kg/m^3
Mean particle size (d_{50})	20 - 30	1100 - 1500	microns
Specific surface area	3 - 12	2 - 4	m^2/gramme
Bitumen index	52 - 57	30 - 34	
pH 1 min.	11.7	11.9	
pH 10 min.	12.2	12.2	

Table 8.9 gives a view how chemical composition of FBC-ash varies with the kind of process and place of arising.

Table 8.9: Results from Chemical Analyses of Waste Products (Nilsson, 1987)

Substance	BFBC	Multibed			CFBC		PFBC		PF	
	cyclone	bed	cyclone	filter	bed	filter	bed	cyclone	fly ash	FGD
As	15–29	10–26	10–26	11–27	20–23	20–31	13–20*	18–30	19–23	18–26
Cd	0.5–1.3	0.3–1.7	0.4–1.2	0.8–1.6	0.4–1.6	0.3–1.3	0.1–1.3	0.4–1.5	0.2–1.3	0.2–0.8
Cr	16–33	42–86	21–113	<1–95	20–38	32–49	26–74	29–79	345–1784	53–266
Cu	13–42	20–34	15–58	12–58	34–69	25–49	3–13	17–27	18–37	32–47
Hg	<0.5	<0.5	<0.5	<0.5–1.7	0.8–2	<0.5	<0.5	<0.5–0.8	<0.5	<0.5–2.9
Ni	15–36	15–22	15–37	15–20	18–55	13–62	12–34	12–22	9–15	16–22
Pb	12–31	13–16	1–13	5–21	6–15	10–13	7–25	8–23	5–12	2–14
chloride*	10–1100	8–82	6–160	6–4270	220–1300	4–1580	5–96	7–170	3–34	90–12,960
fluoride*	0.6–4.4	<0.1–2.3	1.9–3.8	1.2–4.8	0.6–2.3	1.7–4.9	<0.1–3.2	<0.1–3.1	<0.1–3.7	3.6–5.9
sulphite*	1–34	≤1	5–99	3–644	131–578	3–19	1–9	1–21	≤1	<1
sulphate*	21–1735	1432–1747	333–1714	17–1972	1747–2184	1525–2022	1440–1881	1282–1808	20–1327	299–2111
pH	11.7–12.6	12.1–12.6	11.8–12.7	12.3–12.6	12.6	10–12.6	11.9–12.5	10.9–12.6	11.6–12.4	11.5–12.6

* mg/l

Whereas PF ash can be used as the pozzolan (a pozzolan is a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious property but which will, in finely divided form, combine the CaO in the presence of water to form cement) it is the CaO in AFBC residues which can be used to make cement. There appears to be some confusion in the literature as to whether AFBC residues are pozzolans. Some authors from the FRG refer to the pozzolanic activity of AFBC residues as similar to that of PF ashes. On the other hand researchers in Canada consider that AFBC residues are not pozzolans like PF ashes; further, that failure to consider this distinction has led some previous authors to suggest uses for AFBC residues which are inconsistent with their unique properties (Smith, 1989).

AFBC residues are primarily a heterogeneous mixture of CaO and $CaSO_4$ (see figure 8.11) with minor and trace inclusions of the elements normally found in coal ashes and limestone. There are three main properties which characterize AFBC residues and which can therefore be exploited for utilization; the residues are:

- potential sources of low grade CaO
- granular
- somewhat cementitious.

Uses are being demonstrated for AFBC residues in a variety of industries and their potential uses assessed (see figure 8.10). However, as Gerritsen (1988) points out, in terms of development status FBC technology has entered the medium term phase during which research on the application of residues in the short term can be started.

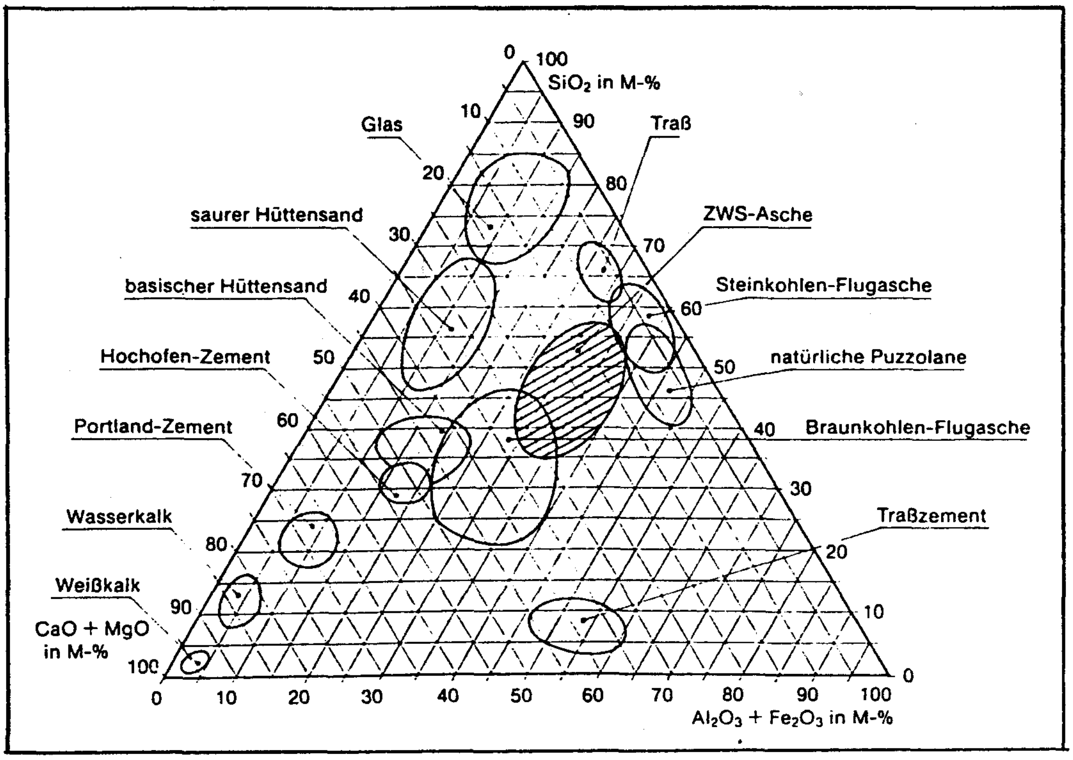


Figure 8.11: Circulation Fluidized Bed Furnace Ash and Pozzolanie Materials in the Ternary Systems $CaO-SiO_2-Al_2O_3$

A wide range of utilization options have been demonstrated for AFBC residues (see figure 8.10) but none has really reached commercial status. Agricultural uses of AFBC residues as a liming agent, soil nutrient source and in minesoil rehabilitation have been studied extensively in the US and are of interest in other countries such as Canada, the FRG and Finland. There is concern in all these countries about the possible release of harmful trace elements and indeed in the Netherlands the application of AFBC residues on agricultural land is not permitted for this reason. Studies have demonstrated the effectiveness of AFBC residues in agriculture and have revealed no deleterious effects on crops, or livestock feeding on pasture grown on soil amended with AFBC residues. Also, compared with sewage sludge which is used in agriculture, AFBC residues contain lower concentrations of heavy metals. However, this use might be less promising for residues from future commercial AFBC because improvements in sulphur capture will reduce the available lime in the residues.

AFBC residues cannot be used like fly ash in building and structural materials as they are not glassy pozzolans. Cements, mortars and concretes made with AFBC residues have unique cementitious properties including the slow development of good strength properties owing to their content of CaO and $CaSO_4$. The expansion on curing of AFBC mortars and concretes can be exploited in mines for low strength strata control applications. AFBC residues can also be used in synthetic aggregate for lightweight concrete mixes. The direct use of AFBC residues in Portland cement production is not advocated in the Netherlands and Sweden because of their high sulphate content and variability. Appropriate mixes in which AFBC residues are well diluted with other raw materials have been successful in cement production in the US and the concept of an integrated AFBC/Portland cement industrial complex is being evaluated.

Examples of the use of AFBC residues in road construction, that is for soil stabilization and as fillers in road bases or asphalt have been demonstrated in Canada, the FRG, Finland, the Netherlands and the US. Although the performance of AFBC residues is good in these applications there is still concern about long term performance under freeze-thaw conditions.

Various masonry units made with BFBC residues and PF ash in the FRG and the US appear to give satisfactory performance but the residues need to be more consistent in order to find uses in high quality construction materials. This problem is similarly a disadvantage to their use in bricks - an application which is being pursued otherwise with success in Australia, the FRG, the Netherlands, the UK and the US.

The free lime, water absorbing capacity and cementitious properties of AFBC residues are useful for neutralizing and stabilizing acidic wastes and sludges. Here AFBC residues would reduce costs by replacing the lime or Portland cement which is currently used with PF ash for this purpose. The low permeability of AFBC residues suggests their use as liner materials at waste disposal sites. This application was not ranked high by EPRI in the US but preliminary results are satisfactory in the FRG and Japan.

Materials recovery from AFBC residues would facilitate their further disposal or utilization by removing some undesirable components. However, the economic feasibility is poor for aluminium recovery. Sulphuric acid production appears more promising in an integrated industrial complex. The separation of activated carbon is under investigation.

There are many potential uses for AFBC residues but a major handicap is the wide variability of their composition. The technology would lose one of its main advantages if this variability were reduced by limiting the variety of fuel used.

Fortunately, it appears that much of the variability in the characteristics of AFBC residues is due to different operating conditions and sizes of plant. This could improve in future, larger commercial units. Whilst there are methods of controlling the characteristics of AFBC residues these might not always be desirable to the operator for other reasons. Problems of long term leaching behaviour at disposal sites are exaggerated by standard tests and require further investigation using realistic criteria. In terms of development status, research is still in progress on the management of AFBC residues from relatively small plants. This will form the basis for future progress in commercialization of AFBC technology.

8.2.1.2 Pressurized Fluidized Bed Combustion

There are clear incentives to develop commercial outlets for ash residues form power stations in order to reduce operational costs and minimize the overall environmental impact of ash disposal. Laboratory-scale experiments have shown that there are possible commercial applications for PFBC ash. The applications investigated include: structural fill, grouts, cement replacement, asphalt aggregate, road base material, sand/lime-type bricks and blocks, neutralizing agent for acidic materials, fixation of toxic wastes, synthetic aggregate, filler in plastics, alumina extraction and soil conditioner. (Anon, 1989)

8.2.2 Disposal

In principle all concerns made on disposal in chapter 2.4 has to be regarded when by-products from FBC will be disposed. Figure 8.12 shows possible alternatives for the AFBC Disposal Management.

Safe disposal is strongly influenced by the leaching characteristics of the by-products. The following tables show data from different leaching procedures as well as for different fuels and plant types.

Table 8.10: Results of Leaching Tests (Using the Swedish Leaching Procedure) for Various By-Products of Different FBC-Systems. Used Coal was U.S. Hard Coal (Nilsson, 1987)

Material	pH	COD_{Cr} mg/l	Flourine mg/l	Chlorine mg/l	Sulphite mg/l	Sulphate mg/l	As µg/l	Cd µg/l	Cr µg/l	Cu µg/l	Hg µg/l	Ni µg/l	Pb µg/l
CFBC - Fly Ash													
1 : 1	12.55	90	1580	4.9	19	1715	25	0.33	32	25	< 0.5	62	10
1 : 4	12.20	42	60	4.0	14	1674	24	1.22	40	49	< 0.5	43	13
1 : 8	9.95	< 10	94	1.9	6	1674	22	1.30	49	40	< 0.5	26	13
1 : 12	10.35	< 10	24	2.0	4	1525	20	1.25	41	40	< 0.5	13	13
1 : 16	10.35	10	4	1.7	3	2022	31	1.33	39	36	< 0.5	19	12
CFB - Bed Material													
1 : 1	12.60	880	1300	1.9	578	2184	22	0.39	20	69	1.6	55	15
1 : 4	12.55	470	350	0.6	265	1943	23	1.38	38	52	2.0	21	10
1 : 8	12.55	300	264	0.6	144	1915	20	1.42	38	42	1.2	25	6
1 : 12	12.55	230	220	2.3	131	1747	20	1.38	27	38	0.8	18	8
1 : 16	12.55	340	226	2.0	194	1966	20	1.56	21	34	0.8	18	12
AFBC													
1 : 1	11.65	95	1100	4.4	34	1735	15	1.25	16	42	< 0.5	15	12
1 : 4	12.55	39	260	3.2	20	1470	27	0.91	33	22	< 0.6	36	26
1 : 8	12.55	< 10	90	3.0	4	1317	28	0.64	22	13	< 0.5	27	26
1 : 12	12.55	< 10	19	0.6	1	1005	29	0.54	19	19	< 0.5	22	27
1 : 16	12.40	< 10	10	1.0	1	21	26	1.00	17	14	< 0.5	19	31

The results obtained in this leaching test show primarily salts (e.g. chloride and sulphate). The leaching of trace elements (As, Hg, Ni, Cr, Cu, Pb) generally occur slowly, propably due to the high alkalinity of the materials.

Table 8.11: Leaching of Ash from Different FBC-Systems and one Using a Binder. Used leaching method was DEV-S4 (Kautz, 1986). All data in mg/l.

	AFBC total ash	AFBC filter ash	CFBC filter ash	CFBC filter ash with 5 volume % lime after 28 days
Ca	960	878	420	5
SO_4	720	977	1214	80
Cl	< 10	34	28	20
As	0.001	0.002	0.01	< 0.001
Cr	< 0.01	0.01	0.01	< 0.01
Pb	< 0.01	< 0.01	< 0.01	< 0.01

At present however most of the FBC ash generated still has to be disposed due to lack of suitable possibilities of utilization.

As far as there are little information on performance of FBC ash on disposal in detail in FRG and Austria it is considered to be hazardous or special waste.

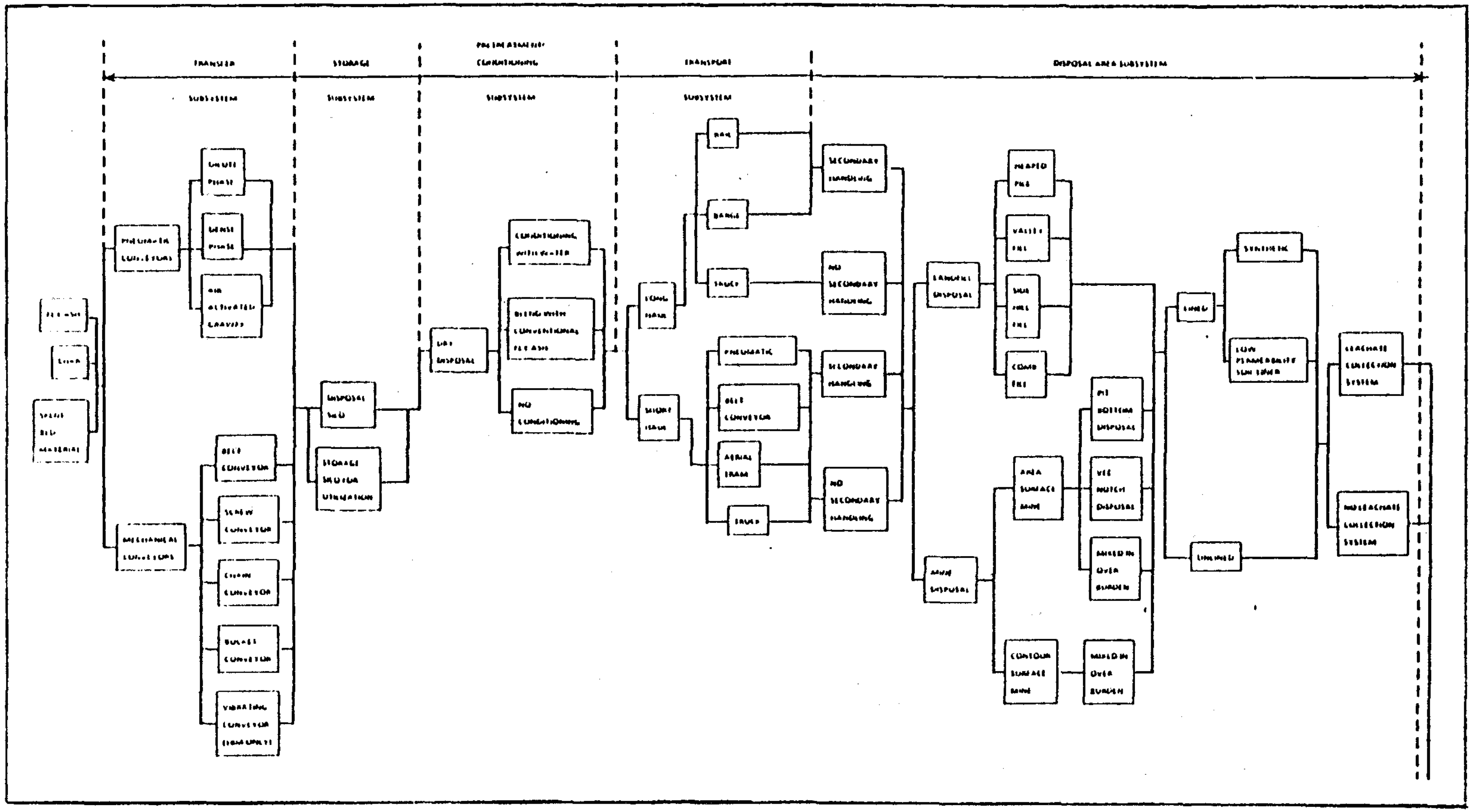


Figure 8.12: Typical AFBC Waste Management Alternatives (Lees et al., 1988)

9 BY-PRODUCTS AND WASTE FROM GASIFICATION PROCESSES

According to the ECE-Task Force Report on gasification, i.e. for Integrated Coal Gasification Combined Cycle the abbreviation IGCC is used (IGCC Task Force, 1988). Table 9.1 gives prospected amounts of by-products from coal gasification.

Table 9.1: Projected Amounts for the Year 2000 for By-Products from Gasification Processes in Member Countries (data provided by member countries)

Country	Actual amount	Amount 2000	Unit	Remarks
AUSTRIA	none	probably none		
CANADA	none	expected		
FEDERAL REPUBLIC OF GERMANY	200.000		t	slag
	7.000	no data available	t	fly ash and filter cake
	1.800		t	sulphur
FINLAND	none	probably none		
ITALY	none	100.000		
MALTA		none		
NETHERLANDS	none	170.000	t	slag
SWEDEN	none	none		
UNITED KINGDOM	none	probably none		
UNITED STATES OF AMERICA	no data available			

9.1 Current Status of IGCC Technology

The commercial status of gasification processes available is not in all cases completely proven and requires further scale up and research (IGCC Task Force, 1988).

However, considerable cost savings are to be expected in the future for an IGCC power plant in comparison to a pulverized coal fired plant. IGCC plants offer some special features such as (IGCC Task Force, 1988):

- Unlike conventional coal fired plants, IGCC plants have the proven capability to remove sulphur to almost any extent required at low incremental cost and without producing gypsum. Consequently, the possibility exists to process high sulphur coal in an IGCC plant and still meet the emission standards at marginally higher cost.

- Potentially the overall thermal efficiency of IGCC power plants will tend to increase over the years mainly because of advances in gas turbine technology to be expected in the future.

- The availability of the IGCC power plant is estimated by Fluor Daniel for Netherlands circumstances to be of the same order of magnitude as for a conventional pulverized coal fired power plant. Since the gasification section of the plant can be "backed up" with natural gas, the total plant equivalent availability would be approximately that of the combined cycle portion of the IGCC.

- Phased construction option. Phased capacity addition is characterized by low capital investment and short construction periods for the early phases. Previous studies in the United States of America indicate that on an instantaneous basis the overall investment for a phased IGCC plant is about five percent more than for an "unphased" plant.

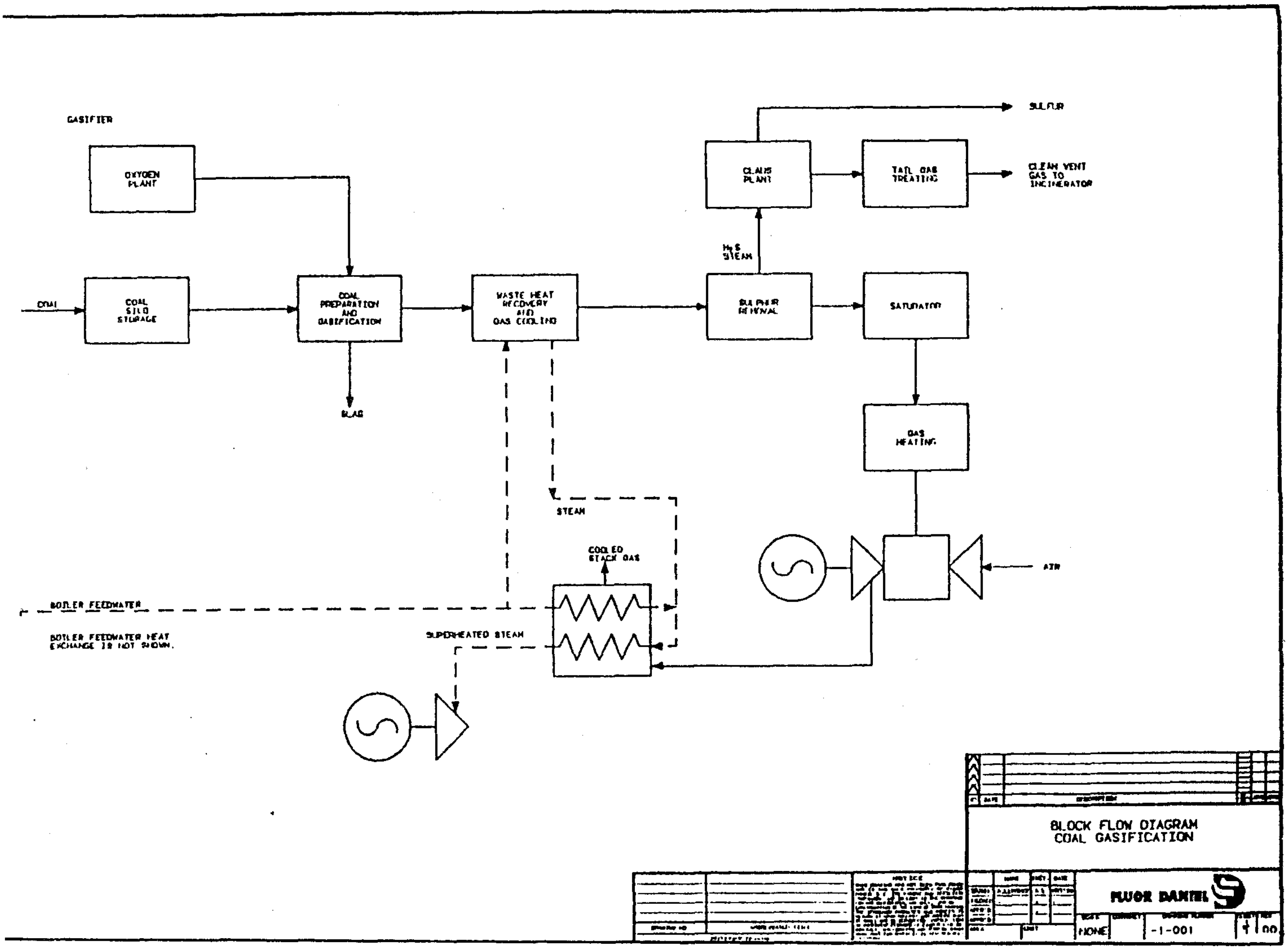


Figure 9.1: Block Flow Diagram Coal Gasification (IGCC Task Force, 1988)

Phased construction offers the possibility to build the gasificatiion section at a later moment. Also in a phased construction project, the earliest start is determined by the commercial availability of the advanced gas turbines.

9.2 Environmental Impacts and By-Products of IGCC Power Plants

Figure 9.2 gives an overview about possible effluents from an gasifier plant.

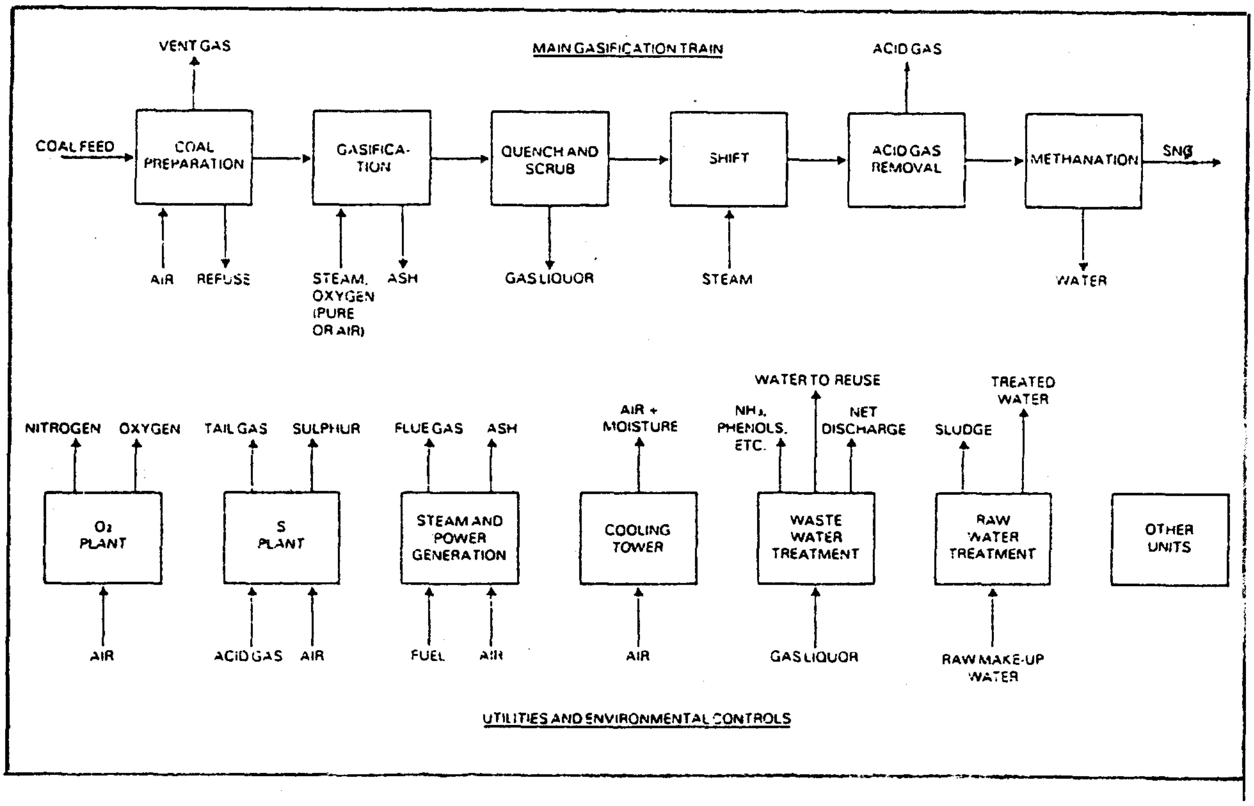


Figure 9.2: Flow Plan for Coal Gasification (Eriksson and Prior, 1979)

9.2.1 SO_2-Emissions

Sulphur contained in the coal will mainly be converted into H_2S in the gasification process. Next to H_2S a lesser amount of COS is formed. The COS formation is strongly dependent upon the gasification process, and can vary from 5 to 20 % of the total available sulphur. H_2S is removed from the raw gas by absorption in a selective solvent, stripped off from this solvent and then converted into elemental sulphur in the Claus sulphur recovery process. COS is, depending on the process, removed to a lesser extent by the absorption process and depending upon the degree of desulphurization required, hydrolysis of COS to H_2S may be required as an extra step.

The tail gas from the Claus process still contains small amounts of sulphur oxides which can be reduced to H_2S by several commercially proven processes, concentrated by means of absorption/stripping processes and recycled to the Claus unit for final sulphur recovery.

In practise the following processes for selective sulphur removal have been applied:

- Selexol^R process by Texaco
- Hot potassium carbonate and Rectisol^R processes by British Gas and Lurgi
- MDEA processes by Shell and Krupp Koppers.

These processes are easily capable of sulphur removal in excess of 99 %. High sulphur removal is currently demonstrated at the Cool Water IGCC plant, where sulphur removal rates over 98 % with high sulphur feedstocks have been demonstrated. It has been shown that virtually complete (down to below 1 ppm) sulphur removal from the fuel gas is achievable using the Rectisol process.

All these processes have in common that the gas from the gasification section must be cooled to about 35 - 45 ^{o}C. The gas is then routed upwards through an absorption column where entering from the top and leaving at the bottom the absorption liquid removes the H_2S and other sulphur compounds. The liquid from the bottom of the absorber is then sent to the top of a stripping column where the H_2S is stripped from the absorption liquid. The H_2S leaves the top of the stripper and in a suitably concentrated form to be used as feed gas in a sulphur recovery unit.

9.2.2 NO_x-Emissions

The gas turbines are the primary sources of NO_x emissions. Control of the formation of NO_x in the gas turbine combustion chamber is achieved by the injection of inert fluids, e.g. nitrogen, water or steam. This results in NO_x-emission levels below 135 g/GJ (300 mg/m^3, 6 % O_2), based on LHV of coal gas. With catalytic reduction, it is possible to reduce the emission of NO_x to 40 - 70 g/GJ (110 - 190 mg/m^3, 6 % O_2). It is expected that in the future emission levels can be achieved of 50 - 70 mg NO_x per GJ (140 - 190 mg/m^3, 6 % O_2) even without catalytic reduction.

British Gas/Lurgi based IGCC plants have a second source of NO_x emissions, the gas liquor incinerator. However, NO_x-emissions levels from this source result in an additional NO_x-emission of 2 % only.

9.2.3 Particulates Emissions

Particulate emissions are negligible (less than 2 mg/m^3 off-gas) due to the fact that practically all dust is removed in the raw gas cleaning section. Low particulate content of the fuel gas is also a must because of the gas turbine requirements.

Particulate emissions also occur from the coal feed system and the ash handling facilities. Water sprays, bag houses and covered conveyors can be used to control emissions from these facilities.

9.2.4 Liquid Effluents

Effluents from gasification processes can be complex mixtures. They need to be analyzed, not only to assess any potential market value of components or their heat value but also to assess the success of any stage of proposed effluent treatment. Typical analyses are shown in table 9.2 and 9.3. Table 9.4 shows an analysis of nitrogen compounds.

Further analyses are given within Eriksson and Prior (1979, Ahrabi (1988), Ebbins and Ruhl (1988). The effluents are very different, depending on

- the type of coal used
- the type of process used.

Table 9.2: Main Components of Aqueous Liquor from an British Gas HCOM Methanation Process (Ahrabi, 1988)

Component	Concentration (mg/l)
Free NH_3	550
Fixed NH_3	6500
Phenols	5500
Carbonates	7500
Thiocyanates	1000
Cyanides	100
Sulphides	3200
Nitrates	20
Hydantoins	220
COD	20000
TOC	5500
Chlorides	1000
Trace elements (total)	45

Table 9.3: Phenols in Aqueous Liquor > 20 mg/l (Shephard and Watkins, 1985)

Compound	Concentration (mg/l)
Phenol	5000
Cresols + ethylphenols	4400
Xylenols	700
Naphthols	20
Trimethylphenols	50
Quinol	30
Resorcinol	90
2-Methyl resorcinol	60
4-Methyl resorcinol	100
5-Methyl resorcinol	140
Catechol	270
3-Methyl catechol	130
4-Methyl catechol	100

Table 9.4: Analysis of Aqueous Liquor for Nitrogen Compounds (Shephard and Watkins, 1985)

Compound	Concentration (mg/l)
Aniline	105
Methyl aniline	35
Dimethyl aniline	8
Pyridine	210
2-Methyl pyridine	18
3- and 4-Methyl pyridine	30
Ethyl pyridine	5
Quinoline/isoquinoline	35
Methyl quinoline	5

Several methods of treating organic and inorganic constituents of effluent from the slagging gasifier have been and are under study, but the initial studies focused on a conventional route involving dephenolation, ammonia removal, biological treatment and polishing with active carbon. Laboratory studies have already shown that all the species of interest to date can be treated to a quality that could be accepted for discharge to all but top quality fishing water (IGCC Task Force, 1988). Some work in the USA on a gasification effluent containing similar types of compounds has shown that it can be treated successfully. Thus substantial progress has been made in treating such effluents in a conventional way.

There is every confidence that other approaches will provide viable alternatives. Incineration or catalytic wet air oxidation are other options for the disposal of effluent.

The liquid effluents to be treated are:

- Process condensate from gasification, ash handling, acid gas removal and tail gas treating
- Storm water run-off
- Utility waste water.

The main liquid waste stream is the process condensate. There are several methods to treat this waste stream. In general this stream will be treated in a process condensate treating unit designed to remove formates, sulphides, ultrafine ash particles, hydrogen cyanide and ammonia from the water using the following steps:

- Steam stripping
- Chemical addition with precipitation
- Filtration
- Settling   or incineration
- Bio treatment

The effluent water from the process condensate treating unit should be suitable for discharge or re-use. However, if salinity is too high for discharge, installation of an evaporator or a reverse osmosis installation should be considered. The resultant concentrated salts solution could be incinerated resulting in a solid, saltcake product, containing trace metals etc. for disposal.

Precipitate and biotreater sludge if produced can be combined with the ash cake for disposal. Ammonia and sulphur compounds (sour gas) stripped from the water are routed to the sulphur plant furnace.

In British Gas/Lurgi based IGCC plants the process condensate, which contains some organic material, is incinerated in the gas liquor incinerator, resulting in zero liquid effluent discharge. Alternatively the condensate can be treated by a biological oxidation route as described above.

Storm water run-off and utility waste water are subjected to clarification, bio treatment and deep bed filtration for oil removal.

9.2.5 Solid Effluents

Solid wastes can be put in the following four categories:

- Gasifier slag and fly ash (N.B. recycling of fly ash is expected to produce 100 % slag. Fixed bed reactors do not produce fly ash).
- Wastes from liquid effluent handling (waste sludge and incineration salts)
- By-product sulphur
- Process wastes (Tail Gas Treating, Claus and acid gas treatment wastes and demineralization plant regeneration waste).

Each waste/by-product will be discussed below.

9.2.5.1 Gasifier Slag and Fly Ash

During gasification, most of the mineral matter in the coal is converted into molten slag, which subsequently falls into a water quench chamber where it is solidified into a glassy slag. Gasifier slag is obtained as a frit. It is wet, from water granulation, typically containing 10 - 15 % moisture. Apparent particle density is 2.900 kg/m^3. The slag grains are irregularly shaped and fall within a narrow size range, 90 % less than 2.5 mm.

Gasifier slag consists of three major components, silica and alumina (derived from the minerals in coal) and lime (mainly from added flux) (see table 9.5). In this respect it is intermediate in composition between pulverized fly ash and blastfurnace slag, as indicated on the phase diagram, figure 9.3.

Table 9.5: Chemical Analysis of a Typical Gasifier Slag (wt %). Analysis Carried Out by X-Ray Fluorescence (fused bead) (Shepperd, 1984)

SiO_2	35
Al_2O_3	20 - 25
CaO	20 - 25
Fe_2O_3*)	15 - 20
MgO	1
Na_2O	1
K_2O	1
TiO_2	1
P_2O_5	0.3
SO_3	1
Gain on ignition (1025 °C)	2

*) Total Fe as Fe_2O_3: Fe 5 %, FeO 6 %, Fe_2O_3 < 1 %

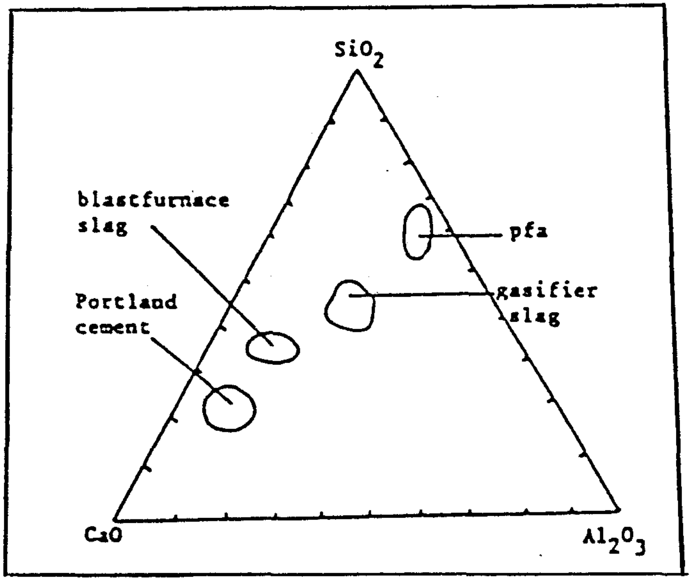


Figure 9.3: Location of Gasifier Slag in the SiO_2-Al_2O_3-CaO System (Shepperd, 1984)

Several potential uses for water granulated slag are currently under investigation. By far the most extensive study has been on its cementious properties and applications analogous to those for granulated blastfurnace slag and PFA. But gasifier slag presents an excellent oppurtunity to develop the technology and markets to suit an emerging product while there is still the chance to tailor both the chemical composition and physical form of that product (at least to some extent) to make it more valuable. Hence some more speculative uses are also being considered.

As slag contents up to 25 % Al_2O_3 it is an attractive potential source of alumina. A preliminary study has demonstrated a route for the recovery of alumina that is technically and economically feasible. Oxides of Ti, Fe and Mn can also be extracted.

The free iron in the slag is an obvious starting point. Tests have shown that this can be easily and efficiently removed by conventional magnetic separation equipment. This leaves a clean slag fraction (< 0.2 % iron) but the iron content of the magnetic fraction is generally only 50 - 80 %. Besides adhering slag, the iron itself may contain a percent or more of carbon, sulphur and phosphorus as well as certain trace metals (notably chromium, cobalt and nickel) which appear to concentrate in the iron.

Gasifier slag is a pozzolanic material, behaving essentially like PFA but with enhanced activity, presumably due to its higher lime content. Standard tests for pozzolanicity and strength development of mortar and concrete cubes have been carried out.

Grit blasting trials with gasifier slag have shown it to be as effective as conventional materials like chilled iron and copper slag. It is quite hard, but not as dense as non-ferrous slags and may be most suitable as a diluent for these materials.

A gasifier slag ceramic has been made by adding a nucleating agent to slag and carefully cooling the melt. The composition of the gasifier slag is close to the optimum and needs only slight adjustment. The material produced is extremely dense and highly resistent to abrasion, much like blast furnace slag ceramics.

Slag also appears to be a good medium for plant propagation; cuttings rapidly produce roots in what is essentially a sharp sand, and will grow on in slag provided some nutrients are added. Other uses being studied include concreting sand, glass fibres, decorative facing, and high temperature aggregate. The suitability of gasifier slag as a binder in road making (i.e. similar to the grave-laitier process with granulated blastfurnace slag) will also be investigated. Van der Sloot et al. (1988) gave a list of possible enduses for TCGP slag which can be found in table 9.6.

Table 9.6: Possible End Uses for TCGP Slag Studied in the EPRI Report (van der Sloot, de Groot and Wijkstra, 1988)

Agriculture
- Soil conditioner
- Acid-soil neutralizer
- Low grade fertilizer

Industrial materials
- Roofing granules
- Filter media
- Industrial fillers
- Sandblasting abrasives
- Mineral wool production

Cement and concrete
- Concrete aggregate
- Mortar/grouting material
- Pozzuolanic admixtures
- Raw material for Portland cement production
- Masonry unit production

Road construction and maintenance
- De-icing grit
- Fine aggregate for bituminous pavement
- Base aggregate
- Sub-base aggregate
- Seal-coat aggregate

Synthetic aggregate
- Lightweight construction aggregate
- Landscaping material
- Sand substitute

Landfill and soil stabilization
- Soil conditioner for improving stability
- Structural fill
- Embankment material

Resource recovery
- Source of carbon
- Source of magnetite
- Source of iron, aluminium and other metals

In the Texaco process practically all the fly ash entrained in the raw gas is captured in the gas scrubbing unit. The ash slurry from the slag quench chamber and the fly ash slurry produced in the gas scrubbing unit flow to the ash dewatering unit. The slurry is clarified and filtered to yield gasifier slag, ash cake and water. The gasifier slag and the ash cake are transported to off-site storage.

In the British Gas/Lurgi (BGL) process virtually all the dust and tar entrained in the raw gas is captured in the gas liquor separation unit and recycled to the gasifier, so that the ash present in the feed coal ends up in the slag. The slag is de-watered and transported to off-site storage. No fly ash is produced.

In the Shell process and the PRENFLO process the bulk of the fly ash entrained in the raw gas is captured in the dry fly ash separators. The removed fly ash is mixed with precipitate cake and biotreater sludge and transported to off-site storage. Any residual fly ash in the raw gas is removed to a level of less than 1 mg/m^3 by water scrubbing. The blowdown stream from the wet scrubbing unit is withdrawn to the liquid effluent treating system. Slag is dewatered and transported to off-site storage.

In Sweden, residual products from a Japanese Texaco coal gasifier have been investigated. The chemical composition is shown in table 9.7. There is an uncertainty regarding the mercury analysis. A comparison of the metal contents in the slag and the aqueous paste showed that there was no great difference between them for this plant.

Very few leaching tests on coal gasification products have been made. The results are not conclusive as to whether the slag from coal gasification is better or worse than bottom ash from grate firing. The concentrations of heavy metals is higher in leachate from aqueous paste than from slag (Hartlen et al., 1989).

Slag from the Japanese Texaco gasifier was regarded suitable for use as a friction material (sand) and may be used for fillings, road construction and house foundations. The potential environmental impact has to be judged, and special care should be taken when the slag is used in ground water.

The aqueous paste was not considered usable (Hartlen et al., 1989).

Table 9.7: Chemical Composition of Slag and Aqueous Paste (mg/kg) (Hartlen et al., 1989)

Element	Slag	Aqueous Paste
As	< 10	47
Cd	5	5
Co	0	34
Cr	547	359
Cu	114	176
Hg	0.02	0.02
Mo	33	16
Ni	53	71
Pb	20	107
V	146	185
Zn	21	149

Leaching tests had been conducted on slag from a BGL-gasifier. For the purposes of leaching tests the slag was separated into three portions whole slag, the iron fraction and separated slag (whole slag less the iron fraction).

Four leaching tests (see Annex I) were performed on each slag protion, these were:

1) American Society for Testing and Materials Method A (ASTMA)
2) American Society for Testing and Materials Method B (ASTMB)
3) Carbonic Acid Extractions (CAE)
4) Modified Environmental Protection Agency Extraction Agency Procedure (EPMOD).

A comparison of the leachate concentrations and the US Resource Conservation and Recovery Acts (RCRA) guidelines and other guidelines derived from the US Secondary Drinking Water Standards, Irrigation Water Standards (IW) and EEC Drinking Water Maximum Advisable Concentrations (MAC) is given in table 9.8.

From table 9.8 it may be seen that the leachate concentrations are well below the FRG legal guidelines with the exception of iron.

Table 9.8: Comparison of Legal Guidelines and Maximum Leachate Concentrations (Ebbins and Ruhl, 1988)

Element	Standard	Limit Value (mg/l)	Maximum Concentration in Lechate (mg/l)		
			Whole Slag	Separated Slag	Iron Fraction
Arsenic	RCRAx100	5.0	0.003*	0.0036**	0.00063**
Barium		100.0	0.402*	0.265*	0.115*
Cadmium		1.0	0.0015*	0.0033**	-
Chromium		5.0	0.053+	0.019**	0.031**
Lead		5.0	0.0068*	0.018**	0.0082**
Mercury		0.2	-	0.0013++	-
Selenium		1.0	-	0.007*	0.009**
Silver		5.0	0.001**	0.0036**	0.0006**
Copper	SDWx100	100.0	0.83++	1.16+	0.25++
Iron		30.0	1803.5	411.1*	1370**
Manganese		5.0	2.06*	0.49*	2.81**
Zinc		500.0	0.11*	0.098*	0.102**
Aluminium	IWx100	200.0	2.1+	14.8*	0.053**
Berylium		5.0	-	0.001	-
Boron		20.0	1.07+	0.564+	4.02++
Cobalt		50.0	0.025*	0.069*	0.032**
Molybdenum		0.5	0.0031*	0.0016**	0.013**
Nickel		20.0	0.075*	0.30*	0.047**
Sodium	EECx100	15000.0	1.35++	0.62+	1.48++
Potassium		1200.0	2.02*	4.46*	1.22++
Antimony		1000.0	0.011++	-	0.044++

-	not detected
*	concentration as determined by ASTMB test
+	concentration as determined by ASTMB test
**	concentration as determined by EPMOD test
++	concentration as determined by CAE test

9.2.5.2 Wastes from Liquid Effluent Handling

Wastes from liquid effluent handling systems are generated on a regular basis. The charateristics and quantities of these wastes are dependent on feedstock properties and used technology. Table 9.9 summarizes the possiblities of three considered processes for liquid effluent handling.

Low-volume waste sludge streams contain considerable amounts of toxic trace elements. The sludge could be incincerated.

Incineration (like the Lurgi process; Ahrabi, 1988) leads to the generation of incineration salts. This residue contains highly soluble components which necessitates careful, dry disposal of the material. This waste represents a risk of ground water contamination due to its high solubility and is subject to special disposal in a dry area.

However, the waste (arising mainly from the chlorides which are present in the coal) is invariably produced and must be discharged either as a solid salt as above or in solution in the treated waste water (IGCC Task Force, 1988).

Table 9.9: Summary of the Results of the Comparison of the Incineration Process by Lurgi, the Catalytic Wet Air Oxidation Process (CWAO) and a Conventional Effluent Treatment Route (Ahrabi, 1988)

Lurgi Incineration	CWAO	Conventional Route	
Atmospheric discharges	Dissolved gases to Claus plant and no hydrocarbons, NO$_x$ and SO$_x$ produced in the flue gas	Dissolved gases oxidized to base chemicals and no NO$_x$ or SO$_x$ produced	The stripped gases to Claus plant
Water discharges	None	Saline effluent with trace metals, not suitable for river discharge	Saline effluent with trace metals, not suitable for river discharge
Process for further treatment of water	None	Reverse osmosis to produce a permeate for re-use	Reverse osmosis to produce a permeate for re-use
Secondary effluent	(1) Salt cake	(1) Concentrate	(1) Concentrate (2) Wasted sludge
Process for further treatment of secondary effluent	None	Evaporation	Evaporation of RO concentrate
Final secondary effluent for disposal	(1) Salt cake	(1) Salt cake	(1) Salt cake (2) Wasted sludge
Disadvantages running costs	(1) High capital and used as catalyst (2) Evaporation of water in the effluent	(1) Rare metal is process upsets (2) High running cost with no process integration	(1) BIOX prone to (2) High capital cost (3) Several process steps
Advantages	(1) Limits for discharge met, no further processing required	(1) Single process step to remove the bulk of contaminants	(1) Proven technology (2) Low running cost (3) By-products for re-sale, e.g. phenols

9.2.5.3 Sulphur

High purity (99.5 %) sulphur is recovered in the Claus sulphur recovery process. This by-product is not considered a waste, but has a certain market value as a raw material for sulphuric acid production.

9.2.5.4 Process Wastes

Process units generate intermittent low-volume waste streams. The Claus and Tail Gas Treating units periodically require new catalysts.

The spent catalysts require reclaiming by the manufacturers or disposal. Some of the acid gas treatment units and the tail gas units require periodic solvent blowdown. These streams are hazardous and can best be disposed of by incineration or at the process condensate treating unit. The Rectisol process does not require solvent blowdown.

Demineralizer regeneration wastes are hazardous due to their corrosive nature and should be neutralized before leaving the demineralizer.

10 BY PRODUCTS FROM MUNICIPAL WASTE COMBUSTION

10.1 Flue Gas Treatment of Municipal Waste Combustion

The processes for flue gas treatment of municipal waste combustion can be divided in three different methods (just like processes for FGD) characterizing the physical condition of the reagents:

* Wet processes: Reactant is a washing solution, the untreated reaction products are wet. Special regard must be emphasized on waste water treatment.

* Quasi-dry processes: The washing solution is injected by special jets into the flue gas where it vaporizes. The dry reaction products are precipitated.

* Dry processes: The dry reagent is added to the flue gas. A dry reaction product is formed.

The air pollutants, e.g. HCl, HF, SO_2, particulates containing heavy metals and organic substances are separated from the flue gas. In general the main part of the particulates are precipitated before these processes by electrostatic precipitators.

A flow sheet of an Austrian waste incineration plant is given in figure 10.1.

Although a prognosis for the amounts of by-products or wastes from waste combustion plants is hard to be made (because of the uncertain number of plants to be built as well as future legal emission limits), table 10.1. give rough data for a prognosis.

Table 10.1: Actual Data and Rough Calculations for the Year 2000 of By-Products and Wastes from Municipal Waste Combustion Plants. The Prognosis does not Include Possible Changes of the Heating Value of the Municipal Waste. Amounts are Given in Metric Tons.

Country	Amount	Year	Proposed Data for 2000
Austria	135.000	1989	200.000
Canada	320.000	1986/87	750.000
Federal Republic of Germany	3.160.000	1989	4.500.000
Finland	20.000	1987	> 20.000
France	2.000.000	1989	> 2.000.000
Italy	1.000.000	1989	1.250.000
Netherlands	1.000.000	1988	2.000.000
Sweden	460.000	1989	450.000
Switzerland	646.000	1987	678.000
United Kingdom	965.000	1989	> 1.000.000
USA	5.500.000	1987	5.500.000

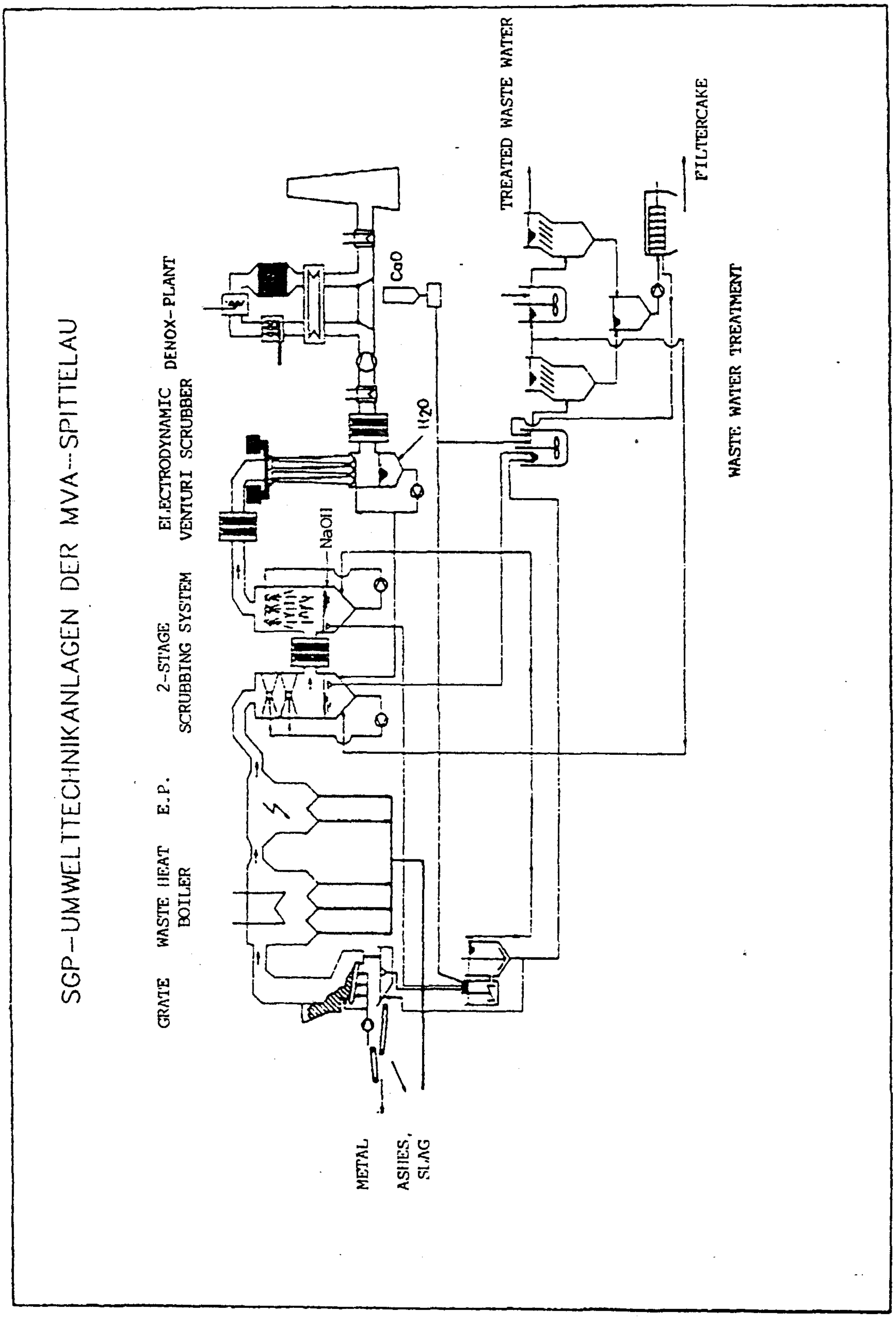


Figure 10.1: Flow Sheet of an Austrian Waste Incineration Plant with Integrated FGD and $DeNO_x$ (SGP, 1990)

10.1.1 Wet Processes

The flue gas is treated with a washing solution. A mass-transport of the air pollutants from the gas phase to the liquid phase takes place, the gas is absorbed. The efficiency of absorption depends upon different factors:

* availability of active surface of exchange
* fluid dynamic parameters of mass-transfer
* chemical reaction in the liquid phase
* retention time
* selection of the washing solution.

Usually particulates are separated before the wet cleaning processes which reduces the volume of the residues of the wet flue gas treatment.

Wet processes for the flue gas treatment of municipal waste combustion plants usually operate in two steps. In the first step (first washer) mainly HCl and HF are absorbed at low pH-range (from 0.5 to 1.5). For the absorption of SO_2 a second step (second washer) must be installed. In the second step SO_2-absorbtion takes place at pH-values from 3.5 - 5. As neutralization medium generally calcium carbonate, calcium hydroxide or sodium hydroxide is used.

10.1.2 Quasi-Dry Processes

For the quasi-dry flue gas treatment the so-called spray absorption is applied. The main characteristic is the vaporizing of water from the washing solution in the flue gas in order to get dry products. The washing solution is dispersed with jets into the flue gas.

The additive reacts with the acidic flue gas compounds such as HCl, HF, SO_2, SO_3 and CO_2. Dry neutral salts are produced.

Inert particles are precipitated before the reaction tower. The dry reaction products are separated after the reaction tower.

All quasi-dry cleaning system are operating with an excess of neutralization agent. Depending on the boundary conditions the stoichiometric factor is between 1.5 to 4.

10.1.3 Dry Processes

Using dry processes the air pollutants are adsorbed by the reagent. The dry reagent is added into the flue gas. In some cases the flue gas is conditioned by injected water.

The dry processes operate also with stoichiometric excess.

10.2 Mass-Flow and Residue-Flow of Municipal Waste Combustion

The original motive for municipal waste combustion is the reduction of waste volume using its calorific value. The nature and properties of the residues vary with the type of combustion.

Residues from municipial waste combustion may be divided into the following main types:

* bottom ash
* particulates or fly ash
* residues from the flue gas treatment.

Depending on the composition of the municipal waste and the working condition of the plant following amounts of residues are obtained per ton of burnt waste:

200 - 450 kg	bottom ash
40 - 70 kg	fly ash
5 - 15 kg	residues from the wet flue gas treatment.

As an example for the quantity of produced by-products per ton waste, figures of the municipal waste combustion plant in Vienna (Flötzersteig) are given:

330 kg	slag
30 kg	fly ash
15 kg	residues from the wet flue gas treatment.

Analyses of the discharges from waste incinerators show that the inorganic substances are bound to the bottom ash, fly ash of the electrostatic precipitator; residues from the flue gas treatment process and in the clean gas. If combustion is complete, organic substances are transformed to carbon dioxide and water. Incomplete combustion results in the emission of hydrocarbons (e.g. polyaromatic hydrocarbons), carbon monoxide, carbon and reaction products with anorganic compounds, e.g. dioxins and furans.

Inorganic compounds such as metal oxides and salts are primarily found in the bottom ash, fly ash and in residues from the flue gas cleaning.

The different main components of waste are transfered in the following way:

* Carbon is transfered to the gas phase as carbon dioxide and carbon monoxide.
* 80 - 90 % of the chlorine contents of waste converts to hydrochloric acid and metal chlorides. The rest is bound to the bottom ash.
* 10 - 15 % of the fluorine contents is emitted as hydrogen fluoride.
* About 90 % of the mercury is emitted as mercury vapor.
* Iron and copper remain in the bottom ash (Bundesamt für Umweltschutz, 1987)

Approximately 50 % of the content of lead, cadmium and zinc vaporizes. During cooling and cleaning of the flue gas these elements are precipitated on the fly ash in the electrostatic precipitator.

The numerous organic substances have very complex properties. So there is little knowledge about their mass flow.

The separated organic substances are mainly found in the fly ash and the residues from the secondary treatment process due to its adsorption on the inorganic residues.

Referring to literature (Bundesamt für Umweltschutz, 1987; Thomé-Kozmiensky, 1985; Hagenmaier and Kraft, 1986; Hutzinger and Karasek, 1986) during municipal waste combustion radicals are created in reducing zones with insufficient oxygen. During cooling in the electrostatic precipitator these radicals recombine to aromatic compounds such as benzol and phenol (Lustenhower, Olie and Hutzinger, 1980). These substances react with free chlorine to chlorobenzene and chlorophenol. The metal oxides in the fly ash are thought to catalyze reactions to dioxins, furans and to aromatic compounds. Therefore the concentration of toxic organic substances in fly ash is very high compared with the bottom ash. Table 10.2 shows the analysis of PCDD and PCDF of the fly ash from a municipal waste combustion in Vienna named "Flötzersteig" from 1983.

Investigations of polychlorinated dioxins in Swedish municipal waste incinerators gave values of estimated dioxine contents around 5 g TCDD equivalents (according to Eadon) per 1000 tons of fly ash, and 1 g TCDD equivalents per 10000 tons of bottom ash (Swedish Environmental Protection Board/National Swedish Energy Administration, 1986). No leaching of dioxins or dibenzofurans has been recorded from any of the products, despite very low detection limits (approx. 1 - 10 pg/l). Nor has it been possible to demonstrate any leaching of other organic material. The leaching tests were performed as column tests with melted snow (Hartlen and Elander, 1986).

Table 10.2: Contents of PCDD and PCDF in the Fly Ash (Löffler, 1986)

Fly Ash	(µg/kg)
T4CDD	38.6
P5CDD	98.6
H6CDD	281.0
H7CDD	508.0
O8CDD	1243.6
total	2169.8
T4CDF	27.0
P5CDF	64.7
H6CDF	147.3
H7CDF	182.2
O8CDF	152.3
total	573.5

The volatile metal oxides, metal halides and gaseous compounds such as hydrochloric acid must be separated by different cleaning processes mentioned above. Depending on the applied flue gas treatment process, wet or dry residues are obtained.

Table 10.3: Pollutants in Solid By-Products from Municipal Waste Incineration in Switzerland (Bundesamt für Umweltschutz, 1987)

Element	Municipal Waste		Slag		Fly Ash		Slime from FG-Washing	
	content (ppm)	amount (t/a)	content (g/kg)	amount (t/a)	content (g/kg)	amount (t/a)	content (g/kg)	amount (t/a)
Chloride	8000	20000	2.8	1680	55	2200	5 1)	30
Pb	500	1250	1.3	780	7.7	308	3	18
Cd	10	25	0.01	6	0.5	20	0.1	0.6
Hg	4	10	0.0002	0.12	0.02	0.8	1	6
Zn	1500	3750	2.8	1680	26	1040	8	48
Cu	400	1000	1.6	960	1.5	60	0.3	1.8

1) depending on type of washing system

10.3 Characterization of the Residues from Municipal Waste Combustion

10.3.1 Bottom Ash

The main components in the bottom ash are amorphous material such as silicates, oxides, metals and unburnt waste. High contents of chlorides may also occur. The principal chemical composition is shown in figure 10.2.

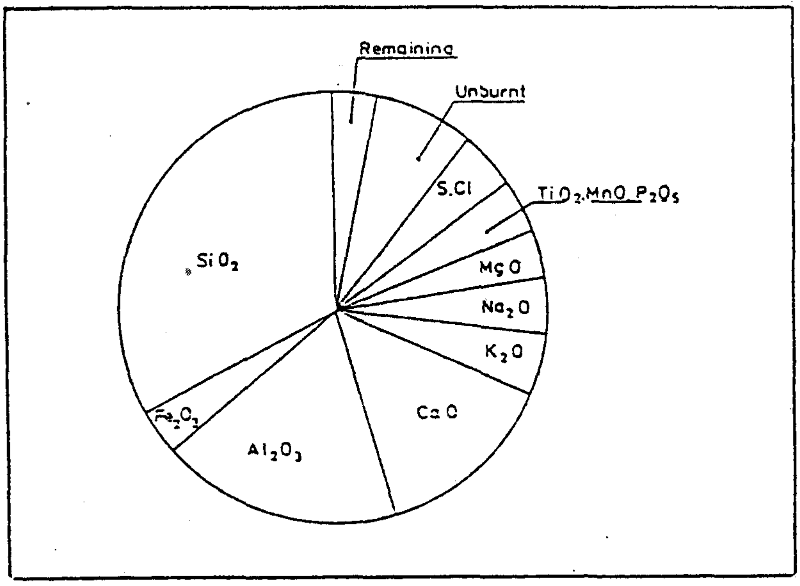


Figure 10.2: Principal Chemical Composition of Bottom Ash (Ahrtlen and Elander, 1986)

Potential environmental impacts by leachable substances such as heavy metals and also organic compounds must be taken into account before utilization of bottom ash. Chlorides and sulphates of heavy metals, sodium and calcium are highly soluble salts.

Table 10.4: Composition of Bottom Ash from the Municipal Waste Incineration Plant Horgen (single measurement) (Bundesamt für Umweltschutz, 1987) and 6 Swedish MSWIs (Ahrtlen and Elander, 1986)

Element	Content in % Bottom Ash	
	Bundesamt für Umweltschutz, 1987	Ahrtlen and Elander, 1986
Si (as SiO_2)	41.0	49.8 - 60.0
CaO	11.0	11.0 - 13.6
Al	4.6	11.2 - 13.6 (as Al_2O_3)
Fe	4.6	5.3 - 7.0
total carbon, as C	3.3	3.0 - 4.9
carbonate, as C	0.93	-
Na	0.9	4.8 - 6.9 (as Na_2O)
Mg	0.7	2.1 - 3.2 (as MgO)
K	0.5	1.6 - 2.7 (as K_2O)
Zn	0.3	-
Cu	0.3	
total sulphur, as S	0.3	0.2 - 0.8
sulphate, as S	0.22	
chloride	0.28	0.3 - 0.9
Ba	0.1	
Mn	0.1	< 0.1 - 0.2 (as MnO)
Pb	0.09	
Cr	0.08	
Sn	0.03	
Ni	0.02	
Cd	less than 0.01	

Table 10.5: Contents of Trace Elements in the Bottom Ash (Ahrtlen and Elander, 1986) from 6 Swedish MSWIs

Element	Bottom Ash (mg/kg)
Arsenic (As)	20 - 80
Barium (Ba)	900 - 1600
Lead (Pb)	1300 - 5400
Cadmium (Cd)	4 - 40
Cobalt (Co)	< 10 - 40
Copper (Cu)	900 - 3200
Chromium (Cr)	300 - 600
Mercury (Hg)	< 0,01 - 3
Molybdenum (Mb)	20 - 40
Nickel (Ni)	60 - 160
Strontium (Sr)	190 - 350
Tin (Sn)	< 100 - 1300
Thorium (Th)	70 - 300
Vanadium (V)	50 - 90
Wolfram (W)	< 20 - 50
Zinc (Zn)	1800 - 5900

Table 10.5 records the contents of trace elements in the bottom ash.

The heavy metal contents are lower in bottom ash than in particulates. But if attention is paid to the fact that the volume of bottom ash is about ten times greater than the volume of particulates, many heavy metals will be found to be predominant in bottom ash.

In the case of cadmium more than 50 % is found in the bottom ash, despite the fact that cadmium is regarded as comparatively volatile. On the other hand, by far the largest part of the mercury is captured in the flue gas treatment stage. However, even highly volatile mercury is captured to a large extent in the bottom ash. This may be due to batteries and other material having such durability that mercury in them is never released.

Studies show a concentration of dioxins and furans (PCDD/PCDF) in the bottom ash in the range of 5 ppb (Pietrzeniuk, 1985). In the bottom ash of a municipal waste incinerator Vienna ("Flötzersteig"), dioxines and furans were not found. Results of an investigation in the Federal Republic of Germany (Bundesamt für Umweltschutz, 1987; Hagenmaier and Kraft, 1986) about the contents of PCDD and PCDF and other harmful substances in slags and boiler ashes are shown in tables 10.6, 10.7 and 10.8.

Table 10.6: PCDD- and PCDF-Concentration in the Bottom Ash (Hagenmaier and Kraft, 1986)

	Bottom Ash (ng/g)
2,3,7,8-TCDD	< 0.02
Total Tetra-CDD	0.1
Total Penta-CDD	0.3
Total Hexa-CDD	0.3
Total Hepta-CDD	0.6
Octa-CDD	1.0
Total Tetra-CDF	0.5
Total Penta-CDF	0.4
Total Hexa-CDF	0.4
Total Hepta-CDF	0.3
Octa-CDF	0.1

Table 10.7: Concentration of Heavy Metals and Chloride in the Bottom Ash (mg/kg) (Thomé-Kozmiensky, 1985)

		minimum	maximum	mean
Cadmium	Cd	< 5	11	< 5
Chromium	Cr	1100	12000	5700
Copper	Cu	2200	7000	3500
Nickel	Ni	900	4300	2000
Lead	Pb	< 100	600	230
Zinc	Zn	800	7600	2550
Chloride	Cl	800	16000	4350

Table 10.8: Concentration of Heavy Metals and Chloride in the Boiler Ash (mg/kg) (Thomé-Kozmiensky, 1985)

		minimum	maximum	mean
Cadmium	Cd	220	680	440
Chromium	Cr	1300	3100	2250
Copper	Cu	2600	9800	5550
Nickel	Ni	2200	4100	2550
Lead	Pb	29000	95000	54300
Zinc	Zn	17000	34000	23500
Chloride	Cl	8000	24000	16500

10.3.2 Fly Ash

The main components of the fly ash are similar to those in the bottom ash (Figure 10.2). These components are silicates, oxides, metals and unburnt waste, too. Figure 10.3 shows the principal chemical composition of fly ash.

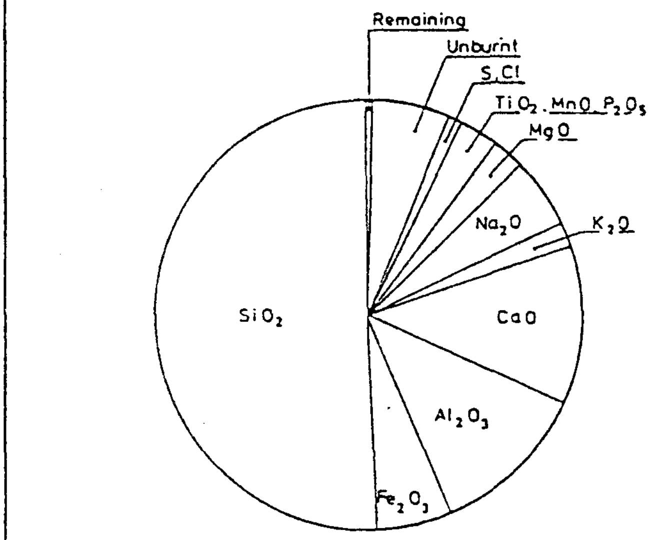


Figure 10.3: Principal Chemical Composition of Fly Ash (Hartlen and Elander, 1986)

10.3.3 Inorganic Compounds

The volatile heavy metals from municipal waste combustion are concentrated in the flue gas and the particulates. The chemical behaviour of the heavy metals determines the distribution rate between flue gas and bottom ash, respectively gas and particulates. The volatile metals and their compounds such as mercury, cadmium, zinc, lead and their chlorides are vaporized at a temperature between 800 °C to 1.100 °C (Bundesamt für Umweltschutz, 1987). By cooling of the untreated flue gas the particulates are acting as condensation nuclei. Therefore high concentration of cadmium, lead and zinc chlorides and sulphates are found in the particulates.

Table 10.9 shows the contents of trace elements in fly ash.

Table 10.9: Contents of Trace Elements in Fly ash from 6 Swedish MSWIs (Hartlen and Elander, 1986)

Element	Fly Ash (mg/kg)
Arsenic (As)	40 - 140
Barium (Ba)	870 - 2300
Lead (Pb)	1200 - 3600
Cadmium (Cd)	0.3 - 110
Cobalt (Co)	< 10 - 15
Copper (Cu)	700 - 5000
Chromium (Cr)	260 - 2400
Mercury (Hg)	2 - 40
Molybdenum (Mb)	15 - 50
Nickel (Ni)	80 - 200
Strontium (Sr)	270 - 550
Tin (Sn)	< 100 - 810
Thorium (Th)	80 - 180
Vanadium (V)	60 - 110
Wolfram (W)	< 20 - 90
Zinc (Zn)	2500 - 14000

Table 10.10 shows the result of an analysis of the fly ash from the two municipal waste combustion plants in Vienna.

Table 10.10: Fly Ash from Two Municipal Waste Combustion Plants in Vienna (Fuchs, 1985)

	Flötzersteig	Spittelau
SO_3 %	12.69	11.86
Loss at red heat %	6.0	6.5
Pb (mg/kg)	2300	2200
Zn	10250	10010
Ni	220	136
Hg	4	5
Cr	243	175
Cu	298	330
Sb	35.7	37.2
Cd	176	129
Sr	680	356
Co	43	30

The results of examinations of fly ash and their leaching behaviour are listed in table 10.11. It can be seen that lead, cadmium and zinc are highly soluble with solubility increasing at lower pH-values.

Table 10.11: Analysis of Fly Ash and their Leaching Behaviour (Thomé-Kozmiensky, 1985)

Designation	Total Concentration		Leachate	DEV S4
	Mean	Variation	H_2O	pH = 4
mg/kg TS	mg/kg TS	mg/l	mg/l	
1	2	3	4	5
pH-value	11.7	11.5 - 12.4	11.7	4
Loss at red heat	2.5	0.95 - 3.7	-	-
BSB	20	-	-	-
CSB	(1250)	1020 - 1450	-	-
Cl-	40200	17570 - 43000	4000	-
SO_4	42800	20980 - 94000	2480	-
F-	180	60 - 310	6.5	-
NO_3	510	480 - 550	0.2	-
Pb	5250	4140 - 6340	3.2	4.3
Cd	325	100 - 486	0.05	28.1
Zn	15325	9000 - 21250	1.5	753
Ni	140	74 - 302	0.04	0.61
Hg	3.9	1.4 - 18.9	0.0018	0.0015
Cr	207	154 - 279	0.043	0.057
Cu	1105	738 - 1530	0.053	2.59
Ti	0.8	0.21 - 1.6	0.02	-
Sb	(672)	290; 1054	-	-
Ag	(40)	31; 50	-	-
Br	(175)	50; 305	-	-
Se	(17)	17	-	-
Co	(38)	38	-	-
Fe	(30500)	28000; 33000	-	-

Table 10.12: Leaching of Heavy Metals out of ESP Fly Ash in Dependence of pH-Value and Time (Bundesamt für Umweltschutz, 1987)

Element	Total Eluted Mass (g/kg) at						
	pH	1	4	7.0	7.8	9.5	max. leachable
	24 h	0.25 h	0.25 h	8 h	8 h	8 h	°/oo x)
Cn	400	182	117.6	0.6	0.6	0.6	706
Cr	4	n.	1.0	3.0	2.0	2.0	200
Fe	4	21	0.04	0.24	0.04	0.04	600
Cd	925	750	925	750	275	7.5	925
Hg	n.	n.	n.	n.	n.	n.	n.a.
Pb	73	67	4.2	4.2	0.67	0.25	667
Zn	694	167	556	111	0.194	0.06	694

n. ..... not found
n.a. ..... not analyzed
x) by leaching with kingswater (Aqua-Regia)

10.3.4 Main Organic Compounds

It is known that in zones of low temperature and low turbulence incomplete combustion occurs resulting in the formation in trace quantities of many (over 300) complex organic compounds such as PAH, etc. Many of those, in addition to their basic toxicity, combine with the ever present chlorine to form more highly toxic compounds such as chlorophenols. These conditions can occur in most incinerators, particulary during start up and shut down. Volatile organic substances can be found in the residues of the flue gas treatment. Tables 10.13, 10.14 and 10.15 show the contents of organic toxic substances in the fly ash.

Table 10.13: Contents of Chlorophenols in the Fly ash of the Electrostatic Precipitator (Bundesamt für Umweltschutz, 1987)

CHLOROPHENOL	QUANTITY (µg/kg, ppb)
2,4,6-Trichlorophenol	trace (about 10 ppb)
2,3,4,6-Tetrachlorophenol	250
Pentachlorophenol	400
TOTAL CHLOROPHENOL	660

Table 10.14: Contents of Chlorobenzols in the Fly Ash of the Electrostatic Precipitator (Bundesamt für Umweltschutz, 1987)

CHLOROBENZOL	QUANTITY (µg/kg, ppb)
Trichlorobenzol	trace (about 10 ppb)
Tetrachlorobenzol	180
Pentachlorobenzol	335
Hexachlorobenzol	375
TOTAL CHLOROBENZOL	910

Table 10.15: Contents of PCDD and PCDF in the Fly Ash of the Electrostatic Precipitator (Bundesamt für Umweltschutz, 1987)

	CHLOR-DIBENZO-p-DIOXIN (µg/kg, ppb)	CHLOR-DIBENZO-FURAN (µg/kg, ppb)
Tetra-	1.4	10
Penta-	4	27
Hexa-	18	28
Hepta-	77	77
Octa-	710	120

10.4 Residues from Flue Gas Treatment

10.4.1 Residues from the Wet Flue Gas Treatment

Heavy metals and gaseous compounds such as HCl or SO_2 are washed out by the wet process. The sludge from the washing process mainly consists of calcium sulphate, carbonates and heavy metals. Separated chlorides are emitted in the waste water.

The organic substances are also reduced by the flue gas treatment and are found in the residues and in the waste water. It is possible to eliminate about 80 % chlorophenols from water by precipitation (Bundesamt für Umweltschutz, 1987)

The very acidic waste water produced by the washing process contains a high concentration of dissolved salts and heavy metals, especially mercury, cadmium and nickel. Additional treatment is necessary to reduce the toxicity of this waste water before discharge to the environment.

By adding a neutralization agent such as lime (water), sodium hydroxide or sodium carbonate the main part of heavy metals in the waste water is precipitated as hydroxides or carbonates. The efficiency of precipitation of mercury, nickel and cadmium is very little by using the neutralization agents mentioned above and it decreases with the increase of the contents of chloride. Using this method only 40 % of mercury and 70 % of cadmium are bound in the neutralization sludge (Thomé-Kozmiensky, 1985). The other heavy metals are precipitated up to 90 %.

In order to increase the efficiency of precipitation of mercury, zinc and cadmium hydrogen sulphide or sodium sulphide can be added. But these agents are highly toxic and the resulting sulphide floc is difficult to separate. In general this method is not used.

However, nowadays a substance called TMT 15 (Trimercapto-s-triazin, $C_3H_3N_3S_3$) is used as precipitating agent, especially for mercury, nickel and cadmium. Therefore it becomes possible to separate these heavy metals also up to 90 % from the waste water.

Table 10.16 shows the results from an examination of sludge from the wet flue gas treatment.

After neutralization and precipitation of heavy metals the amount of about 20 % of chlorophenols are in the waste water (Bundesamt für Umweltschutz, 1987).

Table 10.17 gives the results of the analysis of the pressed and dewatered filter cake from the municipal waste combustion plant "Flötzersteig" in Vienna.

Table 10.16: Examination of Residues from the Wet Flue Gas Treatment (Thomé-Kozmiensky, 1985)

Designation	Total Concentration		Leachate	DEV-S4
	Mean	Variation	H_2O	pH = 4
	mg/kg TS	mg/kg TS	mg/l	mg/l
1	2	3	4	5
pH-value	9.7	9.4 - 9.9	7.5	4
Loss at red heat	-	-	-	-
BSB	(40)	20; 60	-	-
CSB	(450)	340; 550	-	-
Cl-	166000	156000 - 174000	8670	-
SO^2-	4100	2590 - 5550	253	-
F-4	(40)	40	4.8	-
NO_3-	900	810 - 960	86	-
Pb_3	2785	2020 - 3490	0.21	2.2
Cd	170	140 - 360	0.035	7.4
Zn	6400	5080 - 8800	0.04	175
Ni	835	430 - 1650	0.019	4.08
Hg	1900	1320 - 2975	0.0012	0.0018
Cr	186	104 - 332	0.006	0.04
Cu	385	320 - 450	0.006	0.66
Ti	0.45	0.25 - 0.62	n.n.	n.n.
Sb	(730)	730	-	-
Ag	(9)	9	-	-
Br	(120)	120	-	-
Se	(120)	120	n.d.	n.d.
Fe	(31000)	31000	-	-

n.d. ...... not detectable

Table 10.17: Analysis of the Pressed and Dewatered Filter Cake from the Municipal Waste Combustion Plant "Flötzersteig" in Vienna (Wruss, 1986a)

Filtercake 4 Elementary Analysis	Air-Dried	105° Dried	Dim.
	HNO_3-Disintegration		
pH-value	n.a.	n.a.	n.a.
conductivity	n.a.	n.a.	n.a.
dry substance	50.8	42.2	%
insoluble residue (HNO_3-disintegration)	39.3	37.9	%
soluble in HNO_3	60.7	62.1	%
Polyc. Ar. (PAK)	n.a.	-	-
Phenols	n.a.	-	-
Hydrocarbons	n.a.	-	-
CSB	n.a.	-	-
Antimony	5.00	0.10	mg/kg
Arsenic	11.98	8.99	"
Barium	290.3	318.4	"
Beryllium	2.60	3.15	"
Lead	6512.9	7067.5	"
Boron	20.57	23.46	"
Cadmium	358.7	411.4	"
Chromium total	225.5	283.3	"
Iron (soluble)	12.141	14.012	"
Cobalt	20.39	22.95	"
Copper	899.7	1062.8	"
Manganese	604.3	724.9	"
Nickel	62.18	70.80	"
Mercury	459.4	444.3	"
Selenium	3.50	3.99	"
Silver	17.44	22.57	"
Thallium	1.60	2.20	"
Vanadium	44.25	54.46	"
Zinc	15000	16738	"
Tin	124.8	109.8	"
Calcium	100733	122610	"
Magnesium	13228	14870	"
Strontium	170.4	176.6	"
	soda extraction		
TS	50.8	42.2	"
Fluoride	3353	3666	"
Chloride	8575	9075	"
Cyanide total	7.48	0.47	"
Rhodanide*)	54.08	50.07	"
Sulphide	676.0	604.7	"
Sulphate	321255	352942	"
unsolvent residue	80.7	85.7	%

n.a. ... not analyzed *) Thiocyanates

In the waste water from the flue gas treatment no dioxins and furans were detected (Wruss, 1986a). Table 10.18 gives the results from the analysis of the waste water after heaving passed a rubble-filter, which is discharged into the canal system.

Table 10.18: Waste Water of the Municipal Waste Combustion Plant "Flötzersteig" (Wruss, 1986a)

Sampling	12. November 1985	
pH-value	7.88	
conductivity	8920.0	
Polyc. Ar. (PAK)	n.a.	
Phenols	n.a.	
Hydrocarbons	n.a.	
CSB	n.a.	
Antimony	0.12	mg/l
Arsenic	< 0.003	"
Barium	0.033	"
Beryllium	0.02	"
Lead	0.0004	"
Boron	0.86	"
Cadmium	0.15	"
Chromium total	0.018	"
Iron	0.0018	"
Cobalt	0.00031	"
Copper	0.0027	"
Manganese	0.0076	"
Nickel	0.0081	"
Mercury	0.001	"
Selenium	0.001	"
Silver	0.00083	"
Thallium	0.0718	"
Vanadium	0.00056	"
Zinc	0.078	"
Tin	n.a.	
Flouride	12.9	"
Chloride	3758	"
Cyanide total	n.n.w.	"
Calcium	2367.8	"
Magnesium	35.9	"
Strontium	0.19	"
Rhodanide*)	0.30	"
Sulphide	5.2	"
Sulphate	1178.8	"

n.a. ... not analyzed

*) Thiocyanates

The behaviour of leaching of the filter cake, examined in Austria, is shown in table 10.19.

Table 10.19: Behaviour of Leaching of the Filter Cake, Examined in Austria (Wruss, 1986b)

Date	5.11.85	5.11.85	15.11.85	26.11.85	Dim.
pH-value	7.81	7.64	8.49	7.14	
Conductivity	833	1206	2560	2120	mS/cm
dry substance	33.4	31.9	42.5	42.2	%
Polyc. Ar. (PAK)	< 0.003	< 0.002	< 0.002		
Phenols	n.a.	-	-	-	
Hydrocarbons	n.a.	-	-	-	
CSB	n.a.	-	-	-	
Antimony	< 0.1	< 0.1	0.07	0.002	mg/l
Arsenic	< 0.013	< 0.013	< 0.003	< 0.004	"
Barium	0.003	0.023	0.046	0.063	"
Beryllium	< 0.002	0.004	< 0.002	0.0022	"
Lead	0.0016	0.0004	0.0025	0.00028	"
Boron	0.31	0.14	0.21	0.35	"
Cadmium	0.015	0.011	0.0031	0.0079	"
Chromium total	0.028	0.00	0.104	0.45	"
Iron	0.093	0.086	0.026	0.028	"
Cobalt	0.0013	0.0016	0.0002	0.00035	"
Copper	0.0043	0.0054	0.0026	0.0031	"
Manganese	0.026	0.018	0.021	0.034	"
Nickel	0.0009	n.d.	0.0032	0.0004	"
Mercury	< 0.0015	< 0.0015	< 0.001	< 0.001	"
Selenium	0.002	0.001	< 0.001	< 0.0012	"
Silver	0.004	0.0004	0.0012	0.00084	"
Thallium	0.02	0.02	0.0087	0.012	"
Vanadium	0.0072	0.0039	0.0012	0.004	"
Zinc	0.105	0.130	0.040	0.066	"
Tin	< 0.2	< 0.2	0.1	< 0.1	"
Fluoride	9.5	9.4	5.2	4.45	"
Chloride	191.4	304.9	232.6	326.2	"
Cyanide	0.002	0.004	n.d.	n.d.	"
Calcium	145.4	215.7	699	681.1	"
Magnesium	5.58	6.69	6.11	17.8	"
Strontium	0.312	0.234	0.43	1.16	
Rhodanide*)	0.28	0.26	0.44	0.35	"
Sulphide	3.2	5.2	6.8	5.0	"
Sulphate	149.8	184.4	1475.1	1501.4	"

n.a. ... not analyzed
n.d. ... not detectable

*) Thiocyanates

Table 10.20: Composition of the Residuals of the Wet Flue Gas Treatment of the Municipal Waste Incineration Plant Bern (Bundesamt für Umweltschutz, 1987)

Element	Content (g/kg dried residue; $^{o}/oo$)
	260
Ca	80
Total sulphur, as S	76
Sulphate, as S	52
Total carbon, as C	45
Carbonate, as C	33
Fe	8
Zn	7
Mg	5
Chloride	4
Al	4
Na	3
Pb	2
Sn	2
K	1
Hg	1
B	1
Mn	0,4
P	0,3
Cu	0,1
Cd	0,1
Ti	

10.4.2 Residues from the Quasi-Dry Process

The dry residues from the quasi-dry process are in general remaned by a bag house filter. This method operates with an excess of sorption medium, so the product has a high content of calcium hydroxide. Furthermore the residues contain most of the soluble chloride. Concerning these two facts (high pH-value, chlorides) the mobility of heavy metals increases and the treatment of the residues (e.g. solidification) becomes more difficult. The utilization of this by-product is not possible, because of its high salt content.

By-Products Spray-Drying

Table 10.21 shows the composition of a solid by-product generated in a Swiss spray drying unit of a municipal waste incinerator. The relatively high content of chloride as well as the rather high pH-value enhance the mobility of the heavy metals and hinder the solidification.

Table 10.21: Composition of the Residuals of a Spray Drying Unit for Flue Gas Washing of the Waste Incineration Plant Josefstrasse in Zürich (Bundesamt für Umweltschutz, 1987)

Element	Contents (g/kg dried residue, $^{o}/oo$)
Calcium	230
Chloride	120
Aluminium	48
Total-sulphur, as S	37
Total-hydrocarbons, as C	27
Sulphate, as S	15
Potassium	12
Zinc	12
Carbonate, as C	10
Iron	8
Magnesium	8
Sodium	6
Lead	4
Copper	0.8
Manganese	0.3
Chromium	0.2
Cadmium	0.2
Nickel	0.1
Mercury	0.028

10.4.3 Residues from the Dry-Process

The air pollutants of the untreated flue gas are adsorbed on the dry sorption medium and precipitated in dry condition. In general, calcium hydroxide is used as sorption substance. Because of continuous changes in the flue gas composition and the high gas temperature, the cleaning process must be operated with an excess of sorption medium. So the amount of non reacted calcium hydroxide in the residues is very high and some of the CO_2 in the flue gas reacts to calcium carbonate. The high amount of chloride results from the reaction between hydrochloric acid and calcium hydroxide. The heavy metal chlorides are highly soluble in water and must be taken account of in the case of subsequent treatment.

Table 10.22 shows the composition of the residues produced in flue gas treatment by the dry process.

Table 10.22: Composition of the Dry-Working Flue Gas Cleaning of the Waste Incineration Plant Niederurnen (Bundesamt für Umweltschutz, 1987)

Element	Contents (g/kg dried residue, °/oo)
Calcium	250
Chloride	140
Potassium	32
Total sulphur, as S	29
Sulphate, as S	25
Aluminium	22
Sodium	20
Zinc	17
Total hydrocarbons, as C	9
Lead	7
Magnesium	7
Iron	6
Carbonat, as C	3
Barium	1
Manganese	1
Copper	0.7
Tin	0.5
Cadmium	0.3
Nickel	0.1

10.5 Environmental Impact - a Comparison with Other Residues

The concentrations of a number of important elements (heavy metals) obtained in leaching tests on residues of municipal waste combustion are compared in Figure 10.4 with leachates from deposits of municipal waste (household refuse). Figure 10.4 also shows the comparison between corresponding leachate contents from leaching of residues from combustion of other solid fuels and of drinking water criteria and background contents in natural surface water - freshwater. It can be seen that in leachates from residues obtained from municipal waste combustion a number of metals are found in higher concentration than in leachates from other by-products. This applies especially to the leachates from the residues from dry flue gas treatment mixed with fly ash. The content of lead in the leachate is higher than in other leachates. The high salt content in leachates from fly ash and residues resulting from dry processes must also be taken into account in making an environmental risk evaluation.

It is worth mentioning that if a disposal of residues from municipal waste combustion is built up to the same height as a corresponding deposit of unburnt household refuse, the residues will occupy an area about 12 % of that resulting from direct deposition of household refuse (Ahrtlen and Elander, 1986). If it is furthermore assumed that the same measures are taken to limit the volumes of leachates, this will be about ten times greater in a deposit of unburnt household refuse, than in a deposit of a corresponding volume of combusted waste.

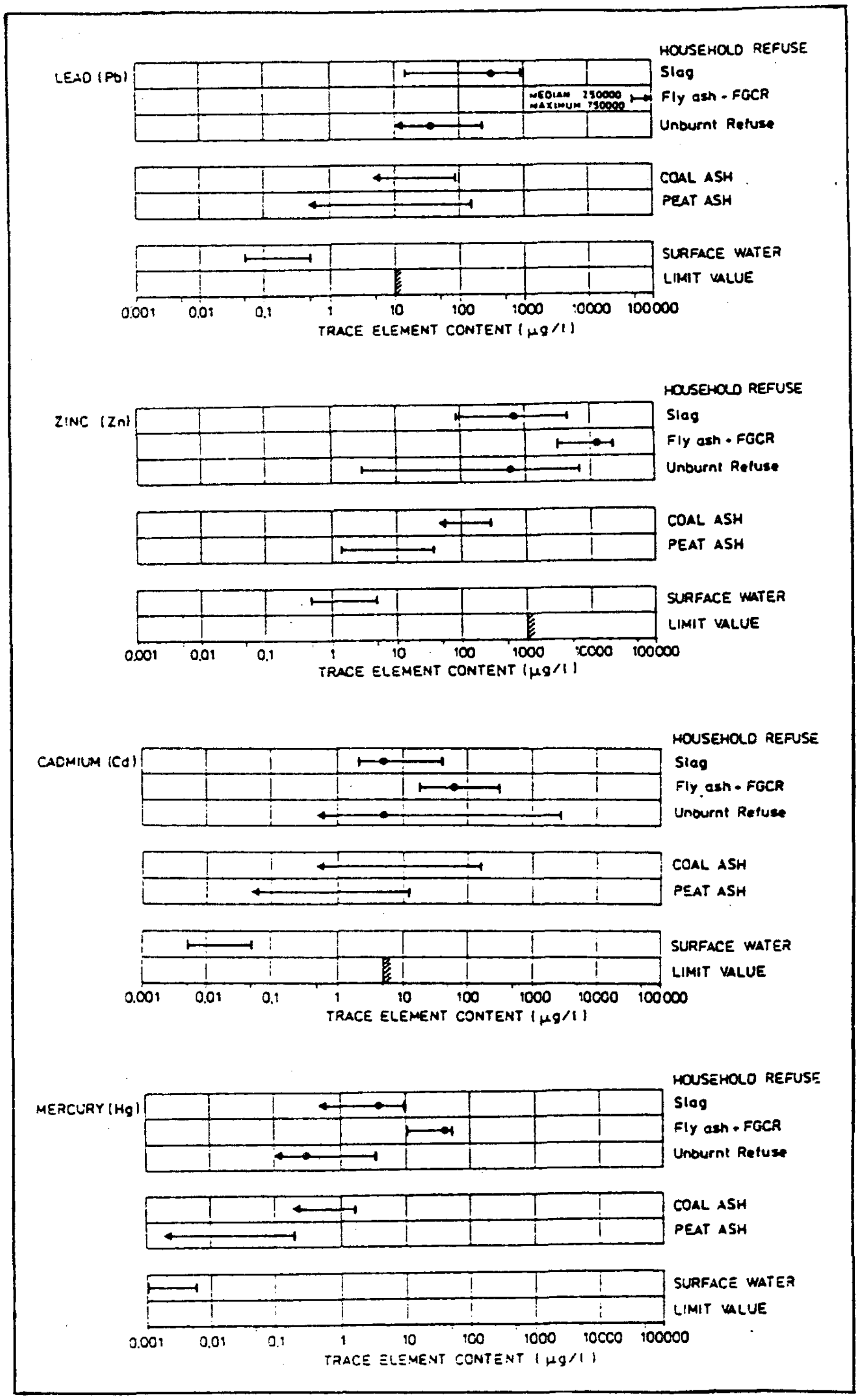


Figure 10.4: Contents of a Number of Important Trace Elements in Leachates from Various Wastes (Range and Median Values) (Ahrtlen and Elander, 1986)
FGCR: Residues of the Flue Gas Treatment by a Dry Process

10.6 Utilization and Disposal of By-Products from Municipal Waste Combustion

One ton of bottom ash contains 120 - 150 kg iron. The recovery of this scrap is carried out by nearly all municipal waste combustion plants.

Bottom ash from the municipal waste combustion has been tested as artificial gravel for building roads in several countries, mainly in Denmark, France, Federal Republic of Germany and the USA. In Denmark extensive studies have been made of the prospects for using bottom ash as a filling material under road pavements (Pietrzeniuk, 1985; Ahrtlen and Elander, 1986). To obtain reasonable efficiency, the slag must be sorted and treated. After treatment it has to consist mainly of mineral constituents with special size distribution for further utilization.

In Austria bottom ash from municipal waste combustion is deposited in a special area of a municipal waste land-fill.

In Sweden bottom ash is used at a number of sites as a covering material for household refuse deposits. This is not regarded as having an impact on the total leaching situation in a refuse deposit. However, bottom ash must not be covered by household refuse owing to the risk of leaching of dioxins and heavy metals through the creation of complexes (Ahrtlen and Elander, 1986).

The separated particulates from municipal waste combustion are usually not utilized because of the high concentration of toxic heavy metals and organic compounds.

Nevertheless, two technical possibilities have been suggested in Pietrzeniuk, 1985:

* incorporation in bricks,
* incorporation in concrete (first the particulates are treated by a thermal process, the binding and fixing agents are added).

In general untreated particulates are deposited in land-fills or mines which have to confirm to a technical standard that reduces migration of leachates into the underground. Furthermore untreated particulates can be windblown when dry.

Recently the treatment of particulates has been stressed. The most favoured treatment is solidification in concrete or mixing with limestone, chemicals or the different by-products from municipal waste combustion.

The Waste Management Concept in the City of Bamberg, FRG (so-called "Bamberg-Modell") is one of the best known examples for a mixture of the residues: A certain amount of particulates is mixed with sludge from the flue gas treatment. Investigations about leaching of the solidified product show that it corresponds to the requirements of third class of the classification of land-fills in the FRG (see chapter 2).

A further improvement of the leaching characteristic of treated particulates is achieved by simultaneous treatment of particles and residues from the wet flue gas treatment.

Austrian investigation of mixtures from particulates and residues from the wet flue gas treatment shows that dioxins and furans are not detectable in the leachate from the leaching test (DEV-S4). In a mixture of 90 % bottom ash, 8 % particulates and 2 % sludge, dioxins and furans were not detected by this leaching test (Wruss, 1986b).

The residues from the wet flue gas treatment arise in a quantity of 10 - 15 kg per ton of municipal waste burned. The composition of the residue is shown in table 10.17. Nearly 95 % of the sludge is a mixture of gypsum and calcium sulphite. Dioxins and furans were not detected in the leachate from the leaching test (Wruss, 1986a). Utilization is not possible.

10.6.1 Fly Ash

Fly ash from Electrostatic Precipitators in waste combustion can be prepared for safe disposal by immobilizing pollutants with one of the following treatments:

- solidification without washing (retaining high contents of chloride and heavy metals)
- solidification after washing with water (retaining low contents of chloride and high contents of heavy metals)
- solidification after acid washing (retaining low contents of chloride and heavy metals).

A comparison of the effects of these treatments is given in table 10.23.

Table 10.23: Effect of Solidification of Electrostatic Precipitator Fly Ash on Eluation (Bundesamt für Umweltschutz, 1987)

Element	Untreated ESP Fly Ash[1)] (mg/l)	Solidified ESP Fly Ash[1)] (mg/l)	Decrease of Pollutants Emission Factor	Washed and Solidified ESP Fly Ash[1)] (mg/l)	Decrease of Pollutant Emission Factor
Pb	29.8	0.073	408	0.011	2709
Cd	3.7	0.0026	1423	0.0013	2846
Cu	4.4	n.	> 880	n.	> 880
Zn	52.3	n.	> 2600	n.	> 2600

n. ...... not found

1) Total of concentrations from 11 eluates

As a result of investigations made in Switzerland disposal of ESP fly ash from municipal waste combustion without being solidified shows very high metal contents in leachates. Fly ashes with high contents of chloride (4 - 8 %) and high contents of sulphate (4 %) solidified with two different kinds of cement and subjected to leaching tests show results which are given in table 10.24. Solidification with some kinds of cement shows satisfactory results, but the high content of cement results in high costs and increased volumes for disposal.

Mixtures of fly ash and bottom ash compressed without adding cement can be disposed of in a controlled landfill site. However, in respect to the content of toxic organic compounds and possible leaching of heavy metals this material cannot used as a base material for roads.

Table 10.24: Effect of Solidification with Different Kind of Cement of Electrostatic Precipitator Fly Ash on Leaching (Bundesamt für Umweltschutz, 1987)

Element	Content in TB (g/kg)	Cumulated Leaching in 14 Days (mg/l)		Specific Concentration Leached in 14 Days (mg/kg TB)		Amount Leached in 14 Days (o/oo of content)		D_E 1) 10^{-x} (m^2/s) x	
	P + L	P	L	P	L	P	L	P	L
Copper	0.7	0.66	n.	4.3	-	6	-	12	-
Zinc	14.7	9.1	n.	59.66	-	4	-	13	-
Lead	4.6	3.5	0.073	22.9	0.39	5	0.085	12	15
Cadmium	0.17	0.15	0.0026	0.98	0.014	5,7	0.083	12	15
Chloride	34.9	2249	1851	14730	9.848	422	282	11	9

n. ..... not found

1) ..... Diffusion coefficient, average value 3.-14. day

P ..... Portland cement

L ..... Lafarge cement

TB ..... Testbrick

Composition of TB:	
Fly ash	38,5 %
Cement	38,5 %
Water	23,0 %
Total	100,0 %

10.6.2 Sludge from Waste Water Treatment of Flue Gas Treatment

As with fly ash, sludge and filtercake from wet treatment plants of FGT have to be prepared for disposal by one of the following treatments:

- solidification without washing (retaining high contents of chloride and heavy metals)
- solidification after washing with water (retaining low contents of chloride and high contents of heavy metals)

- solidification after acid washing (retaining low contents of chloride and heavy metals).

A comparison of the results of leaching tests with these treatments is given in table 10.25.

Table 10.25: Effect of Solidification of Slime from Washing Liquor of FGT (Bundesamt für Umweltschutz, 1987; EPA, 1982)

Element	Untreated slime from FG-washing (mg/l)	Solidified slime from FG-washing (mg/l)	Decrease of pollutants emission factor	Solidified mixture 1)2) (mg/l)	Decrease of pollutants emission factor
Pb	8.6	0.079	110	0.12	70
Cd	0.58	0.076	7.5	0.02	29
Cu	0.75	0.083	9	0.01	75
Zn	12.8	0.84	15	0.17	75
Hg	n.a.	n.			

1) total of concentrations from 11 eluates
2) mixture of sludge from FG-washing and untreated ESP fly ash (1:3)

n. .... not found
n.a. .... not analyzed

10.7 R & D Projects

These projects are aimed at the separation of heavy metals from the by-products. Solidification of the treated residues is usually not necessary.

10.7.1 3 R-Process (Kernforschungszentrum Karlsruhe)

Cadmium and zinc are extracted from the particulates with an acidic washing solution and then adsorbed in an ion exchanger. The treated residue is recycled to the combustion chamber and burnt with the municipal waste in order to destroy organic compounds.

10.7.2 Multi-Recycle-Process (SGP)

The wet product from separation of SO_2 from the flue gas in the second washing tower is combined with the bottom ash and the particulates. The process water is led back to the process. Sodium and calcium from the bottom ash and the particulates are efficient chemicals for the separation of SO_2 in the washing tower. So no more addition of sodium hydroxide and lime milk is necessary. The SO_2-removal efficiency increases.

The chemical reaction to gypsum is performed on the surface of bottom ash and particulates. The basic slurry suspension of bottom ash, fly ash and gypsum is dewatered. This product is rewashed with the processing water from the first washer for HCl removal. This acidic process water extracts the heavy metals from bottom ash and fly ash and basic compounds are dissolved. The process water is recycled to the first washer to offer neutralization compounds.

This process guarantees that most of the gypsum can be deposited with particulates and bottom ash. Sludge contains mainly hydroxides. Sodium hydroxide is only added in cases of interruption or high SO_2-concentration in the flue gas. Milk of lime is only added in the waste water treatment.

10.7.3 Thermal Detoxification

A thermal process splits the ash in two fractions, a small fraction in which the problematic heavy metals are concentrated enough for recycling and a major fraction, that is harmless:

To the end the filter ash is heated in an electrically heated furnace - preferentially located at the waste incinerator site - to about 1300 °C. During the heating most of the heavy metal compounds evaporate. The dioxins and furans are thermally destroyed. The gaseous heavy metals are quenched with cold air, which leads to condensation of the heavy-metal compounds in the form of particles and which prevents the reformation of dioxins during cooling. These particles - about ten percent by mass of the filter ash - are precipitated in a bag filter. Their heavy metal content is so high, that the metals can be recycled in a foundry after a simple pretreatment. The exhaust gas (mainly air with some CO_2 and SO_2) is vented to the incinerator furnace. Since the major component in the filter ash is SiO_2, the non-evaporating fraction of the ash - about 80 % of the mass - forms a glass-like melt at the furnace temperature of 1300 °C.

This glass-like residue is a harmless material suited for normal sanitary landfill or possibly for road construction. It has a volume of only about 25 % of the original filter ash and meets by far the proposed strict Swiss leaching test (e.g. Hirth et al., 1989).

11 LEGAL INSTRUMENTS

The generation of by-products is a result of emission control laws. An overview about emission standards in IEA member states is given by Vernon (1988). Usually these regulations cover emissions of SO_x, NO_x, particles and heavy metals, but not by-product treatment.

Lower emission standards require stronger efforts for flue gas treatment and thereby result in increased amounts of by-products. Many waste management laws and regulations can be applied to the utilization and treatment of these products.

Austria

In Austria the emissions from boilers are limited by the Clean Air Act and the Clean Air Ordinance for Boilers ("Luftreinhaltegesetz für Kesselanlagen", "Luftreinhalteverordnung"). According to the law the emissions of steam boilers have to be limited according to the state of technology. The ordinance therefore gets emission standards for different air polluting substances according to the kind of fuel, size of unit and kind of unit. The standards apply for new as well as for existing plants. The law came into effect January 1, 1989, requiring existing plants to meet the standards at latest until January 1, 1997. Therefore a large number of power plants, industrial boilers and waste incineration units are retrofitted and will produce an increasing amount of by-products.

For other industrial or commercial units the industrial legislation ("Gewerbeordnung") requires licensing of installations that might pollute the air. Licenses for these installations often set maximum possible standards for air pollutants, therefore also resulting in by-products.

On July 1st, 1990 the Waste Management Act (Abfallwirtschaftsgesetz), which supplants and in many areas extends or tightens the provisions of the Special Waste Act (Sonderabfallgesetz 1983) came into force.

The Waste Management was provided in accordance with the technical guidelines on waste management and orientates by similar rules of the Federal Republic of Germany, Denmark and the Global Convention on the Transboundary Movements of Hazardous Waste.

The primary objective of the Act is the avoidance of waste production through the development of production processes which entail the production of little or no waste and through waste minimization on the product level. Non-avoidable waste is to be collected seperately and to be reutilized, most particulary through the development of recycling systems.

If waste products cannot be reutilized in any manner, they may be dumped only after having been treated in accordance to the environment.

The Waste Management Act covering waste in general makes a distinction between waste and hazardous waste, and lays down the terms "salvage" (Altstoffe) for a subgroup of waste and "problem stuffs" (Problemstoffe) for a subgroup of hazardous waste.

The technical standard "ÖNORM S 2101" was made compulsory through the ordinance concerning the determination of hazardous special waste.

As the Waste Management Act orders that this ordinance is put on a level with the fixing of hazardous waste, also after the inactment of the Waste Management Act only this waste can be considered as hazardous waste, that the Special Waste Act has applied to.

Therefore the Federal Ministry of the Environment, Youth and the Family is composing in this connection an ordinance, that on the one hand has to make the ÖNORM S 2101 compulsory and on the other hand has to pronounce a certain waste like slags and ashes of combustion plants, etc. hazardous.

Parellel to that an extention of the ÖNORM S 2101 is in elaboration.

If this extended technical standard should be finished before the enactment of the mentioned ordinance, it could be abstained from an additional list of hazardous waste.

According to the Waste Management Act the Federal Minister of Environment, Youth and the Family has to organize a data bank installed at the Federal Environmental Agency (Umweltbundesamt) which allow the control of the kind, the amount, the origin and the disposal of all hazardous waste.

Impacts on Waters are regulated by the Federal Water Act (Wasserrechtsgesetz 1959), which has strong influence on the location and management of disposal as well as on the discharge of liquid effluents of wet flue gas treatment systems.

Canada

In October 1988, in response to the Brundtland World Commission on Environment and Development, the Canadian Council of Resource and Environment Ministers (CREEM), established a National Task Force on Environment and Economy. The mandate of the Task Force, which supports the main conclusion and recommendations of the World Commission's April 1987 final report, "Our Common Future", was to foster and promote environmentally sound economic development in Canada.

In April 1989 the Canadian Council of Resource and Environment Ministers formally recognized that waste management is an urgent and pressing national problem in Canada. Some jurisdictions are already running out of landfill sites (in a relatively large and unpopulated country). The Ministers agreed that targets and schedules for waste minimization would be established, including a 50 % reduction in waste generation, by the year 2000. These initiatives would be consistent with the "four R's" of waste reduction, reuse, recycling and recovery.

To further encourage and increase the utilization of coal fly ash in cement and concrete products, appropriate government policies may be developed within the next year. To facilitate the utilization of flue gas desulphurization (FGD) by-products, Ontario Hydro (the largest Canadian electric power utility), must design and operate their wet FGD systems to produce commercial quality gypsum for wallboard and similar products. This condition for the Ontario Hydro FGD program was announced July 1989. The utility must also investigate technical options for closed loop operations (i.e. "zero discharge" of FGD process waste water).

Environment Canada has published a series of "Environmental Codes of Practice for Steam Electric Power Generation" (Environment Canada, 1987b; Environment Canada 1985). These Codes are being developed by a federal, provincial and industry Task Force, and identify environmental protection practices for the siting, design, construction, operation and decommissioning phases of electric power plants.

In the Siting Phase Code (Environment Canada, 1987b), criteria are included which will reduce or avoid adverse environmental impacts in the selection of sites for waste disposal. Some of these criteria are presented by table V/1, Annex V. The criteria relate to land use, terrestial ecology, surface water and ground water, aquatic ecology and atmospheric environment.

In the Design Phase Code (Environment Canada, 1985), practices are recommenced that will reduce or eliminate adverse environmental impacts by the appropriate selection and design of power plant systems.

Recommendations that relate to solid waste and waste water systems are presented in table V/2, Annex V. The recommendations relate to ash handling systems, flue gas desulphurization systems, waste disposal, waste liquid containment, seepage control for ground water protection, discharged effluent limits, monitoring facilities and environmental data processing.

In addition to these federal environmental protection standards, various provincial regulations relate to waste management (Table V/3, Annex V).

The Operation and Decommissioning Phase Environmental Codes for Steam Electric Power Generation are currently being developed. Of particular concern is the long-term physical and chemical stability of power plant waste disposal sites, the contamination of ground water by salts and metals, and future land use restrictions of these sites.

In addition to these standards for the management of by-products from the electric power sector, various regulatory guidelines are used for the disposal of wastes from other industrial sectors and the municipal sector. These include national, federal, provincial and municipal requirements and many have been developed by the Canadian Council of Ministers of the Environment (CCME).

Federal Republic of Germany

In the Federal Republic of Germany, the laws governing air-quality control, waste management and the protection of water bodies are the Federal Immission Control Act (Bundes-Immissionsschutzgesetz), the Waste Avoidance and Waste Management Act (Abfallgesetz), and the Federal Water Act (Wasserhaushaltsgesetz). Important regulations in the sector of air quality control include, for instance, the Federal Ordinances on Small (1. BImSchV) and Large (13. BImSchV) Combustion Plants, the Ordinance on Waste Incinerators (17. BImSchV) and the Technical Instructions on Air Quality Control (TA Luft). All regulations concerning these fields are based on two legal-policy principles, namely the principle of precaution and the polluter-pays principle. The measures to be taken as a precaution against harmful effects on the environment include, in particular, emission-reduction measures based on the best available technology.

Article 5, para. 1 No. 3 of the Federal Immission Control Law provides that residues be avoided or utilized, as far as technically feasible and reasonable, or - as a last resort - that they be properly disposed of. The requirement to avoid the generation of residues and to re-use/recycle residues has definite consequences with respect to the development and application of clean air technologies. Processes which do not generate any or only low amounts of residues, or which generate residues that can be re-used/recycled, are to preferably be used in flue gas purification. Operators are required to submit comprehensive recycling schemes. Article 1 a of the Waste Avoidance and Waste Management Act prescribes that the generation of waste be avoided or that waste be re-used or recycled. According to article 3, para. 3 the authorities which are responsible for waste management can reject the acceptance of wastes which due to their quality or quantity cannot be disposed of together with household waste. In such a case the owner of this waste is responsible for its management. In such a case the owner of this waste is responsible for its management. Pursuant to article 7 a of the Federal Water Act, requirements in form of an administrative regulation for the discharge of waste water into water bodies have been established (such as for waste water from flue gas scrubbers in combustion plants). This administrative regulation insists that not only the concentration of pullutants in the waste water should be minimized according to the best available technology but also their freights by recycling the scrubber water.

Thus, the legal regulations have established the following order concerning the management of residues:

- The generation of residues is to be avoided

- Residues which cannot be avoided are to be re-used/recycled.

- Non-reusable/recyclable residues are to be disposed of.

- Residues are to be utilised or disposed of in such a way that the pollution of water bodies is kept to a minimum.

- No additional open land should be used for the depositing of waste.

Finland

Management of non-radioactive wastes formed in energy production is covered by the Waste Management Act. The Waste Management Act applies to community wastes, industrial wastes and those generated in the course of other production (e.g. energy production) as well as hazardous wastes. The Act does not apply to radioactive wastes nor to the management of waste explosives, which are covered by other legislation.

The main principle of the Act is that, to the extent possible, waste management is to be executed in such a manner that wastes can be recycled or otherwise re-used and that they are not detrimental to the environment. This principle is binding and applies to everybody who produces or treats wastes. "To the extent possible" concerns for recycling the financial, technical and organization means to be considered in each particular case. Whenever these possibilities exist, wastes must be used to economic advantage. According to the latter part of the regulation, wastes must not cause harm to the environment.

According to the Waste Management Act, wastes are classified as hazardous waste and non-hazardous waste. The Act gives a general definition of hazardous waste. According to it, waste being difficult to make non-hazardous or difficult to handle due to its toxicity or other quality of waste otherwise especially hazardous to the environment are considered hazardous waste. No classification criteria, such as maximum contents of hazardous substances in the waste, have been suggested.

When a property owner or holder is required to arrange for waste processing himself and hazardous wastes or wastes of otherwise unusual character or in exceptional quantities are produced or treated on the property, he must provide the waste management authorities (municipal or provincial) with a Waste Management

Plan. In approving a Plan, the authorities can impose conditions requiring recycling or re-use or any other measures considered necessary from the viewpoint of environmental protection. Thus, the quality of the waste and the proper method of its handling are usually evaluated case by case by the Waste Mangement Authority.

This procedure has two main purposes: It imposes a statutory obligation on the property owner or holder to plan waste management thoroughly and in a manner meeting the requirements of the Act, in addition to which it constitutes a documentary aid to the authorities responsible for ensuring implementation of the Act.

About 60 % of the fly ash from coal firing is used in the building material industry in the raw powder for cement, as a compound of cement, and as fillers in the manufacture of concrete. Maximum values have been set by the building material industry for the quality of fly ash: for ignition loss and for chloride, magnesium and sulphur contents. The rest of fly ash is used in soil construction works disposed on dumps. The major part of peat fly ash is disposed on dumps.

The desulphurization wastes formed in Finland have so far been on dumps used for soil construction at exactly determined site or disposed in a limestone mine.

In one case disposal of desulphurization wastes as ballast between blasted stone and gravel embankments in an artificial hill has been approved as the method of treatment for the mixture of wet-dry method waste and fly ash (30000 t/a) from a coal-fired power plant. Seepage water is monitored in the area. The aim is to build a ski slope on the artificial hill formed in this way. According to the decision made by the authorities it is also possible to dispose the waste in limestone mine. The authorities have also required that the producer of the waste concerned must survey alternatives of utilization, for example, in the building material industry.

A number of surveys are underway about the use of desulphurization wastes in soil construction works, for example in road construction. Laboratory experiments are being conducted at the Technical Research Centre of Finland and at IVO (the biggest supplier of energy in Finland) to assess properties and potential applications of desulphurization wastes. The studied materials are wastes from the wet-dry process, from fluidized bed combustion and from the Lifac process. Both geotechnical characteristics of wastes and impacts on the environment are being investigated.

There is only one combustion plant for municipal wastes in operation in Finland. The fly ash and slag formed in this plant (20000 t/a) is disposed on a dump for municipal wastes.

Italy

In Italy the provisions for industrial waste disposal are contained in the DPR 915/82 that regulates wastes, that is, any substance or object abandoned or destined to be abandoned. The regulation divides wastes into three categories on the basis of their chemical-physical characteristics: urban wastes, special wastes and toxic and noxious wastes. The last two categories, which cover industrial wastes, differ for the presence in the waste as such of some substances considered dangerous in amounts exceeding values expressely indicated in the regulation.

Different types of discharge are provided for depending on the chemical characteristics of the wastes (test of elution with acetic acid similar to that provided for by EPA in the United States, or treatment with water acidulated with carbonic acid). The coal ash produced at present and the gypsum produced in the future from desulphurization systems fall in the special waste category. Discharges for this type of waste (which pursuant to the regulation are called "second category type B") should have the following general requirements:

- They should be located within a safe distance from inhabited centers and from fresh water supply areas on the basis of the hydrologic characteristics of the site.

- The discharge bottom should be at least 1 m above maximum water-table level.

- The soil at the discharge site should have adequate impermeability and such geologic and geotechnique characteristics as to avoid risk of landslides or failure of the walls or bottom.

The legislation also indicates the general criteria for management of discharges, and requires that the application for authorization and operation of the discharge should specify the type of covering that will be adopted once the discharge is filled, depending on the end-use of the soil.

The regional authorities should identify the discharge sites and provide for their qualificatioin. They should also issue the specific authorization for operation after presentation by the operator of ad-hoc designs. The province authorities should ensure environmental control during operation of the discharge.

Present Experience

The discharges for ash disposal now in operation are generally abandoned quarries or depressed areas located at distances ranging from a few kilometers to a few hundreds kilometers from the stations. Transport is performed with adequate lorries and management of the discharge is entrusted to authorized private operators. Besides compliance with the requisites set forth in the legislation for that specific waste (degree of natural impermeability of the soil, level of the water bed and stability of the soil), further cautionary actions are provided for by some local authorities owing to the limited experience in this field. These actions include lining of the discharge bottom with clayey layers or geomembranes, drainage and canalization of meteoric water, sampling of ground and surface water for periodical quality analyses, system for collection and treatment of percolate, if any.

As concerns management, the ash disposal criteria are defined in the authorization phase and consist mainly of gradual filling of the discharge divided into small sectors in order to reduce the surface exposed to meteoric water and thus the possibility of scouring; of compaction of the daily discharge layer and of levelling and recompaction - at the time intervals required by the different situations - to prevent any instability phenomena; of humidification of the surface layer, when necessary, to avoid eolic resuspension and ash dispersion.

Once the discharge is filled up, the ash are covered with about 30 cm layers of soil suitable for such utilization. In some cases an intermediate layer of low-permeability material 30 - 40 cm thick is required by the authorities. The results of the various controls performed on the underground and surface water by the competent bodies proved that no pollution phenomena due to ash have occurred. Furthermore, in most cases percolate was absent owing to consolidation of the ash layers due to the pozzolanic reaction in presence of water.

Netherlands

Historical Background, Present Situation

In 1971 a preliminary draft of the "Soil Pollution Bill" was submitted to the Lower House of the States General. During the processing of this preliminary draft it became steadily clearer that from the legislative point of view it was not very practical to combine waste disposal and soil pollution in a single, truly integrated, juridical entity. In mid-1972 it was therefore decided to split the preliminary draft into a separate legal statute regulating waste collection and disposal and an act to protect the soil from pollution.

In view of the urgent need for a statute to regulate the disposal of chemical or hazardous waste it was decided at the end of 1972 to draw up as a matter of urgency a separate act regulating this category of waste. This meant splitting the legislation into a law for chemical waste, including oil waste, and a law for the remaining waste substances (insofar as there were no existing requirements imposed by other laws such as for radioactive waste substances).

Presently all necessary procedures are set in train for the integration of the two legal instruments - the Waste Substances Act and the Chemical Waste Act - into one chapter on Waste Mangement of the Bill on General Regulations for Environmental Protection (WABM).

The Waste Substances Act

The passing of the Waste Substances Act created a legal framework aimed at limiting the generation of waste and promoting the recycling and application of waste substances and the adequate disposal of waste flows.

The Waste Substances Act provides a decentralized structure with a co-ordinating role for the provinces and an implementation role, with legal authority, for the municipalities.

The licensing system pursuant to the Waste Substances Act may be regarded as a limited integrated licensing system, with provincial executives acting as primary licensing authorities. However, under Article 33, licensing activities can also be undertaken by the central government via a general administrative order. Practically all environmentally relevant aspects such as danger, damage and nuisance (including air pollution and noise nuisance) caused by a facility for the processing of waste substances are regulated by this licensing system, including ecological aspects. The system is limited in that it excludes the licensing of the pollution of surface water insofar as such pollution is covered by the Pollution of Surface Waters Act.

The Chemical Waste Act

The Act applies to the disposal of chemical waste or waste oil which the holder intends to get rid of by transfer to a second party or by dumping. The Act does not apply to storage or processing within the concern where the waste was produced. Other laws for the protection of the environment, such as the Nuisance Act, may well be applicable. The Act is also inapplicable to disposal by discharge or cumbustion at sea, which is covered by the Pollution of the Sea Act. The disposal of chemical waste substances will normally be associated with transportation of these substances. The Act contains no regulation for this; transportation is covered by what is laid down under or by virtue of the Dangerous Substances Act. The supplementary nature of the Act is particularly evident in Articles 2, 10 and 61.

Article 2 declared the Act to be inapplicable to chemical waste or waste oil derived from households. The Waste Substances Act covers disposal of these wastes.

Article 10, section 2, determines that licenses under the Chemical Waste Act must be refused if licenses required under Nuisance Act, the Air Pollution Act or the Pollution of Surface Waters Act have not been obtained.

Article 61 contains a priority provision for certain acts under which regulations have been drawn up in relation to the disposal of chemical waste or waste oil, such as the Nuclear Energy Act and the Pollution of Surface Waters Act.

In order to determine whether a waste material is to be considered as a chemical (or "hazardous") waste, an investigation must be made with the aid of the Substances and Processes Decree under the Chemical Waste Act. In this connection the Decree contains a list of substances with four limiting concentration values, a list of processes, and a list of exceptions. According to the Decree, waste substances are regarded as chemical waste if incorrect treatment of them in association with their particular properties (toxicity, biological persistence and bio-accumulation) can lead to serious damage to human health or to the environment.

Sweden

Legal Instruments

The Environmental Protection Act (SFS 1969:387) provides a "frame-work legislation" giving a coordinated regulation of air and water pollution, noise, etc. from real estate. A central section in the act lays down rules defining the conditions upon which a polluting activity may be permitted. Details of the regulation are given in ordinances, guidelines, etc. Under a licensing system specifications and other data for new constructions or alterations are required. Public participation is an important element. A licence carries the same legal weight as a court ruling.

Both the siting and the design of disposal sites for combustion residues and the utilization of such residues are controlled by the Environmental Protection Act.

First and foremost, the most suitable site should be chosen in such a manner that the "purpose can be attained with the least possible interference and nuisance, without unreasonable expense". The basis principle is then that disturbances shall be prevented as is practically feasible, and that unnecessary disturbance should not be tolerated under any circumstances. The obligation to take protective action, etc. shall be considered on the basis of what is technically feasible, using the most effective technical devices and methods that are available, the sensitivity of the environment and the cost of the measures.

Slags, ashes and other flue gas cleaning products are not classified as environmentally hazardous waste according to the Swedish law.

General Environmental Policy

The Environmental Protection Agency has defined environmental goals for different categories of pollution and for the protection of ecological systems and human health. Long-term goals have been defined only in a general way: "All nature types should be preserved to such an extent that species diversity and ecological stability is maintained." What the World Commission on Environment and Development describes as sustainable development - to meet the needs of the present without compromising the ability of future generations to meet theirs - is a goal for an environmentally sound economic development supported by the Swedish government.

In a long time perspective, the leaching of heavy metals is considered to be the most serious threat of cumbustion residues to the environment. Heavy metals persist indefinitely and may therefore affect the environment far into the future. The ultimate aim must be that the anthropogenic entry of heavy metals into the environment is so limited that it can safely be assumed that no significant negative effects will occur. This condition ought to be fulfilled if anthropogenic distribution adds little to the natural level of that metal in the environment. The "natural" level is often, however, unknown and one must instead work on the basis of what is known about the possible ecological effects of the metal. This method is, however, more uncertain.

Leachates from combustion residues may pollute ground water and/or surface water. The same environmental criteria should apply in both cases. Drinking water criteria are not sufficient.

Also, the environmental criteria and the environmental demands are the same for the utilization of residual products as for deposits.

Guidelines

Guidelines for the disposal of combustion residues do not include limit values for the emissions. The disposal of ashes, slags and other flue gas cleaning products are judged individually, the conditions being layed down according to the site-specific environmental requirements.

The basic principles for the siting and construction of deposits of combustion residues are:

- limitation of leachate production
- durability in the long-term perspective
- performance independent of maintenance and regular inspection.

The siting of the deposit is most important. An appropriate siting may limit the risk of infiltration of ground water or surface water into the deposit. It may also favour dilution (in time and space) and limit the environmental effects by avoiding emissions into sensitive recipients.

The amount of precipitation percolating into the deposit, and thereby the amount of leachate, may be limited by means of top sealing, protective covering and vegetation. An effective sealing layer may be created out of compacted fly ash of fly ash stabilized with FGD-products, lime or cement. Surface run-off and thus the effect of the sealing layer may be improved by providing a drainage layer above the sealing layer. Finally, the deposit should be covered by soil resistant to erosion and vegetation be established.

For coal and peat ashes the hydrological conductivity of the top sealing and the drainage layer should normally be about 10^{-9} m/s. Based on a judgement of the environmental susceptability and knowledge of the leaching properties of the residues and the dispersal of the substances in the environment, the requirements on protective measures may be set higher than normal. In new plants, the disposal of fly ash and other flue gas cleaning products from municipal waste incineration will require a stabilization of the residues.

Codisposal with organic waste is not recommended.

No ashes may be used on agricultural land.

Economic Incentives and Disincentives

Economic instruments have so far not been used in connection with combustion residues in Sweden.

Results

The environmental demands and the strategy laid down in the guidelines have been established in the conditions for new deposits licensed by the environmental authorities. Until now, however, there is limited practical experience of these deposits and of their environmental consequences.

The environmental demands have had a restrictive effect on the extent of utilization of combustion residues.

Future Outlook

Research is going on to develop utilizable products from combustion residues. Problems involved are connected with quality demands and standard settings. A widespread utilization of residual products have to be evaluated very carefully from an environmental point of view, and the ways in which residual products is used must be controlled. Stringent guidelines should be established. It may also require some legislative measures to be taken and economic instruments.

Further investigations are to be conducted on the stabilization or other treatment of flue gas cleaning products from municipal waste incineration. Also, work is under way to evaluate the long-term environmental consequences of depositing combustion residues on old household waste deposits, using the organic waste as a "filter" for metals.

United Kingdom

Control of Pollution Act, 1974 (COPA)

Part I of COPA empowers or places duties on Waste Disposal Authorities (WDAs) to:

- Investigate and then decide what arrangements are needed to dispose of controlled wastes which are or are likely to be situated within its area.
- Prepare and subsequently review a statement setting out those decisions, consulting widely on its ideas before publicising a final plan.
- Control the disposal of specific wastes by a system of licensing, placing conditions on the operation of waste disposal facilities which have a valid planning permission.
- Control the movement of special (i.e. hazardous) wastes from the point of production to final disposal ("from cradle to grave"), by a consignment note system.
- Monitor and where necessary take enforcement action to ensure that licenses and consignment procedures are compiled with and that waste is not disposed of illegally.

Refuse Disposal (Amenity) Act, 1978 (RDA)

This Act replaces sections in the Civic Amenities Act (1967). It deals with the control of dumping, abandoned vehicles and the provision of RDA facilities (often called Civic Amenity Sites, Household Waste Sites, Skip Tips or Tidy Tips).

Duties are placed on WDAs to:

- Provide places where householders can dispose of (usually bulky) waste which District Councils do not collect.
- Remove and dispose of vehicles abandoned within their areas.
- Take enforcement action against anyone who dumps anything illegally.

Town and Country Planning Act, 1971

Planning permission is almost always required for sites where waste is disposed of or re-loaded or treated. A licence under COPA cannot be issued unless there is a valid planning consent. The County Council determines applications for waste disposal activities as well as subsequently granting licenses under COPA.

Planning deals with matters of principle, amenity, highways and the like, attaching conditions which can remain with the land before, during and after the activities in question.

Licensing deals with detailed measures necessary to safeguard the environment and public health, but, at present, only applies whilst disposal activities are taking place.

To assist in the planning process the County and District Councils prepare:

- A Structure Plan, which sets out the strategic policies and general proposals for development and other uses of land in the County.
- Local Plans, which show in detail how policies in the Structure Plan are applied to precise areas of land (in cities, town and villages).

- Subject Plans, which deal with the application of Structure Plan policies to specific industries or topics (such as minerals or waste disposal).

At present the provisions under COPA apply only to the activity of waste disposal and to the licence holder, whereas planning requirements apply to the land itself. Any requirements that should continue after operations have ceased, such as controls on escaping leachate or gas, and to the rehabilition of surface soils, should therefore be attached to the planning permission rather than the licence.

Other Legislation

Many provisions apply in some way to the waste industry but the ones which have a significant effect are:

The **Liter Act 1983**, although not fully implemented, sets up Litter Authorities and charges County Councils with a duty to investigate and co-ordinate activities to abate litter in their areas, consulting widely with all relevant sectors of the community and industry and publishing a Litter Plan or Statement of Intent.

The **Radioactive Substances Act, 1960** places responsibility for control of all radioactive substances and wastes with the Department of the Environment rather than WDAs. NIREX is the agency appointed to dispose of nuclear wastes within the meaning of the Nuclear Installations Act, 1965.

The **Health and Safety at Work, etc. Act, 1974** places general duties on employers to secure the health, safety and welfare of their employees, as well as anyone else who may be affected by the work concerned. It also requires that the best practicable means is used to control emissions of harmful or offensive substances from their works.

The **Alkali Acts** require registration of, for instance, chemical incinerators, and applies restrictions to control air pollution.

The **Food and Environmental Protection Act, 1985** and other regulations prohibit certain wastes from being disposed of at sea, requiring safe disposal on land. Other legislation requires WDAs to dispose of hazardous materials which are washed up on beaches etc., and to assist in the disposal of oil and other pollutants.

An Environmental Protection Bill is passing through Parliament and will shortly be enacted as the Environmental Protection Act (1990). This will impose a new concept of Ingegrated Pollution Control to all media (air, wateer, land) and will impose new regulations and procedures with respect to waste.

United States

Disposal Regulations

High volume wastes from coal-fired utility boilers had been exempted from the hazardous waste provisions of the 1976 Resource Conservation and Recovery Act pending completion of a comprehensive study by the Environmental Protection Agency (EPA) assessing the adverse effects on human health and the environment. In the interim, regulation of these wastes is primarily carried out under the authority of state solid waste laws which vary widely. It is therefore difficult to generalize about the extent of state regulation of coal combustion wastes; some states have very stringent regulations and/or policies, such as those that impose design and operating standards and on-site and off-site permit requirements, whereas other states have few requirements or exempt on-site disposal from regulation. For a number of states, requirements are determined on a case-by-case basis. This allows the states to take climatic, geologic, and other site-specific characteristics into account for each waste management facility.

The EPA completed and submitted its study to the Congress on March 8, 1988. The primary tentative recommendations are as follows:

- Ash, slag and FGD wastes from coal-fired boilers generally do not exhibit hazardous waste characteristics and EPA does not intend to regulate these wastes under the RCRA hazardous waste provisions.

- Certain low volume wastes from metal and boiler cleaning operations may exhibit hazardous characteristics in terms of corrosivity or toxicity. EPA will consider whether such wastes should be regulated as hazardous.

- EPA encourages the utilization of coal combustion wastes as one method for reducing the amount of wastes that need to be disposed of to the extent such utilization can be done in an environmentally acceptable manner.

Prior to reaching any regulatory determinations concerning these preliminary findings, a six-month period is provided for public hearings, consultations with other agencies, and further analysis. To date (10/90) EPA has not proceeded further on regulating coal wastes.

12 CONCLUSIONS AND RECOMMENDATIONS

12.1 Conclusions

1. As efforts for the reduction of SO_2- and NO_x-emissions from stationary sources to comply with environmental goals (e.g. fuel cleaning and flue gas treatment) are enforced in the member states the amounts of by-product will increase.

2. Due to changing energy scenarios in different countries an accurate forecast of future volumes of by-product generated is difficult and results therefore in uncertainty of the data.

3. Volumes of by-products are now substantial. Within countries contributing data, by-products generated in the late eighties are projected to increase until the year 2000,

   from oil and gas treatment by about 15 %,
   from FGD by about 200 %,
   from conventional combustion by about 50 %,
   from FBC by about 60 % and
   from municipal waste combustion plants by about 20 %.

4. The reclamation and decommissioning of emission control waste disposal sites warrants careful investigation so the land is suitable for beneficial uses by future generations, unrestricted by environmental and health concerns.

5. If by-product management is to be successful, it is important that no product is considered in isolation and that no generalized decisions are made. As a result of differences in fuel quality, origin and types of raw material, treatments, combustions systems and flue gas treatment technology the physical and chemical properties of by-products vary considerably. Therefore generalized decisions in favour of specific forms of utilization and disposal are meaningless.

6. Environmental concerns associated with by-products from Flue Gas Emission Control Systems can be reduced or eliminated by the application of available environmental protection technologies and practices.

7. Certain by-products may require disposal. Many countries have classifications systems and legislation governing the utilization and disposal of waste.

8. Conventional coal cleaning results in a waste which is usually disposed of. Treatment of liquid and gaseous fuels results in a usable by-product (sulphur).

9. Conventional coal combustion processes produce large amounts of ash and slag which it is possible to utilize. However, ashes under some conditions cannot be utilized.

10. In all member countries utilization of these ashes is basically to be considered as a state of the art. In some member countries up to 80 % and more of the arising amount is utilized.

11. The number of FGD installations is increasing rapidly within the ECE region. Currently the lime/limestone gypsum processes are the most commonly used. By-products and wastes from desulphurization processes are:

Usable:	Gypsum Magnesia compounds Sulphur, sulphur dioxide and sulphuric acid Ammonium sulphate

Probably usable (R & D):	Mixtures of $CaSO_3$, $CaSO_4$, $CaCO_3$ and fly ash
- Not usable:	Condensates Waste water Sludges from waste water treatment

12. The decision on the technology to be used for desulphurization of flue gases has far reaching and long term consequences. The impact on the environment caused by the technology chosen is to a great extent dependent on the manner of utilization and disposal of the by-products from the selected technology.

13. The only one of the combined systems for SO_x- and NO_x-removal which is commercially available, the activated carbon process, generates usable by-products.

14. $DeNO_x$-processes (primary and secondary) may influence fly ash in a negative manner with respect to utilization (e.g. carbon and NH_3 content).

15. FBC is an available technology to reduce both the SO_2- and NO_x-emissions. At present there is no large scale utilization of the by-products.

16. At IGCC-plants the sulphur content of the fuels is recovered in an usable form. The main residues are slag and sludge from waste water treatment. Data on uses and properties of these latter materials are sparse. However, this technique will not contribute a significant amount to the total formation of by-products till the year 2000.

17. By-products from municipal waste incineration plants are to be considered separately due to their contents of toxic compounds. In some countries slag is utilized for road construction, while in other countries it has to be disposed of, sometimes with pretreatment. In some countries flue gas treatment by-products and filter cakes from waste water treatment have to be handled the same way like toxic materials.

18. In all contributing countries enhanced R & D is done in most of the following fields:

    - improving the quality of usable products
    - development of further processes to generate usable by-products
    - treatment of yet unusable by-products to receive usable ones
    - treatment of toxic by-products to produce less or not toxic ones.

19. The practical utilization of by-products from dry FGD systems, sorbent injection systems and fluidized bed combustions, warrants further reasearch, development and demonstration. Full consideration should be given to all environmental and health concerns.

20. The appropriate management of by-products from thermal power emission control systems, provides practical opportunities to apply the principle of "sustainable development" as advocated by the Brundtland World Commission on Environment and Development. The United Nations Economic Commission for Europe is playing an important role in encouraging these opportunities.

12.2 Recommendations

1. By-product utilization and waste management from fuel treatment and combustion systems, should be consistent with "Sustainable Development".

2. The process of energy production and consumption has to be viewed by all parties as one system whereas the fuel treatment and flue gas treatment is only one part of the whole. Considerations concerning by-products are strongly influenced by energy saving measures and the energy conversion efficiency. Therefore these parts of the energy life cycle have to be handled with priority and will also result in a lower amount of by-products.

3. An integrated approach to environmental protection should be adopted and the management and fate of by products should be considered for the whole cycle at the earliest possible stage of the selection, planning and operation of any energy conversion system.

4. The aim should be to avoid the production of waste where possible.

5. Where residuals are generated they should be produced and/or treated in a way that will encourage their utilization rather than disposal. By-products should be used in an environmentally acceptable manner.

6. The concept of clean technologies should be enforced within power plants and other industrial installations. This has been shown in many cases to have long term economic and environmental benefits.

7. The decision on utilization of by-products should be based on chemical and physical properties and environmental goals. There are today available different test methods which could be used to classify residuals and to evaluate environmental effects.

8. To ensure the proper management of residuals in the long term, new possibilities for utilization should be explored and R & D should be implemented. This not only applies to by-products now utilized (e.g. FGD gypsum), but especiallly to residuals which have not yet been widely utilized (such as FBC ash).

9. In many cases the utilization of residuals is still governed by economic considerations. Residuals often compete with natural materials. One must ensure that the utilization of residuals is not hampered by inappropiate product norms. Fiscal and regulative measures can be used to promote the replacement of natural materials and the utilization of by-products.

10. The use of residuals for landfilling, land reclamation, soil conditioning or other applications with characteristics similar to disposal has to comply with environmental goals and long term land uses. Environmental pollution by long term processes (e.g. leaching) must be considered. Methods for the analyses and assessment of land fill products should reflect the actual and long term behaviour of substances in a land fill as accurately as possible. The leaching methods, for example, have to be reviewed with this respect.

11. Even where a high degree of utilization can be achieved it will still be necessary to have contingency plans for storage and disposal.

12. The primary method of fulfilling environmental criteria should be to minimize and contain the waste and not solely to dilute the residue with other material.

13. If utilization is not possible, it should be the aim to produce residuals that have minimum impact on the environment.

    If material has to be disposed of, the siting and design of the site must take account of all relevant physical and chemical characteristics of the waste, future uses for the site and environmental goals. It should be the aim to avoid long-term technical interventions but technical (e.g. monitoring) and financial provisions should be made as appropiate to ensure that future generations are protected.

14. With the use of advanced disposal techniques the cost of disposal can be expected to rise and therefore encourage the utilization of by-products and the adoption of clean technologies. Disposal sites should be carefully regulated by the responsible authorities.

15. Further R & D and exchange of information between member countries of ECE should be implemented in order to help to achieve these recommendations.

16. The subject of "By-Product Utilization and Waste Management from Fuel Treatment and Combustion" should be a major topic during the next seminar of ECE.

ANNEX I

LEACHING PROCEDURES

1.) Leaching Test According to the ASTM

This selection of tests covers a wide range of situations which could occur in an actual dump. The ASTMA is a pure water extraction test and is used to simulate rainwater percolating through a stable landfill. ASTMB uses a more aggressive leaching media (sodium acetate-acetic acid) and is considered to give an indication of longer term leaching. The CAE method attempts to simulate an actively decomposing landfill which releases volatile organic acids.

2.) DEV-S4 (German Standard Leaching Test)

10 grams of a dry probe is shaked slowly with one liter of double distilled water for 24 hours and filtered afterwards. Filtrate is used for analyses.

3.) The Swedish Leaching Procedure

The sample and water (acidified with sulphuric acid to pH 4) are shaken for about 24 hours and the mixture is then filtered. The test is repeated according to procedure shown in figure I.1. The amount leached from the waste is dependent on the total amount of water contacted a certain waste amount. The quality of the leachate is described as a function of the liquid-solid ratio (L/S). (Lundgren and Elander, 1986)

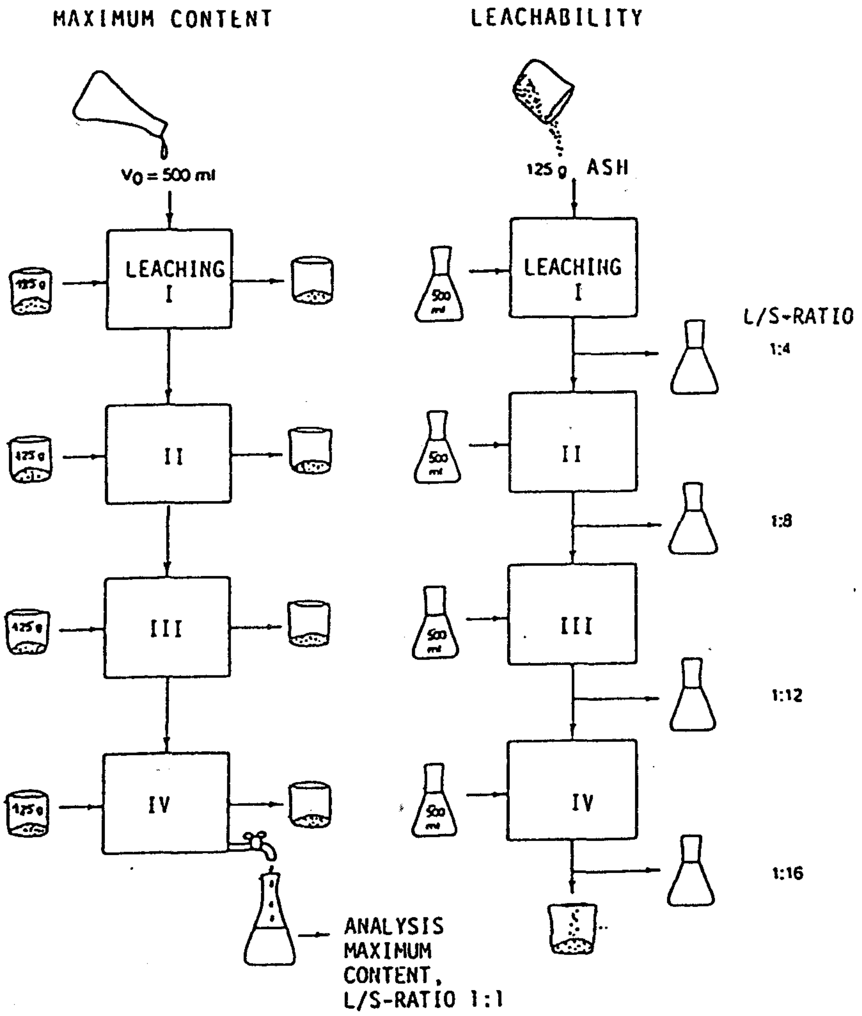


Figure I.1: Flow Sheet of the Swedish Leaching Procedure

4.) Canadian Leachate Extraction Procedure (164-GP-1 MP)

1 Apparatus

1.1 Sieve, 9.5 mm mesh opening, stainless steel or plastic material.

1.2 Stainless steel filtration unit, 142 mm diameter, minimum 1 L capacity, capable of sustaining a pressure of 500 kPa, applied to the solution to be filtered.

1.3 Membrane filter, 142 mm diameter, 0.45 µm diameter pore size, made of synthetic organic material such as teflon, cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is campatible with the leachate to be filtered. Teflon is recommended for organic constituents.

1.4 Glass fibre prefilter, 124 mm diameter, 3 µm to 12 µm pore size range.

1.5 Vacuum filtration unit, 90 mm diameter.

1.6 Membrane filter 90 mm diameter, 0.45 µm diameter pore size, made of synthetic organic material such as teflon, cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is compatible with the leachate to be filtered. Teflon is recommended for organic constituents.

1.7 Glass fibre filter 70 mm diameter, 3 µm to 12 µm pore size range.

1.8 Solid waste rotary extractor - a device that rotates the bottles end over end about a central axis through 360 °, with a speed of 10 rpm. The dimensions of the box will depend on the needs of each laboratory.

1.9 Structural Integrity Tester with a 31.8 mm diameter hammer weighting 0.33 kilogram and having a freee fall of 152.4 mm.

1.10 pH meter, with a readability of 0.01 pH unit and accuracy of ± 0.1 pH units.

1.11 Cylindrical bottles, wide mouth, 1250 mL capacity, polyethylene or glass with lined cap for inorganic constituents; glass with Teflon-lined cap or Teflon bottles for organic constituents.

2 Reagents and Materials

2.1 Acetic acid 0.5 N. Dilute 29.4 mL of concentrated acetic acid (American Chemical Society (ACS) reagent grade) to 1000 mL with reagent water.

2.2 Reagent water, Type IV in accordance with ASTM Specification D 1193 "Reagent Water". For organic parameters, the reagent water shall be free of any organic substances to be analyzed, Type I in accordance with ASTM Specification D 1193.

2.3 Nitric acid, 10 % (v/v). Add 100 mL of concentrated nitric acid (ACS reagent grade) to 900 mL of reagent water.

2.4 Nitrogen gas, pre-purified, scrubbed through a molecular sieve.

3 Sampling

3.1 Collect a sufficient amount of sample to provide approximately 100 g of solid material, using techniques set out in US EPA SW-846 "Test Methods for Evaluating Solid Waste".

4 Preparation of Apparatus

4.1 All glassware and equipment that comes into contact with the sample shall be cleaned in the following way before each use.

4.2 Wash with a non-phosphate detergent solution.

4.3 Rinse twice with tap water.

4.4 Rinse twice with reagent water.

4.5 Wash with 10 % nitric acid.

4.6 Rinse several times with reagent water.

4.7 Store bottles filled with 10 % nitric acid, until ready to use.

4.8 Rinse several times with reagent water before use.

4.9 Rinse clean oven dried bottles with methylene chloride, followed by methanol, for organic constituents.

5 Procedures

5.1 Separation Procedure

5.1.1 If the sample contains a distinct liquid and a solid phase, separate it into its component phases using the following procedure.

5.1.2 Determine the dry mass of the solids in the sample at 60 °C, using a well homogenized sample. Use this mass to determine the amount of material to be filtered.

5.1.3 Assemble the filtration unit with a filter bed consisting of a 0.45 µm pore size membrane filter and a coarse glass fibre pre-filter upstream of the membrane filter (per manufacturer's instructions).

5.1.4 Select one or more blank filters from each batch of filters. Filter 50 mL portions of reagent water through each test filter and analyze the filtrate for the analytical parameters of interest. Note the volume required to reduce the blank values to acceptable levels.

5.1.5 Wash each filter used in the leach procedure with at least this predetermined volume of water. Filter under pressure until no water flows through the filtrate outlet.

5.1.6 Remove the moist filter bed from the filtration unit and determine its mass to the nearest ± 0.01 g.

5.1.7 Re-assemble the filtration unit, replacing the filter bed, as before.

5.1.8 Grind the sample with a mortar and pestle, to a size that will pass through the opening of the filtration unit (less than 9.5 mm).

5.1.9 Agitate the sample by hand and pour a representative fraction of the solid and liquid phases into the opening of the filtration unit. Filter a sufficient amount of the sample to provide at least 60 g of dry solid material.

5.1.10 Pressurize the reservoir very slowly with nitrogen gas by means of the regulating valve on the nitrogen gas cylinder, until liquid begins to flow freely from the filtrate outlet.

5.1.11 Increase the pressure step-wise in increments of 50 kPa to a maximum of 500 kPa, as the flow diminishes. Continue filtration until the liquid flow ceases or the pressurizing gas begins to exit from the filtrate outlet of the filter unit.

5.1.12 De-pressurize the filtration unit slowly using the release valve on the filtration unit. Remove and weigh the solid material together with the filter bed to ± 0.01 g. Record the mass of the solid material.

5.1.13 Measure and record the volume and pH of the liquid phase. Store the liquid at 4 °C under nitrogen until required in 5.2.13.

5.1.14 Discard the solid portion if the mass is less than 0.5 % (w/v) of the fraction taken. If not, carry out the extraction procedure in 5.2.

Note: For mixtures containing coarse grained solids, where separation can be performed without imposing a 500 kPa differential pressure, a vacuum filtration unit with a filter bed as described in 5.1.3 may be used. Vacuum filtration must not be used if volatile organic compounds are to be analyzed.

5.2 Extraction Procedure

5.2.1 Prepare a solid sample for extraction by crushing, cutting or grinding, to pass through a 9.5 mm mesh sieve. If the original sample contains both liquid and solid phases, use the solid material from 5.1.14. The structural integrity procedure in 5.3 should be used for monolithic wastes which are expected to maintain their structural integrity in a landfill (e.g. some slags and treated solidified wastes).

Note: Do not allow the solid waste material to dry prior to the extraction procedure.

5.2.2 Determine the moisture content of the de-watered sample, by drying a suitable fraction to constant weight at 60 °C in an oven. Discard the dried solid material.

5.2.3 Place the equivalent of 50 g dry mass of the de-watered undried material into a 1250 mL wide mouth cylindrical bottle. Use additinal bottles, if a larger volume of leachate is required for the analysis.

5.2.4 Add 800 mL (less the moisture content of the sample in mL) of reagent water to the bottle.

5.2.5 Cap the bottle and agitate it in the rotary extractor for 15 minutes before measuring the pH.

5.2.6 Measure and record the pH of the solution in the bottle using a pH meter, calibrated with buffers pH 7.00 and pH 4.00. The solution should be stirred during the pH measurement.

5.2.7 If the pH is less than 5.2, carry out the procedure commencing at 5.2.10.1.

5.2.8 Add a sufficient volume of 0.5 N acetic acid if the pH is greater than 5.2 to bring the pH to 5.0 ± 0.2.

Note: Maximum Amount of Acid: No more than 4 mL of 0.5 N acetic acid per gram of dry mass of sample may be added during the entire procedure. If the pH is not lowered to 5.0 ± 0.2 with this amount, proceed with the extractioin.

5.2.9 Cap the bottle and place it in the solid waste rotary extractor. Rotate the bottle and its contents at 10 rpm for 24 hours at room temperature (20 °C to 25 °C).

5.2.10 Monitor, and manually adjust the pH during the course of the extraction, if it is greater than 5.2. The following procedure should be carefully followed:

5.2.10.1 Measure the pH of the solution after 1 hour, 3 hours and 6 hours from the starting time. If the pH is above 5.2, reduce it to pH 5.0 ± 0.2 by addition of 0.5 N acetic acid. If the pH is below 5.0 ± 0.2, do not make any adjustments.

5.2.10.2 Adjust the volume of the solution to 1000 mL with reagent water, if the pH is below 4.8 after 6 hours.

5.2.10.3 Measure and reduce the pH to 5.0 ± 0.2, if required, after 22 hours and continue the extraction for an additional 2 hours.

5.2.11 Add enough reagent water at the end of the extraction period so that the total volume of liquid is 1000 mL. Record the amount of acid added and the final pH of the solution.

5.2.12 Separate the material into its component liquid and solid phases as described under the Separation Procedure (5.1). Discard the solid portion.

<u>Note:</u> It may be necessary to centrifuge the suspension at high speed before filtration, for leachates containing very fine grained particles.

5.2.13 Calculate the amount of free liquid from 5.1.13 corresponding to 50 g of the dry solid material. Add this amount to the leachate from 5.2.12.

<u>Note:</u> If the analysis is not performed immediately, store separate fractions of the leachate at 4 ^{o}C, after adding appropriate preservatives for the analytical parameters of interest (see "US EPA SW-846 "Test Methods for Evaluating Solid Waste").

5.2.14 Analyze the combined solutions from 5.2.13 using methods set out in US EPA SW-846 "Test Methods for Evaluating Solid Waste" and which are capable of detecting the contaminants, that are likely to be present at the detection limits specified for each contaminant.

5.2.15 Report concentrations of contaminants in the combined leachate and the free liquid solution as mg/L.

5.2.16 Carry a blank sample through the entire procedure, using dilute acetic acid at pH 5.0 ± 0.2.

5.3 Structural Integrity Procedure

5.3.1 This procedure may be required prior to extraction for some samples as indicated in 5.2.1. It may be omitted for wastes with known high structural integrity.

5.3.2 Fill the sample holder with the material to be tested. If the sample of the waste is a large monolithic block, cut a portion from the block measuring 33 mm in diameter by 71 mm in length. For a treated waste (e.g. solidified waste) samples may be cast in a form with the above dimensions for the purposes of conducting this test. In such cases, the waste should be allowed to cure for 30 days prior to further testing.

5.3.3 Place the sample holder in the structural integrity tester, then raise the hammer to its maximum height and allow it to fall. Repeat this procedure 14 times.

5.3.4 Remove the material from the sample holder, and perform the extraction procedure (5.2). If the sample has not disintegrated, it may be sectioned; alternatively use the entire sample (after weighing) and a sufficiently large bottle as the extraction vessel. The volume of reagent water to be initially added is 16 mL/g of dry sample mass. The maximum amount of 0.5 N acetic acid to be added is 4 mL/g of dry sample mass. The final volume of the leachate should be 20 mL/g of dry sample mass.

ANNEX II

FBC PLANTS

Table II.1: FBC-Plants in Operation in the FRG in Mid of 1988 (Wein, 1988)

	I. Stationary Atmospheric Bed Combustion		
Owner	Location	Thermal Capacity	Year of Starting Operation
1. Ruhrkohle AG	Recklinghausen	6 MW_{th}	1979
2. SW Düsseldorf	Düsseldorf	35 MW_{th}	1979
3. Saarbergwerke AG	Afferde	5 MW_{th}	1980
4. Ruhrkohle AG	Dortmund	35 MW_{th}	1981
5. Bayer AG	Dormagen	30 MW_{th}	1982
6. HASTRA	Lüneburg	2 x 7 MW_{th}	1983
7. Sporthotel	Bad Honnef	0,5 MW_{th}	1983
8. Saarbergwerke AG	Völklingen	2 x 80 MW_{th}	1983
9. EW Wesertal	Hameln	124 MW_{th}	1984
10. Ruhrkohle AG	Niederberg	11 MW_{th}	1984
11. Bergbauforschung	Essen	3 MW_{th}	1984

	II. Circulating Pressurized FBC		
Owner	Location	Thermal Capacity	Year of Starting Operation
1. RWTH	Aachen	20/40 MW_{th}	1985
2. Babcock	Friedrichsfeld	15 MW_{th}	1988

Table II.1: FBC-Plants in Operation in the FRG in Mid of 1988 (Wein, 1988)

	III. Circulating Atmospheric FBC		
Owner	Location	Thermal Capacity	Year of Starting Operation
1. VAW	Lünen	84 MW_{th}	1982
2. SW Duisburg	Duisburg	226 MW_{th}	1985
3. SW Flensburg	Flensburg	117 MW_{th}	1985
4. Köhler	Oberkirch	74 MW_{th}	1987
5. Rheinbraun		2 x 150 MW_{th}	1988
6. SW Flensburg	Flensburg	117 MW_{th}	1988
7. SW Offenbach	Offenbach	2 x 80 MW_{th}	1988
8. BEWAG	Berlin	240 MW_{th}	1989
9. PREAG	Kassel	140 MW_{th}	1989
10. SW Wuppertal	Wuppertal	2 x 130 MW_{th}	1989
11. Bayer AG	Leverkusen	105 MW_{th}	1988
12. Volkswagen AG	Wolfsburg	2 x 150 MW_{th}	1988
13. TW Stuttgart	Gaisburg	100 MW_{th}	1988
14. SW Pforzheim	Pforzheim	80 MW_{th}	1988
15. Sachtleben	Duisburg	100 MW_{th}	1989
16. GEW Köln	Köln	220 MW_{th}	1989
17. Harpener AG	Dortmund	42 MW_{th}	1989
18. Thyssen	Kassel	38 MW_{th}	1988
19. SW Saarbrücken	Saarbrücken	116 MW_{th}	1989
20. Rheinbraun	Berrenrath	2 x 210 MW_{th}	1991

Table II.2: FBC-Plants Applied in Austrian Industrial Plants (Weisser and Hanzenberger, 1988)

Owner	Kind of Industry	Kind of Process (Thermal Capacity)	Degree of Desulphurization	Year of Starting Operation
Frantschacher Papier- u. Zellstoffabrik (Frantschach)	paper and pulp	CFBC with additives (63 MW)	95 %	1983
Papierfabrik Hamburger AG (Pitten)	paper	FBC with additives (67 MW)	95 %	1984
Leykam-Mürztaler Papier- u. Zellstoff-fabrik (Gratkorn)	paper and pulp	CFBC with additives (130 MW)	90 %	1987
Lenzing AG (Lenzing)	pulp and viscose	CFBC with additives	-	1987

ANNEX III

EXTRACT BASEL CONVENTION

1) BASEL CONVENTION ON THE CONTROL OF TRANSBOUNDARY MOVEMENTS OF HAZARDOUS WASTES AND THEIR DISPOSAL (extracted)

Article 2

Definitions

For the purpose of this Convention:

1. "Wastes" are substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law.

2. "Management" means the collection, transport and disposal of hazardous wastes or other wastes, including after-care of disposal sites.

3. "Transboundary movement" means any movement of hazardous wastes or other wastes from an area under the national jurisdiction of one State to or through an area under the national jurisdiction of another State or to or through an area not under the national jurisdiction of any State, provided at least two States are involved in the movement.

4. "Disposal" means any operation specified in "Disposal Operations" later on.

5. "Approved site or facility" means a site or facility for the disposal of hazardous wastes or other wastes which is authorized or permitted to operate for this purpose by a relevant authority of the State where the site or facility is located.

6. "Competent authority" means one governmental authority designated by a Party to be responsible, within such geographical areas as the Party may think fit, for receiving the notification of a transboundary movement of hazardous wastes or other wastes, and any information related to it, and for responding to such a notification, as provided in Article 6.

7. "Focal point" means the entity of a Party referred to in Article 5 responsible for receiving and submitting information as provided for in Articles 13 and 16.

8. "Environmentally sound management of hazardous wastes or other wastes" means taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against the adverse effects which may result from such wastes.

9. "Area under the national jurisdiction of a State" means any land, marine area or airspache within which a State exercises administrative and regulatory responsibility in accordance with international law in regard to the protection of human health or the environment.

10. "State of export" means a Party from which a transboundary movement of hazardous wastes or other wastes is planned to be initiated or is initiated.

11. "State of import" means a Party to which a transboundary movement of hazardous wastes or other wastes is planned or takes place for the purpose of disposal therein or for the purpose of loading prior to disposal in an area not under the national jurisdiction of any State.

12. "State of transit" means any State, other than the State of export or import, through which a movement of hazardous wastes or other wastes is planned or takes place.

13. "States concerned" means Parties which are States of export or import, or transit States, whether or not Parties.

14. "Person" means any natural or legal person.

15. "Exporter" means any person under the jurisdiction of the State of export who arranges for hazardous wastes or other wastes to be exported.

16. "Importer" means any person under the jurisdiction of the State of import who arranges for hazardous wastes or other wastes to be imported.

17. "Carrier" means any person who carries out the transport of hazardous wastes or other wastes.

18. "Generator" means any person whose activity produces hazardous wastes or other wastes or, if that person is not known, the person who is in possession and/or control of those wastes.

19. "Disposer" means any person to whom hazardous wastes or other wastes are shipped and who carries out the disposal of such wastes.

20. "Political and/or economic integration organization" means an organization constituted by sovereign States to which its member States have transferred competence in respect of matters governed by this Convention and which has been duly authorized, in accordance with its internal procedures, to sign, ratify, accept, approve, formally confirm or accede to it.

21. "Illegal traffic" means any transboundary movement of hazardous wastes or other wastes as specified in Article 9.

Article 3

National Definitions of Hazardous Wastes

1. Each Party shall, within six months of becoming a Party to this Convention, inform the Secretariat of the Convention of the wastes, other than those listed in Annexes I and II, considered or defined as hazardous under its national legislation and of any requirements concerning transboundary movement procedures applicable to such wastes.

2. Each Party shall subsequently inform the Secretariat of any significant changes to the information it has provided pursuant to paragrah 1.

3. The Secretariat shall forthwith inform all Parties of the information it has received pursuant to paragrahs 1 and 2.

4. Parties shall be responsible for making the information transmitted to them by the Secretariat under paragraph 3 available to their exporters.

Categories of Wastes to be Controlled

Waste Streams

Y1 Clinical wastes from medical care in hospitals, medical centers and clinics

Y2 Wastes from the production and preparation of pharmaceutical products

Y3 Waste pharmaceuticals, drugs and medicines

Y4 Wastes from the productions, formulation and use of biocides and phytopharmaceuticals

Y5 Wastes from the manufacture, formulation and use of wood preserving chemicals

Y6 Wastes from the production, formulation and use of organic solvents

Y7 Wastes from heat treatment and tempering operations containing cyanides

Y8 Waste mineral oils unfit for their originally intended use

Y9 Waste oils/water, hydrocarbons/water mixtures, emulsions

Y10 Waste substances and articles containing or contaminated with polychlorinated biphenyls (PCBs) and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs)

Y11 Waste tarry residues arising from refining, distillation and any pyrolytic treatment

Y12 Wastes from production, formulation and use of inks, dyes, pigments, paints, lacquers, varnish

Y13 Wastes from production, formulation and use of resins, latex, plasticizers, glues/adhesives

Y14 Waste chemical substances arising from research and development or teaching activities which are not identified and/or are new and whose effects on man and/or the environment are not known

Y15 Wastes of an explosive nature not subject to other legislation

Y16 Wastes from production, formulation and use of photographic chemicals and processing materials

Y17 Wastes resulting from surface treatment of metals and plastics

Y18 Residues arising from industrial waste disposal operations

Wastes having as Constituents

Y19 Metal carbonyls
Y20 Beryllium; beryllium compounds
Y21 Hexavalent chromium compounds
Y22 Copper compounds
Y23 Zinc compounds
Y24 Arsenic; arsenic compounds
Y25 Selenium; selenium compounds
Y26 Cadmium; cadmium compounds
Y27 Antimony; antimony compounds
Y28 Tellurium; tellurium compounds
Y29 Mercury; mercury compounds
Y30 Thallium; thallium compounds
Y31 Lead; lead compounds
Y32 Inorganic fluorine compounds excluding calcium fluoride
Y33 Inorganic cyanides
Y34 Acidic solutions or acids in solid form
Y35 Basis solutions or bases in solid form
Y36 Asbestos (dust and fibres)
Y37 Organic phosphorous compounds
Y38 Organic cyanides
Y39 Phenols; phenol compounds including chlorophenols
Y40 Ethers
Y41 Halogenated organic solvents
Y42 Organic solvents excluding halogenated solvents
Y43 Any congenor of polychlorinated dibenzo-furan
Y44 Any congenor of polychlorinated dibenzo-p-dioxin
Y45 Organohalogen compounds other than substances referred to in this Annex (eg. Y39, Y41, Y42, Y43, Y44).

Categories of Wastes Requiring Special Consideration

Y46 Wastes collected from households
Y47 Residues arising from the incineration of household wastes

List of Hazardous Characteristics

UN Class*)	Code	Characteristics
1	H1	Explosive An explosive substance or waste is a solid or liquid substance or waste (or mixture of substances or wastes) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings.
3	H3	Flammable liquids The word "flammable" has the same meaning as "inflammable". Flammable liquids are liquids, or mixtures of liquids, or liquids containing solids in solution or suspension (for example, paints, varnishes, lacquers, etc., but not including substances or wastes otherwise classified on account of their dangerous characteristics) which give off a flammable vapour at temperatures of not more than 60.5 °C, closed-cup test, or not more than 65.6 °C, open-cup test. (Since the results of open-cup tests and of closed-cup tests are not strictly comparable and even individual results by the same test are often variable, regulations varying from the above figures to make allowance for such differences would be within the spirit of this definition.)

4.1 H4.1 Flammable solids

Solids, or waste solids, other than those classed as explosives, which under conditions encountered in transport are readily combustible, or may cause or contribute to fire through friction.

4.2 H4.2 Substances or wastes liable to spontaneous combustion

Substances or wastes which ae liable to spontaneous heating under normal conditions encountered in transport, or to heating up on contact with air, and being then liable to catch fire.

4.3 H4.3 Substances or wastes which, in contact with water emit flammable gases

Substances or wastes which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

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*) Corresponds to the hazard classification system included in the United Nations Recommendations on the Transport of Dangerous Goods (ST/SG/AC.10/1/Rev.5, United Nations, New York, 1988).

5.1	H5.1	Oxidizing Substances or wastes which, while in themselves not necessarily combustible, may, generally by yielding oxygen cause, or contribute to, the combustion of other materials.
5.2	H5.2	Organic Peroxides Organic substances or wastes which contain the bivalent-O-O-structure are thermally unstable substances which may undergo exothermic self-accelerating decomposition.
6.1	H6.1	Poisonous (Acute) Substances or wastes liable either to cause death or serious injury or to harm human health if swallowed or inhaled or by skin contact.
6.2	H6.2	Infectious substances Substances or wastes containing viable micro organisms or their toxins which are known or suspected to cause disease in animals or humans.
8	H8	Corrosives Substances or wastes which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport; the may also cause other hazards.
9	H10	Liberation of toxic gases in contact with air or water Substances or wastes which, by interaction with air or water, are liable to give off toxic gases in dangerous quantities.

9	H11	Toxic (Delayed or chronic) Substances or wastes which, if they are inhaled or ingested or if they penetrate the skin, may involve delayed or chronic effects, including carcinogenicity.
9	H12	Ecotoxic Substances or wastes which if released present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems.
9	H13	Capable, by any means, after disposal, of yielding another material, e.g., leachate, which possesses any of the characteristics listed above.

Disposal Operations

A. Operations which do not lead to the possibility of resource recovery, recycling, reclamation, direct re-use or alternative uses

Section A encompasses all such disposal operations which occur in practice.

D1 Deposit into or onto land (e.g., landfill, etc.)

D2 Land treatment (e.g., biodegradation of liquid or sludgy discards in soils, etc.)

D3 Deep injection (e.g., injection of pumpable discards into wells, salt domes or naturally occurring repositories, etc.)

D4 Surface impoundment (e.g., placement of liquid or sludge discards into pits, ponds or lagoons, etc.)

D5 Specially engineered landfill (e.g., placement into lined discrete cells which are capped and isolated from one another and the environment, etc.)

D6 Release into a water body except seas/oceans

D7 Release into seas/oceans including sea-bed insertion

D8 Biological treatment not specified elsewhere in this Annex which results in final compounds or mixtures which are discarded by means of any of the operations in Section A

D9 Physico chemical treatment not specified elsewhere in this Annex which results in final compounds or mixtures which are discarded by means of any of the operations in Section A (e.g., evaporation, drying, calcination, neutralization, precipitation, etc.)

D10 Incineration on land

D11 Incineration at sea

D12 Permanent storage (e.g., emplacement of containers in a mine, etc.)

D13 Blending or mixing prior to submission to any of the operations in Section A

D14 Repackaging prior to submission to any of the operations in Section A

D15 Storage pending any of the operations in Section A

B. Operations which may lead to resource recovery, recycling, reclamation, direct re-use or alternative uses

Section B encompasses all such operations with respect to materials legally defined as or considered to be hazardous wastes and which otherwise would have been destined for operations included in Section A

R1 Use as a fuel (other than in direct incineration) or other means to generate energy

R2 Solvent reclamation/regeneration

R3 Recycling/reclamation of organic substances which are not used as solvents

R4 Recycling/reclamation of metals and metal compounds

R5 Recycling/reclamation of other inorganic materials

R6 Regeneration of acids or bases

R7 Recovery of components used for pollution abatement

R8 Recovery of components from catalysts

R9 Used oil re-refining or other reuses of previously used oil

R10 Land treatment resulting in benefit to agriculture or ecological improvement

R11 Uses of residual materials obtained from any of the operations numbered R1 - R10

R12 Exchange of wastes for submission to any of the operations numbered R 1 - R11

R13 Accumulation of material intended for any operation in Section B

2) EEC DEFINITIONS

The EEC definition from 1978 is as follows (Council of European Communities Directive on Toxic and Dangerous Waste; 78/319/EEC-OJ L 84, 31 March 1978):

"(a) "Waste" means any substance or object which the holder disposes of or is required to dispose of pursuent to the provisions of national law in force.

(b) "Toxic or Dangerous Waste" means any waste containing or contaminated by the substances or materials listed in the Annex to this Directive of such a nature, in such quantities or in such concentrations as to constitute a risk to health or the environment.

(c) "Disposal" means
- the collection, sorting, carriage and treatment of toxic and dangerous waste, as well as its storage and tipping above or under gorund.
- the transformation processes necesseary for its recovery, re-use or recycling."

ANNEX IV

STANDARDS FOR DISPOSAL FOR WASTE

Canada

Guidelines for the disposal of municipal and other wastes have been developed by the Canadian Council of Ministers of the Environment (CCME). These guidelines cover the characterization of wastes and the siting, design, construction, operation and closure of waste disposal sites.

Federal Republic of Germany

The Länder Arbeitsgemeinschaft provides guidelines, updated June 1986, as follows:

a) Landfills must have a sealed base.

b) Leachate treatment must be provided.

c) Fly ash must be dampened, conditioned or packaged so as to prevent windblown dust or dust being washed away by rain during filling operations.

d) The landfill must be operated in such a way that the fly ash does not come into contact with leachate containing oils or solvents.

e) When the landfill or section of the landfill is completed it should be capped to prevent erosion and leachate infiltration. This need not to be done if the fly ash has been packaged or solidified.

f) The solidification of the fly ash may be considered as an additional safety measure.

g) Bottom ash may be deposited advantageously with fly ash on account of its pozzuolanic properties.

In Bavaria they have tried a solidification process to prevent leaching of heavy metal.

Netherlands

Under the Chemical Waste Act (although the ash is exempted as such) would cause it to be just on the borderline of being classed as a chemical waste. The Dutch have great problems with landfill disposal as there is risk of contaminating the high water table. There are only a few sites licensed to accept chemical wastes some municipal waste fly ash has been sent to special sites in Belgium and Germany. Nowadays it is partly disposed off, in the Netherlands, partly utilized.

A preliminary draft of an ordinance on soil protection from the use of building materials is in discussion. This ordinance can influence the application of combustion residues in or as building materials. Building materials will be classified according to their contents of heavy metals, aromatics, PAH's, mineral oil and chlorinated organic compounds. The ordinance holds for bulk material as well as for ready products.

Switzerland

The Swiss Commission for Wastes has set up a list of requirements and standards concerning the treatment and disposal of wastes (Bundesamt für Umweltschutz, 1987).

Main points are:

A) A minimum of 90 % of the matrix of a residue has to be known by chemical analysis, including trace elements.

B) Within the residue of combustion the total organic carbon (TOC) should not exceed 5 % (TF weight) and the content of soluble salts should not exceed 5 % (TF weight).

C) For disposal it is necessary that the leachate generated in a special standardized test does not exceed those standards which are given in "Verordnung über Abwassereinleitungen vom 8. Dezember 1975" for discharge surface water. Furthermore the amount of a single pollutant leached out in a test should not exceed 0,5 ^{o}/oo of the original content.

D) Test bricks have to have a mechanical stability of 1 N/mm^3 (10 kg/cm^2) after a hardening period of 7 - 14 days.

United Kingdom

Municipal waste fly ash is normally landfilled in the United Kingdom but the levels of heavy metals are insufficiently high for them to be classed as "Special Wastes" under Section 17 of the Control of Pollution Act 1974. However, all landfill sites are licensed and the licence conditions should take note of the national guidelines in the Waste Management Papers on landfilling wastes, cadmium and mercury bearing wastes. The licence conditions are site specific and site selection is regarded as an all important factor.

United States of America

The US Environmental Protection Agency (EPA) has started to develop a regulatory programme for MSW ash. The programme, which has long been requested by environmentalists and congress, will be based on voluntary guidelines for ash handling and disposal at first. At the same time it will stimulate research on recycling and re-use technology.

According to EPA standards, ash that passes the Extraction Procedure (EP) test may be recycled or placed in a solid waste landfill, which might not be lined or monitored for ground water pollution. Ash that fails the EP test may be placed in a sanitary landfill with ground water monitoring, leachate collection and two liners. The lower liner must be a composite with a flexible membrane liner and a natural material such as compacted clay with a hydraulic conductivity below 1×10^{-7} cm/s.

The EPA's Office of Solid Waste has asked the 140 operators of US waste incinerators to provide information on ash handling. The OSW has also notified the operators that all facilities accepting wastes other than household refuse must have their ash tested for hazardous constituents.

The EPA intends to study possible air pollution from ash dust as well as ground water and surface water contamination from ash dust. This research, together with information from the facilites, will be used to develop appropriate regulations.

ANNEX V

ENVIRONMENT REGULATIONS CANADA

Table 11.1: Summary-Selected Site Selection Criteria for Waste Disposal Sites (Environment Canada, 1987b)

CRITERIA	
Land Use	
	Agriculture
C101	- Avoid areas which have prime agricultural capability on a regional scale.
	Forestry
C 102	- Avoid areas within or adjacent to blocks of intensively managed forest lands.
	Recreation
C103	- Avoid areas adjacent to relatively large designated or formally proposed federal, provincial or regional parks.
Terrestrial Ecology	
	Dedicated Ecological Lands
C104	- Avoid all federal, provincial and regional lands dedicated to the protection of flora, fauna and unique, natural, historical and archeological features.
	Wetlands
C105	- Avoid all large wetlands or wetland complexes in southern Canada.

Table 11.1: Summary-Selected Site Selection Criteria for Waste Disposal Sites (continued) (Environment Canada, 1987b)

CRITERIA

Rare and Endangered Species and Critical Wildlife Habitat

C106 - Avoid all known concentration areas of rare or endangered floral and faunal species, along with a buffer zone appropriate to the sensitivity of the individual species.

C107 - Avoid rare and endangered species habitat, other critical wildlife habitat including wildlife corridors, critical nesting areas and winter ungulate concentration areas, along with a buffer zone appropriate to the sensitivity of the species.

Ground Water

C112 - Avoid areas of highly fractured bedrock.

C113 - Avoid areas of thick, highly permeable sands and gravels.

C114 - Avoid areas of major recharge which are upgradient to major ground water users.

Aquatic Ecology

Major Fisheries and Spawning Grounds

C115 - Avoid areas near a major fishery or spawning ground.

Unique or Sensitive Aquatic Species

C116 - Avoid all areas of a water body containing known concentrations of unique or sensitive species.

C117 - Avoid areas adjacent to anadromous salmon streams.

Table 11.1: Summary-Selected Site Selection Criteria for Waste Disposal Sites (continued) (Environment Canada, 1987b)

CRITERIA	
	Sensitive Aquatic Environments
C118	- Avoid all areas adjacent to estuaries or coastal wetlands.
	Salt Marshes
C119	- Avoid all salt marshes and salt marsh complexes.
Atmospheric Environment	
	Officially Designated Areas and International Boundaries
C120	- Avoid areas close to the boundary of preserved national, provincial or other designated parklands, or close to international borders.
	Poor Air Quality Areas
C121	- Avoid areas where existing air quality is near or exceeds national or provincial air quality objectives, criteria and/or regulations.
	Urban Population Centres
C122	- Avoid locating stations near large urban centres.
	Unfavourable Topographic Areas
C123	- Avoid areas with poor atmospheric dispersion characteristics due to the influence of terrain features.

Table 11.2: Summary of Selected Recommendations Related to Waste Waters Disposal Sites and Waste (Environment Canada, 1985)

NUMBER	SUBJECT	SUMMARY OF RECOMMENDATION
Minimization of Contaminants and Waste Water Volumes		
R204	**Ash Handling** - System Selection	Select i) dry fly ash ii) recirculating bottom ash, unless demonstrated that alternatives will produce less waste water.
R205	**Flue Gas Desulphurization (FGD)** - System Selection/ Design	Select system, or design for zero discharge of process waste water, to extent practicable.
R206	**Water Reuse** - Design Provisions	If practicable, design for i) reuse of auxiliary cooling discharge ii) reuse of other waste waters.
R207	**Waste Disposal**	Design ash, FGD and refuse sites for i) modular development during operation ii) chemical and physical stability suitable for land re-use iii) site contouring and capping iv) reclamation prior to abandonment.

Table 11.2: Summary of Selected Recommendations Related to Waste Waters Disposal Sites and Waste (continued) (Environment Canada, 1985)

NUMBER	SUBJECT	SUMMARY OF RECOMMENDATION
Containment of Waste Waters and Waste Residues		
R208	**Waste Liquids** - Segregation and Containment	Design for i) containment of all waste waters ii) collection of similar waste waters iii) separate containments for hazardous wastes (e.g., PCBs, metal cleaning, radioactive) iv) separate containment for incompatible bulk chemicals.
R 209	**Containment Facilities** - Sizing Criteria	Design containments for normal volumes of waste water and i) maximum 24-hour waste water ii) maximum spills or leaks, or iii) 100-year 24-hour precipitation event for outside containments.

Table 11.2: Summary of Selected Recommendations Related to Waste Waters Disposal Sites and Waste (continued) (Environment Canada, 1985)

NUMBER	SUBJECT	SUMMARY OF RECOMMENDATION
R 210	Seepage Control - Permeability Criteria	Ensure that natural or constructed barriers exist between the bottom of the waste disposal site and the underlying aquifer, with minimum flow resistance equivalent to material 1 metre thick, of the following permeabilities: i) 1×10^{-7} cm/s for high sulphur (> 1 % s) coal piles, chemical and radioactive wastes ii) 5×10^{-7} cm/s for ash, FGD waste lagoons iii) $< 1 \times 10^{-6}$ cm/s for low sulphur coal piles (1 % s), dry ash (except for ash disposal in mines) and dry FGD waste sites iv) 1×10^{-5} cm/s for other areas.

Table 11.2: Summary of Selected Recommendations Related to Waste Waters Disposal Sites and Waste (continued) (Environment Canada, 1985)

NUMBER	SUBJECT	SUMMARY OF RECOMMENDATION
Treatment of Waste Waters Prior to Discharge		
R211	**Discharged Waste Waters** **- Effluent Limitations**	Design so that waste waters discharged to once-through cooling or receiving waters do not exceed following concentrations: pH 6.5 to 9.5 Fe 1.0 mg/l Cr, Cu, Ni, Zn 0.5 mg/l Cr (hexal) 0.05 mg/l TSS 25 mg/l Oil and Grease 15 mg/l TRC 0.2 mg/l

Table 11.3: Summary of Selected Recommendations Related to Monitoring of Waste Disposal Sites

NUMBER	SUBJECT	SUMMARY OF RECOMMENDATION
R210	Monitoring Facilities	Design so that they can be safely accessed and used.
R304	Discharged Waste Waters - Monitors	Provide for i) representative sampling ii) integrated flow monitors (± 10 % accuracy) iii) on-line pH, TRC or other monitors.
R305	Inplant Waters - Monitoring Considerations	Consider flow monitors and sampling facilities for in-plant water streams.
R306	Ground Waters - Monitors	Provide permanent piezometer/ well systems at coal storage and waste disposal sites.
R307	Ground Waters - Pre-operational Monitoring	Conduct pre-operational monitoring starting at least one year before construction.
R308	Aquatic Environment - Pre-operational Monitoring	Conduct pre-operational monitoring starting at least one year before construction to determine baseline data for biota, water quality and sediment.
R309	Environmental Data - Processing	Provide appropriate facilities for analyses, alarms, and data storage and retrieval.

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