CPD NR 3269

Conceptual Process Design
Basis of Design

Process Systems Engineering
DelftChemTech - Faculty of Applied Sciences
Delft University of Technology

Subject

Flue gas treatment system for new waste incineration plant (AVI) Amsterdam

Authors

Erkan Terli	015-2783568
Jan van Erven	015-2783568
Bas van Laarhoven	015-2783568
Koen van der Nat	015-2783568

Keywords

Waste incineration, Flue Gas Cleaning, DeNOx, DeSOx, Dioxins, High Temperature dust removal

Assignment issued	:	**10/15/01**
Report issued	:	**28/11/01**
Appraisal	:	**30/11/01**

Preface

This rapport is a result of a three months of teamwork of four students at the Delft University of Technology, the Netherlands. This project is a coöperation from AVI-Amsterdam, a waste incinerator. The scope of this project is to make a conceptual process design for aflue gas cleaning system a waste incinerator. Several possible ways to clean gases have been considered and compaired. A selection has been made from these options.

A high temperature ceramic filter (to remove particulates) followed by a SCR-unit (to remove NOx) next an absorber and two wetscrubbers are used (to remove acids, sulphur compounds and heavy metals).

Acknowledgements

There a number of people to whom we wish to express our gratitude.

Saul Lemkowitz We want to especially thank you for the many interesting meetings we had, in the beginning you provided us with some good literature. At times when we had trouble overlooking the project you helped us with a schematic approach.

Cor de Vries We thank you for helping us getting started with our project. You were always there for us to help us with your practical knowledge and experimental data.

D.H. Grunwald We enjoyed the meeting that we had with you and experienced it as very usefull. We think that good teamwork and creativity plays a very important role in a project like this CPD-project, and that "coaching" from a psychologist has a broadning effect.

We would also like to express our acknowledgements to the following people:

Mr. Regenauer (BASF AG)
Mr. A.B. Jensen (Haldor Topsøe)
Mr. R. Holste (BB-Power)
Mr. M. Joisten (Siemens)
Mr. B. Vissers (DSM)
Mrs. H. Gablinger (VonRoll)
Mr. J. Luteijn (AVR)
Mr. H. Wassenaar (AVR)

Mr. R. Sleijster (Huisvuilcentrale NH)
Mr. C. Stuart (Sita ReEnergy)
Mr. C. de Vries (AVI-Amsterdam)
Mr. B.Schneibner (USF Schumacher)
Mr. A. Sweers (Pall filtration company)
Mr. P.L.J. Swinkels (TU-Delft)
Mr. F. Kaptein (TU-Delft)
Mr. K.B. Geerse (TU-Delft)
Mr. M.T. Kreutzer (TU-Delft)
Mr. M. Makkee (TU-Delft)

Contents

Chapter 1

Introduction

1.1 Background

As a result of the growing prosperity in the western world, consumption is increasing. The growing consumption rate and the ever-growing population create a huge waste mountain. Furthermore, the content of hazardous compounds in the waste has increased.

Dutch policy towards the waste problem is based the so-called *"Ladder van Lansink"*(vvav,[1]). This policy gives a heuristic approach to the waste problem in the sense that it creates a hierarchical approach, starting from the best option and proceeding to the worst:

1. Prevention
2. Recycling
3. Incineration with energy generation
4. Deposition

1.2 Incineration

In the Netherlands 4,5 million-ton/annum of municipal waste is collected in 2000 (vvav[1]). From this waste stream 38% is incinerated in municipal waste incinerators (MWI). The rest of this stream is recycled, composted or deposited.

Incineration of municipal solid waste (MSW) has three advantages: reduction of volume by about 90%, reduction of the chemical reactivity of hazardous organic compounds, and the production of energy, typically in the form of steam, which is marketable. These incinerations processes, however, generate two main environmental problems: the solid and gaseous reaction products.

1.3 Emission legislation

During the incineration of the municipal waste and the cooling of the flue gases, many chemical reactions take place. Especially the incineration of chlorinated products (e.g. PVC) can lead to the formation of the highly toxic dioxins. The chemical waste that is present, for instance in the form of household batteries, can lead to the formation and emission of pollutants, like the vapour of elemental Hg and/or Hg and Cd compounds. The concentration of harmful components in the effluent gas stream should not exceed the values stated in the '1993 Regulations covering Refuse Incineration Air Emissions: BLA (See table 1.1 taken from: GDA information folder [2]). This is a standard for the maximum concentrations of various pollutants that a municipal and industrial waste incinerator is permitted to emit.

Table 1.1: 1993 Regulations covering Besluit Luchtverontreiniging Afvalverbranding: BLA 11 % O2, dry

Compound:	Concentration
Dust	5 mg/m^3
HCl	10 mg/m^3
HF	1 mg/m^3
SO_2	40 mg/m^3
NO_x	70 mg/m^3
CO	50 mg/m^3
Cd	0.05 mg/m^3
Hg	0.05 mg/m^3
C_xH_y	10 mg/m^3
Dioxin	0.30 ng/m^3

1.4 Expansion AVI Amsterdam

According to the Kyoto Convention (1997), the Netherlands must reduce it's CO2 emission by 5% (1990 taken as a basis) in the period 2008-2012 (vrom [3]). In order to reduce the CO2 emission, 10% of the total energy production must come from sustainable sources. The Dutch government has acknowledged waste for 50% as a sustainable energy source (van Berlo [4]). Because of this acknowledgement, the income of electricity production is 1.7 ct/kWh higher then normal.

In order to satisfy the increasing demand of waste processing capacity in the Netherlands, a total incineration capacity increase of 2.5 Mton/a is needed (vvav[1]). The MWI in Amsterdam (AVI-Amsterdam) has four incineration lines with a total capacity of 800,000 tons/a. In order to fulfil the need for incineration capacity expansion, AVI-Amsterdam has scheduled a capacity increase of 500,000 tons/a. Because of the provided subsidy on the "green" electricity, AVI Amsterdam has chosen for a high thermal efficiency boiler concept.

1.5 Project formulation

The design of the boiler and the incineration process is beyond the scope of this design. The existing flue gas treatment section will be the starting point of our design. A process flow scheme of the existing treatment section and a description of all the units and their (dis)advantages are made. A mass/component balance over the different units is made to give insight in the performance of each unit. The information used to setup the component balance is based on the measured stream compositions of the effluent streams from the different units from AVI-Amsterdam.

A flow diagram of the flue gas cleaning system that is currently used at AVI Amsterdam is shown if figure 1.1.

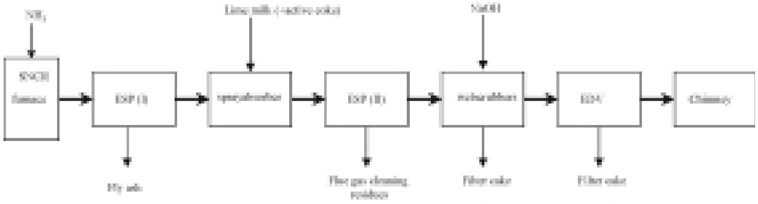


Figure 1.1: Process Flow Diagram, flue gas cleaning section, AVI Amsterdam

The feedstock composition of the new flue gas treatment section is the flue gas composition leaving the existing boiler section. From Dutch law (Besluit Luchtemissies Afvalverbranding, BLA) we know the maximum allowable concentrations of many pollutants in the effluent gas stream. Therefore the mass flow in and the mass flow out of the process. The flue gas cleaning systems is represented by a black box, see figure 1.2.

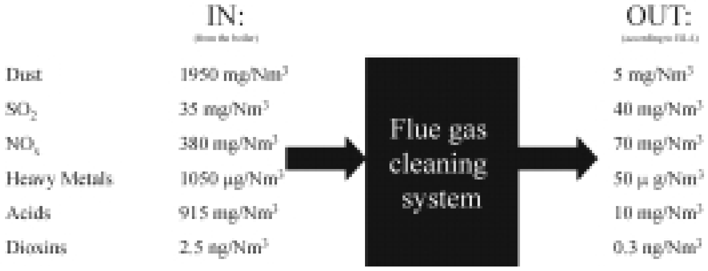


Figure 1.2: Concentration of pollutants in and out of the Gas cleaning system.

An important restriction in the design is the cost price of the flue gas treatment that strongly determines the cost of incineration. This cost price should be low in order to safeguard the commerciality of the AVI. This is especially important because in the near future the European market for waste use will open. This limits many technically feasible flue gas treatment processes.

A sustainable approach in the design of the new flue gas treatment section

will be preferable. With a sustainable approach the authors mean:
Minimize:

- The use of non-renewable energy sources (e.g. oil, natural-gas and coal)
- Emissions/spills/losses.
- Wastes.

Maximize:

- Ratio renewable/ non renewable energy sources
- Thermal and energy efficiency
- The production of useful by-products.

Chapter 2

Process options and selection

2.1 Introduction

2.1.1 Design philosophy

Immediately after choosing the topic of our CPD, the flue gas treatment of incineration of municipal waste, we had to choose whether we would perform our design in terms of existing technology or we would take the chance of choosing a new approach. We chose the latter as we felt this would be more challenging. In order to try to be creative we:

1. Looked at other industries (e.g. coal gasification, oil refineries and coal combustion processes)
2. Regularly performed brainstorm sessions
3. Discussed existing and evolving gas cleaning techniques and equipment with specialists, within the TU Delft and also from equipment supplying companies and process engineers of different MWIs
4. Visited two other MWIs, respectively the largest and the smallest in capacity in the Netherlands.
5. Did not hesitate to use relatively new process equipment, when we felt we had sufficient reason to believe that this would lead to improvements driven by interest
6. Had a review session with Dr. D.H. Grunwald about creativity

While talking to engineers involved in designing or re-designing these systems, it was noticed that from the beginning, when legislation and, in particular, emission standards, on polluting flue gas components first started (datum) until now, when Dutch emission standards are world's strictest (i.e. lowest emissions), the existing systems have always been simply extended to meet the latest legislation. In other words, the basic design was not changed. Rather, an extra gas cleaning apparatus was added to the existing system. For instance,while building the waste incinerator in Amsterdam, extremely strict legislation on maximum dioxins was enacted. To meet this new demand, an extra wetscrubber was inserted in the system. This 'reactive, add-on approach' we wanted to avoid. So, in order to prevent us from following that same approach, we decided to take a fresh look at the nature of cleaning flue gas.

2.1.2 Process options and selection

We also considered alternative process routes which would strongly determine the optimal type of flue gas treatment. Such alternatives routes include:

1. waste gasification
2. biological reduction
3. prevention of waste production at the source

All alternatives were rejected, however, because they were in our opinion not economicly or technically or socially feasable.

When the incineration process was chosen, the flue gas treatment section could be designed. In order to adapt a sustainable approach we focussed on minimising the formation of hazardous substances and to minimize energy consumption/loss and establish space savings. Ideal in this approach would be the integration of different fluegas treatment units. Especially the removal of dust with a high temperature ceramic filer, which in itself is a new technique, could be combined with the catalyst needed for the removal of NO_X. An example is, coating the filter with a catalytic material like V_2O_5, and thereby using the ceramic material as the support for the catalyst coating. In literature it was found that the catalysts used for the destruction of NO_X can also remove the dioxins from the flue gas by oxidizing them. This means that by adding ammonia (for the removal of NO_X) to the flue gas stream followed by a catalytic filter, the flue gas is all ready free of dust, dioxins and nitrogenoxides.Placing a catalyst just after the furnace causes problem with some pollutants, like Cd, Hg and acids.

After having thought of such a system, it was found that a company in Zurich is at the moment offering similar systems, this means that they were able to find a catalytic material that was capable of handling the several pollutants. Contacting this company, and trying to inquire more detailed information on their system's specification, however, did not pay off as we received too little information, in spite of repeated requests. So, unfortunately it was, near impossible to make a conceptual proces design based on this system, and it was decided to design a high temperature ceramic filter, followed by a SCR-unit.
The first ESP is replaced by a high temperature dust filter followed by the SCR-unit. Downstram the fluegas treatment section is simular to the exsisting section in Amsterdam (see figure 1.1 on page 3), only the second ESP is replaced by a bagfilter and the electrodynamic venturi scrubber (EDV) is left out this design. The reason for replacing the second ESP with a bagfilter is the higher particle collection efficiency at the cost of a higher pressure drop. The EDV is

left out because experience has shown that this device leads to no additional cleaning performance (de Vries, [5]).

2.2 Options: Flue gas cleaning train comparison

Three process options will be compared with the current flue gas cleaning train used at AVI-Amsterdam. The following paragraphs will describe the different process options with their pro's and con's.

2.2.1 Option 1: Current flue gas cleaning train used at AVI-Amsterdam

The flue gas cleaning train that is used at AVI-Amsterdam is shown in the block diagram below.

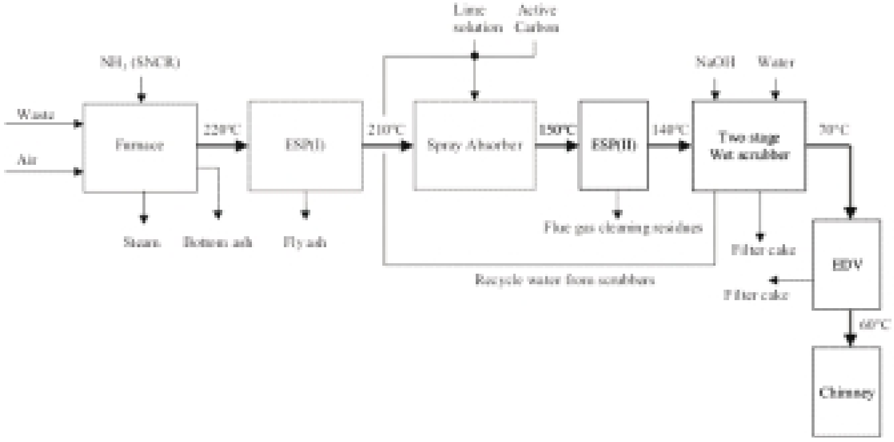


Figure 2.1: Current flue gas cleaning section used at AVI-Amsterdam

Furnace (SNCR)

In order to remove the NO_x from the flue gas, NH_3 is injected into the furnace. An advantage is the relative low investment cost. A disadvantage is that an excess NH_3 has to be added to remove NO_X. Which gives problems downstream because the excess NH_3 must be removed.

Electrostatic precipitator (ESP)

Two electrostatic precipitators are used in order to remove the solid phase from the flue gas stream, this is done with a high efficiency (>99%). The main disadvantage of an ESP is the dioxin forming tendency.

Spray absorber

Gaseous acids (mainly HCl, HF and SO_2) present in the gas are partially removed in the spray absorber. In the spray absorber a lime solution ($Ca(OH)_2$) is added in order to react with the gaseous acids. The solution is prepared with wash water from the wet scrubbers. The wash water is evaporated in the absorber and the solid reaction-salt particles formed, are together with the reamaning fine fly ash particles collected in the second ESP(II).

Wet scrubbers

The partially cleaned flue gas still contains gaseous acids, dioxins and heavy metals. The wet scrubbers consist of two washing towers. In the first scrubber the flue gas is quenched with water from the second wash tower and with the gaseous acids, salt containing acid water is formed. The acidic water reacts with the heavy metals present to the corresponding salts. In the second wash tower NaOH solution is added, here SO_2 reacts with the caustic solution to form Na_2SO_3. In presence of excess O_2 this oxidses to Na_2SO_4. The water from the first scrubber is fed to the upstream spray absorber, where the salts are collected on the fabric filter.

Electrodynamic venturi scrubber

The EDV in the AVI Amsterdam is used as an aerosol separator, to prevent emmisions in the form of aerosol particles from the wet scrubbers.

One of the advantages of the flue gas cleaning section presented above is that no wastewater is produced. The wastewater produced by the wet scrubbers is recycled to the spray absorber and evaporated. Another advantage of this design is the low emissions. Because of the low emissions and the number of apparatus needed the installation is relative expensive. Another disadvantage is the temperature of the gas leaving the chimney. It is relative cold with 70° C and gives problems with the rise power of the plume. And the public refer the plume with environmental pollution.

Table 2.1: Advantages and disadvantages option 1

Advantages	Disadvantages
No waste water	Expensive
Low emissions	Relative cold flue gases
	Additives needed

2.2.2 Option 2a: Waste water free with active carbon filter combined with a SCR-unit

This process can be briefly described as combined semi-dry and wet flue gas treatment section without wastewater production. This system is included with a Selective Catalytic Reduction (SCR) process in order to reduce NO_X with NH_3 over a catalyst to form the environmental harmless N_2 and H_2O. The simplified process flow diagram in block form is presented below.

Only the devices that are currently not used at AVI-Amsterdam will be described.

Cyclone

In this flue gas treatment section, the coarse fly-ash particles are separated from the flue gas by a cyclone.

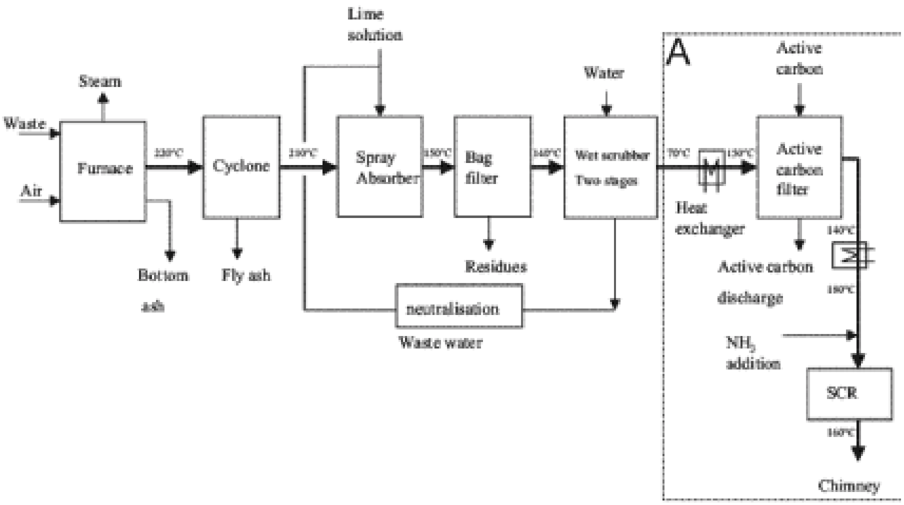


Figure 2.2: Wastewater free; catalytic NO_X removal; block scheme.

Active carbon filter and SCR

The flue gases leaving the wet scrubbers still contain traces of heavy metals and dioxins/furans. In order to protect the downstream SCR-unit from heavy metal deposition which poisons the calalyst, the flue gas passes a active carbon filter. Also dioxins and furans are removed. These filters are only effective at temperatures of 120-150°C hence reheating of the flue gasses is necessary. After the dioxins and heavy metals are removed the flue gas needs to be deNOx'ed which is done by the SCR unit. For removal of NOx in cleaned flue gases with SCR a temperature of 180°C is needed. So the stream is heated to 180°C. The flue gases leave the stack with a temperature of 160°C; this means there is no plume leaving the chimney but this also gives a significant energy loss.

Table 2.2: Advantages and disadvantages of option 2

Advantages	Disadvantages
No waste water	Need of re-heating the flue gas
No cat. poisoning so low SCR operating temperature	Expensive SCR catalyst
No plume leaving the chimney	Energy loss out of chimney

2.2.3 Option 2b: Waste water free with SCR in front of active carbon filter

As an alternative, the SCR can also be used to remove the dioxins/furans through catalytic oxidation, the gas should then have a temperature of around 350°C. Because of the high operating temperature of the SCR-unit the catalyst is less poisoned by heavy metals than in the 2a option. The heavy metals that are still present in the effluent gas stream from the SCR have to be removed with the use of an active carbon filter.

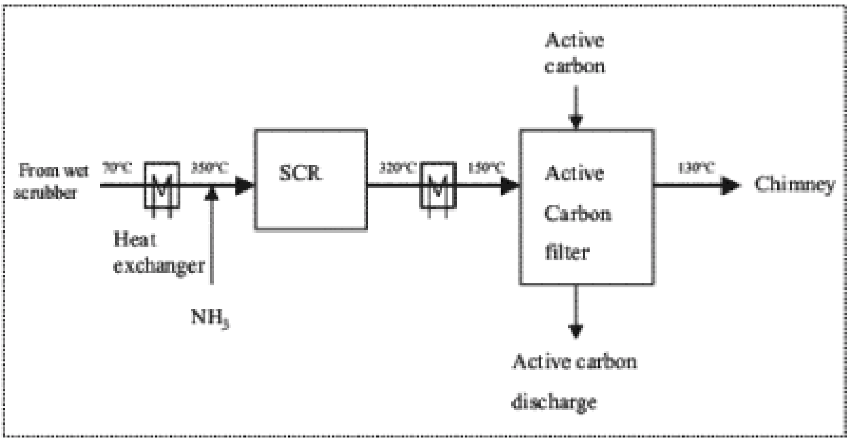


Figure 2.3: Waste water free; catalytic NO$_X$ removal, SCR removes dioxins/furans block scheme.

Table 2.3: Advantages and disadvantages of option 2b

Advantages [1]	Disadvantages
No waste water	Need of re-heating the flue gas
No cat. poisoning so low SCR operating temperature	Expensive SCR catalyst
No plume leaving the chimney	Energy loss out of chimney

2.2.4 Option 3 (Chosen): High temperature dust removal flue gas treatment

In this process particulates are collected at a high temperature in order to minimize dioxin formation and to protect the SCR- unit. The SCR-unit which reduces NO$_X$ present in the flue gas and also destroys eventually formed dioxin/furan traces. Further the system is a conventional wastewater free gas cleaning system with the remark that no ESP is used to collect the particles from the spray absorber but they are separated by a fabric filter. The process flow diagram in block form is presented below:

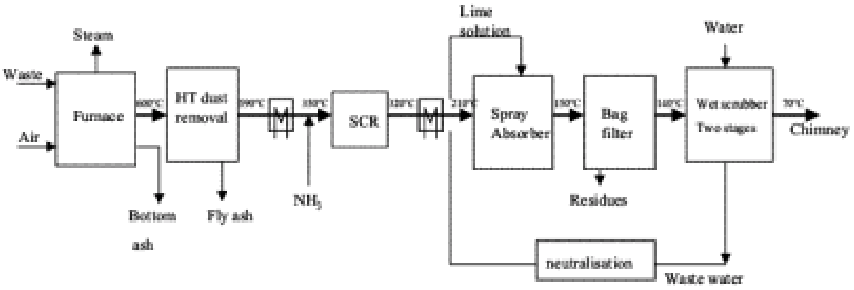


Figure 2.4: Block scheme of the high temperature dust removal flue gas treatment process.

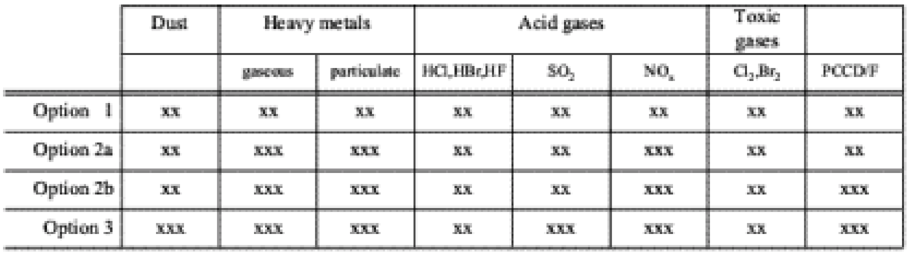
Table 2.4: Advantages and disadvantages of option 3

Advantages	Disadvantages
No waste water	New process HT dust removal
No active carbon addition	Expensive SCR catalyst
No excess NH3 addition	SCR catalyst exposed to acid gases
No re-heating of the streams	Plugging of HT cyclone
Dioxin formation prevented	High pressure drop over dust filters
No ESP's	SCR cat. poisoning
SCR also oxidises heavy metals	Plume out of chimney

The pre-separation of the coarse particulates can be done by a cyclone but not included in this design. The cyclone has an efficiency of 90%, which is not enough for environmental reasons, especially because the fine particles are transmitted. To control the fine particulates a high temperature dust filtration unit is installed, existing of a bundle of candle filters. After the dust filtration the flue gas enters the SCR-unit. In this unit NOx is reduced and the eventual formed dioxins and furans are oxidized. Because the high operating temperature of the catalyst it is less sensitive to heavy metal and sulphur poisoning. The spray absorber and the wet scrubbers are described in the previous process options.

2.3 Comparison

The following table gives an overview of the process options described in the previous paragraphs. The three process options are compared, with respect to their pollutant removal capacities, with AVI-Amsterdam taken as a standard. Option 3 has the best overall pollutant removal performance.



	Dust	Heavy metals		Acid gases			Toxic gases	
		gaseous	particulate	HCl,HBr,HF	SO_2	NO_x	Cl_2,Br_2	PCCD/F
Option 1	xx	xx	xx	xx	xx	xx	xx	xx
Option 2a	xx	xxx	xxx	xx	xx	xxx	xx	xx
Option 2b	xx	xxx	xxx	xx	xx	xxx	xx	xxx
Option 3	xxx	xxx	xxx	xx	xxx	xxx	xx	xxx

Figure 2.5: The pollutant removing capacity for the different process options

Chapter 3

Basis Of Design

3.1 Process definition

A description for the most important components in the flue gas is made in this chapter. Also options for gas cleaning treatment units for every particular component are presented. The most important components treated in this chapter are:

- Dust
- Dioxins
- Nitrogen oxides
- Acid gases
- Sulphur oxides
- Heavy Metals

3.1.1 Dust

Introduction

After the incineration of municipal waste, the amount of particulate matter should be reduced to environmentally acceptable levels as given in Dutch legislation (BLA). At the moment, particulate control of flue gases from municipal waste incinerators (MWI) in the Netherlands is almost exclusively done by electrostatic precipitators (ESP). Operating temperatures of these ESPs are typically in the range of 200 to 300°C. Since "de novo synthesis" of dioxins typically occur in this temperature range, dust separation at a higher temperature would be preferable to prevent dioxin formation.

In the last decade much research has been done in high temperature dust removal in Pressurized Fluidized Bed Combustion (PFBC) and in coal gasification plants. In the Netherlands much experience has been gained with the coal gasification plant Demkolec in Buggenum.

The following demands are made on the devices operating in a MWI:

- Ability to handle high temperature flue gases (max. 850°C).
- Ability to handle corrosive flue gases, including HCl and glass-etching HF.
- High reliability (>8000 hr/a).
- Resistance to abrasion by fly ash.
- Low pressure drop at atmospheric pressure.
- Capable of handling different dust loads.

Candle filters

This is the type of filter that is chosen for the design. A ceramic candle filter is a device in which dirty gas flows from the outside of the candle to the inside. The particulates are collected on the outside surface of the candles, and the clean gas flows to the top. Periodic cleaning of the candles is done by injecting air from a blowback air reservoir. The candle filters are capable of handling high temperatures (up to 1000°C.) and achieve a high particulates removal efficiency (>99.995%). The candle filters are combined together to form large filter installations. These types of filters are used in PFBC and coal gasification units for the high temperature particulate removal of the flue gases. Therefore much practical experience exists with this type of filter. The corrosion resistance of the ceramics against flue gas compounds is good, even at higher temperatures. Because of the low filtration velocity through the filter (up to 0.6 m/s), abrasion by fly ash is not a relevant problem. The pressure drop over the filters is low (typically 20-50 mbar), even at atmospheric pressure.

Conclusion

For the high temperature particulate control in municipal waste incinerators, eventually the combination of a cyclone and candle filters looks very promising. The coarse fly ash particles are pre-separated in the cyclone, and the finer particles are collected in the ceramic candle filters. Only the use of a single candle filter system is incorporated in this design.

3.1.2 Dioxins

Introduction

Dioxins is the generic name for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, which are abbreviated as PCDD/F.

Emission prevention and reduction of dioxins

Figure 3.1 shows the formation routes of dioxins in MWIs.
From figure 3.1 possibilities can be derived for the emission prevention and/or reduction of dioxins. Methods applied in this design are:

1. Prevention of the formation of precursors.
2. Prevention of favourable process conditions.
3. Destruction or immobilisation of formed dioxins.

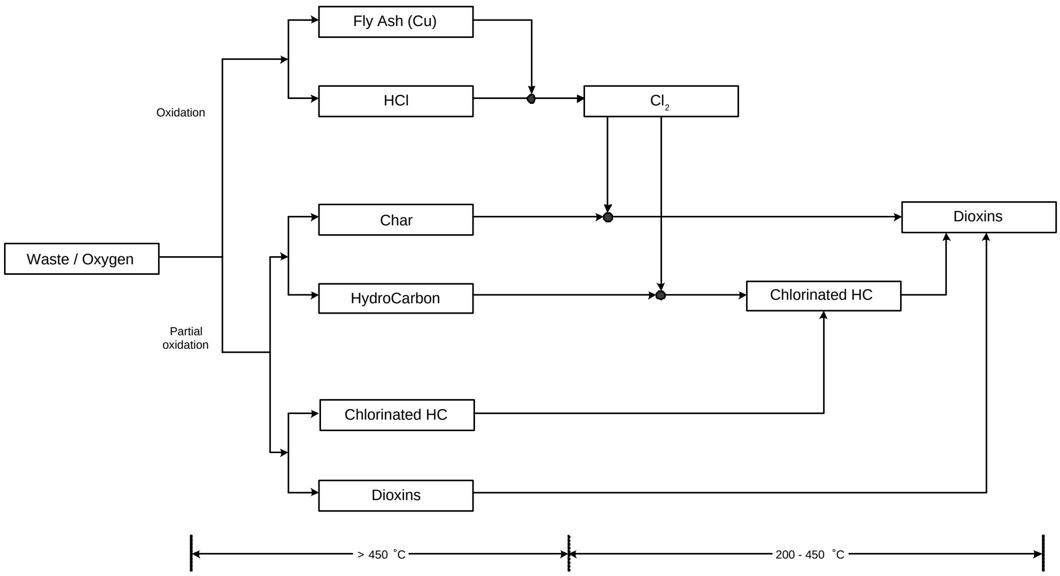


Figure 3.1: Dioxin formation routes in a MWI (Koning [6])

Prevention of the formation of precursors

Taking away one of the precursors prevents the formation of dioxins. A method to prevent formation of chlorine is the removal of the chlorine-producing catalyst by High Temperature dust removal, described in paragraph 3.1.1. The catalyst for the formation of dioxin (mainly Cu) is present in fly ash. By removing the fly ash at a sufficient high temperatures (>500°C) chlorine formation and therefore dioxin formation is prevented.

Prevention of favorable process conditions.

Favorable process conditions for the formation of dioxins are the so-called "de novo" synthesis process and the presence of ESPs. The maximum rate of PCDD/F formation is at a temperature near 400°C. These favorable conditions must be prevented in the new design by:

- Preventing long residence time (>2s.) in the temperature range of 200 and 500°C
- Removing Presence of the precursor chlorine and catalyst Cu.

In many waste incinerators, ESPs are being used for the pre-separation of fly-ash particles. A disadvantage of the use of an ESP is the formation of dioxins, because the ESP is operated in the dioxin formation temperature range. All ESPs release substantial amounts of dioxin. Dioxin formed in an ESP may escape from the stack as a vapor, or be adsorbed on particles that are then released from the stack, or get trapped in the ESP and end up as ad-/absorbed in the fly ash. Dioxin formation can occurs in an ESP at temperatures from 150 to 300° C. For each 30° C increase at the inlet to the ESP, up to 300° C, dioxin concentrations increase by approximately a factor of two (US-Environmental Protection

Agency (USEPA), 1994). However, a the temperature increases beyond 300°C, dioxin formation rates decline. A "cold-sided" ESP generally operates at an inlet temperature below 230° C, while a "hot-sided" ESP generally operates at an inlet temperature greater than 230° C. Hot-sided ESPs are the source of substantially more dioxin formation than cold-sided ESPs, which also produce dioxin. According to the EPA, 85% of all dioxin emissions from municipal waste incinerators are released from incinerators equipped with an ESP. Summarising the use of an ESP is not recommendable.

Destruction or immobilization of formed dioxins.

Preventing dioxins emission in our design is done by catalytic oxidation in a SCR (Selective Catalytic Reduction) unit. Catalysts on basis of TIO_2, used for SCR, are very efficient in removing the dioxins by oxidation in the temperature range of 250-350°C.

Conclusion

- ESPs operating in a certain temperature window, exhibit a dioxin formation tendency and alternative particulate control devices are therefore desirable.
- To prevent chlorine formation and therefore dioxins formation, high temperature dust removal is preferable.
- To prevent the emission of formed dioxins SCR can be used.

3.1.3 Removal of NO_X from flue gas

NO_X consists of approximately 90-95% of the toxic gas nitric oxide (NO); the rest is NO_2 and N_2O. The formation of NO_X causes two separate problems. One is pollution of the environment and the other is personnel exposure. Environmentally, NO_X is a primary factor that increases the lower ozone layer we know as smog. Ozone (O_3) is formed when sunlight decomposes NO_2 to nitric oxide (NO) and atomic oxygen (O). The oxygen atom combines with the natural (O_2) oxygen molecule to form Ozone (O_3). The smog formed is toxic to people and the environment. It's considered the primary cause of the greenhouse effect (IEACR/89, 1996 [7];Vipinc, 2001 [8]).
NO_X is formed during the incineration of waste, the main reactions responsible for the formation of NO_X, are show below.

$$N_2 + O_2 \rightleftharpoons 2NO \tag{3.1}$$

$$NO + \frac{1}{2}O_2 \rightleftharpoons NO_2 \tag{3.2}$$

Selective Catalytic Reduction (SCR)

SCR has a high denox efficiency (80-90%) and that the reactions will occur at low temperatures (300-400°C). The catalysts available are titanium oxide, iron oxide, vanadium oxide, zeolites and active carbon.

The governing chemical reactions that occur in the presence of the SCR catalyst, NO_X reduction and SO_2 oxidation are presented below. The primary NO_X reactions are listed in the equations below.

$$NO + NO_2 + 2NH_3 \longrightarrow 2N_2 + 3H_2O \tag{3.3}$$

$$4NO + NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \tag{3.4}$$

$$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O \tag{3.5}$$

Oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) also occurs on the catalyst, this conversion is greatly increased at temperatures above 370°.

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 \tag{3.6}$$

Theoretically, the amount of ammonia to be injected should be based on a molar ratio of ammonia to NO_X, which is numerically the same as the NO_X removal efficiency. However, since ammonia is not completely and uniformly mixed with NO_X, more than the theoretical quantity is normally injected. The excess residual ammonia in the downstream flue gas is known as the ammonia slip. The NO_X removal efficiency increases with increasing ammonia slip and reaches an asymptotic value at a certain level of excess ammonia. This means that there is a limit to the advantageous effect of excess ammonia in removing NO_X. Furthermore, excess ammonia is environmentally harmful when discharged to the atmosphere through the stack, and, therefore, its quantity should be minimized. The formation of SO_3 can lead to problems in downstream equipment due to corrosion and/or plugging when combined with excess ammonia slip. This means that the SCR should operate at temperatures between 300 and 370°C, because at temperatures lower then 300°C ammonia slip increases and NO_X conversion decreases.

It is important that the flue gases are relatively free of particulate matter, which tends to contaminate or "poison" the catalytic surfaces. Typically, the catalytic reactor is located ahead of the air heater, to take advantage of the temperature regime. Sometimes, however, the reactor may be placed just ahead of the stack and downstream of the particulate collection devices to avoid catalyst contamination. In most cases, however, reactor placement just before the stack requires reheating of the flue gas to meet the catalyst reaction temperature requirements, which in turn adversely increases the cost of the SCR system. In addition, because catalysts lose their effectiveness over time due to contamination or clogging of catalyst pores, they must be replaced periodically.(ThermaloNOx, 2000 [9])

SCR vs. SNCR

The following graph shows the different temperature windows for SCR and SNCR. The SCR can be operated at much lower temperatures, and also less NH_3 is needed(NO_X:NH_3 = 1:1).

Combined SO_2/NO_X removal

The Desonox process also uses NH_3 to remove the NO_X (SCR). An additional step is added to remove the SO_2; a catalyst converts the SO_2 to SO_3. The next step is the cooling of the SO_3 to below the H_2SO_4 dew point, this cause

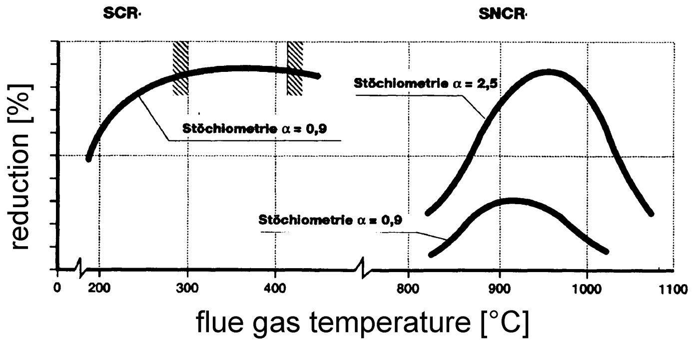


Figure 3.2: Temperature window of SCR vs. SNCR

H_2SO_4 to condense. A wet scrubber and a wet electro filter are used to remove the acids and aerosols. The temperature should be approximately 430-450°C; a 70% H_2SO_4 solution is formed which is a useful product. The combined (Prins *et al.*, 1994 [10]) SO_2/NO_X removal will not be considered.

Selection of the NO_X removal unit

The following table (table 3.1) gives an overview on the different mechanisms that are available for NO_X removal, and their specifications:

Table 3.1: SCR vs. SNCR (Holste, 2001 [11])

	SCR	SNCR
temperature [°C]	300-400	870-1200
pressure drop	moderate	low
efficiency [%]	80-90	45-50
catalyst	yes	no
explosion hazard	yes	yes
capital cost	high	low
residence time [s]	*	> 0.5
NH_3 consumption	low	high
Dioxin-destruction	yes	no
oxidation of heavy metals	yes	no
ammonia-slip [mg/m^3]	3-5	30-40

The use of a catalyst for the reduction of NO_X has more environmental advantages then the use of a non catalytic system (see tabel 3.1), allthough the installation costs will probably be higher because the catalytic material is expensive.

3.1.4 Acid gases

Acids from a MWI flue gas mainly consist of HCl, SO_2, SO_3, and HF. Acids are removed from flue gases by chemical reactions with alkaline substances forming the corresponding salts. Applied processes are, respectively, the semi dry process with limestone (CaO) in a spray absorber and neutralisation with caustic soda (NaOH) in the wet process.

Spray absorber

In a spray absorber, a lime solution in the form of a spray is brought into contact with the hot flue gas. The function of this is to initiate a chemical reaction between the acid gas components and lime. The reactions occur by direct contact between the hot gas and the dispersed droplets of the spray or with the dried lime particulates. The corresponding salts are formed in the solid form. When all liquid of the lime solution has evaporated, the solid products are separated at the bottom of the spray absorber or collected from the exiting flue gas by a fabric filter. The capacity and efficiency of the spray absorber is determined by the specific surface of the droplets, hence the smaller the droplets the larger the efficiency.

Wet scrubber

Wet scrubbers are employed downstream the spray absorber. This sequence is chosen because the produced waste water of the wet scrubbers can be evaporated in the spray absorber. The waste water leaves after evaporation the chimney; the solid residues of the evaporated waste water is collected in the fabric filter of the spray absorber. A typical wet scrubber for refuse incineration is the two stage wet scrubber. The first stage is used for HCl removal and the second stage for SO_2 removal. Water is used to capture HCl, which is extremely water soluble, and caustic soda (NaOH) is used to capture SO_2, which is much less water soluble. In the first (acid) section, heavy-metals are also washed out of the flue gas. The heavy-metal containing HCl stream is treated with the sodium sulfite/sulfate solution from the second stage in a neutralisation/precipitation stage to concentrate the heavy metals and produce salt-containing waste water for the spray absorber. When designing wet scrubbers, corrosion is an important feature that must be accounted for. The scrubbers are therefor lined with a plastic coating. The inlet temperature is limited to protect the plastic coating and is determined by the quench capacity of the spray. The outlet temperature must be over 60°C in orde to ensure sufficient buoyancy of the plume from the chimney.

Conclusion

A combined wet / semi-dry process looks the most promising for SO_2 removal. The wastewater from the wet scrubbers is evaporated in the spray absorber.

3.1.5 Mercury and other gaseous heavy metals

The majority of the range of heavy metals present in the flue gas settle on the fly ash particles. These particles are separated from the flue gas by particulate control devices. Special attention is, however, needed for mercury and cadmium, both of which are extremely toxic. Only mercury present in the particulate form can be captured by particulate control devices. But because of its - for a metal

- very high volatility, significant amounts of mercury are present in the vapor phase, which is not captured by particulate control devices.

Control technologies

Mercury leaves the combustion zone in the vapour phase and cools down as it passes the flue gas treatment section. The amount of unburned carbon and fly ash in the combustion zone determines the mercury concentration in the particulate phase, since these particulates absorb mercury. When it is absorbed by the fly ash particles, mercury is removed by the particulate control devices.

SCR units operating at higher temperatures (300-350°C) oxidise metallic mercury vapour (Hg^o) to Hg(II). Sloss (1995,[12]) reports 80% Hg^o oxidation to Hg(II). Since Hg(II) is removed far more easily than Hg^o in wet scrubbers, SCR benefits the mercury removal efficiency. In the wet scrubbers Hg(II) is removed since it is soluble in acid water. To enhance the mercury removal efficiency, sorbents like sodium sulphite (NaS) can be added [12].

3.2 Basic assumptions

3.2.1 Plant capacity

In order to satisfy the increasing demand of waste processing capacity in the Netherlands, a total incineration capacity increase of 2,5 Mton/a is needed [1]. The MWI in Amsterdam (AVI-Amsterdam) has four incineration lines with a total capacity of 800,000 tons/a. In order to fulfil the need for incineration capacity expansion, AVI-Amsterdam has scheduled a capacity increase of 500,000 tons/a. This waste is processed in two incineration lines, each with a flue gas flow of 156,250 Nm^3. A flue gas cleaning section will be designed to remove all pollutants, to the degree specified by current standards (BLA).

3.2.2 Feedstock

The 500,000 tons/a of waste consists of various components. The composition of industrial waste and bulky refuse is more complicated. The incineration of the waste produces a flue gas with several polluting compounds. This flue gas is the feedstock of the gas cleaning process. The flue gas flow and composistion is based on the existing incineration lines and is translated to the future capacity.

3.2.3 Base chemicals

The following base chemicals are used for the flue gas cleaning section:

Table 3.2: Base Chemicals

Ammonia solution	NH_3 (25% solution)	SCR, removal of NO_x
Catalysts	eg. V_2O_5	SCR
Lime milk	$Ca(OH)_2$	spray absorber, removal of acids $HCl/HF/SO_2$
Caustic soda	NaOH	wet scrubber, removal of acids HF/HCl heavy metals

3.2.4 Products

During the incineration of waste, heat is formed; this heat can be used to create high pressure steam, which can generate electric power. The flue gas cleaning section considered in this report only focuses on the flue gas stream leaving the boiler, so electricity generation will not be included in the design. Between unit operations heat exchangers are installed to generate steam.

3.2.5 By-Products/Waste

None waste water is produced since the license of the MWI in Amsterdam forbids the drainage of waste water. The residues that are generated are the following:

- flue gas cleaning residue
- fly ash

- bottom ash (is produced in the boiler section so not included in this CPD)
- flue gas cleaning residue from the spray absorber and bag filter
- filter cake from wet scrubbers

The by-products that are generated during the flue gas cleaning can, in some cases, be used as useful products. For instance, the fly ash can be used as filler for the asphalt industry. The flue gas cleaning residue and the filter cake, however, must be dumped.

3.2.6 Economic life time

The extension of AVI-Amsterdam should have an economic lifespan of at least 20 years. The Dutch legislation (BLA) is the strictest one in the World. Remaining European countries will first have to adapt to Dutch legislation, before the standards will be made even stricter. This means that the flue gas cleaning section will have a sufficient cleaning capacity for the long term.

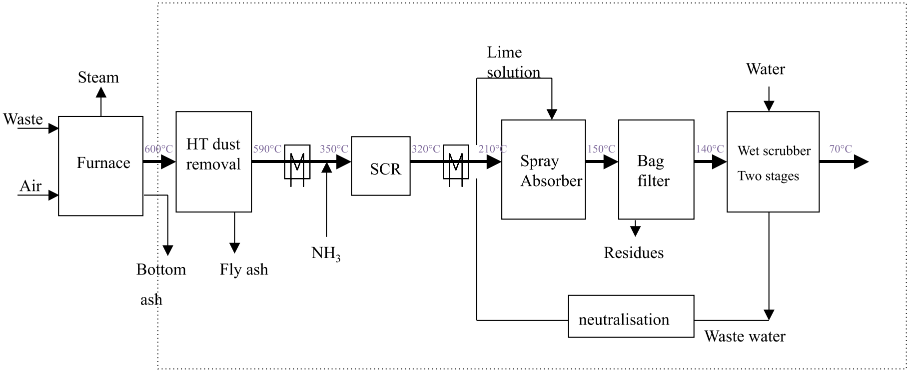
3.2.7 Location

AVI Amsterdam is situated, at the water's edge, Asia Dock, on the western side of the port of Amsterdam. The site itself is an industrial area, with the A10 ring road providing an excellent access to the entire service area. The site can be reached from the Australiëhavenweg. AVI Amsterdam also has a rail link for waste disposal delivery. Slag is temporarily transported from the plant by road; rail and/or ship transportation routes are also planned for the future. The ground that is needed to build the extension is already present. The chimney that is currently used will also be used for the new flue gas cleaning installation.

3.2.8 Battery limit

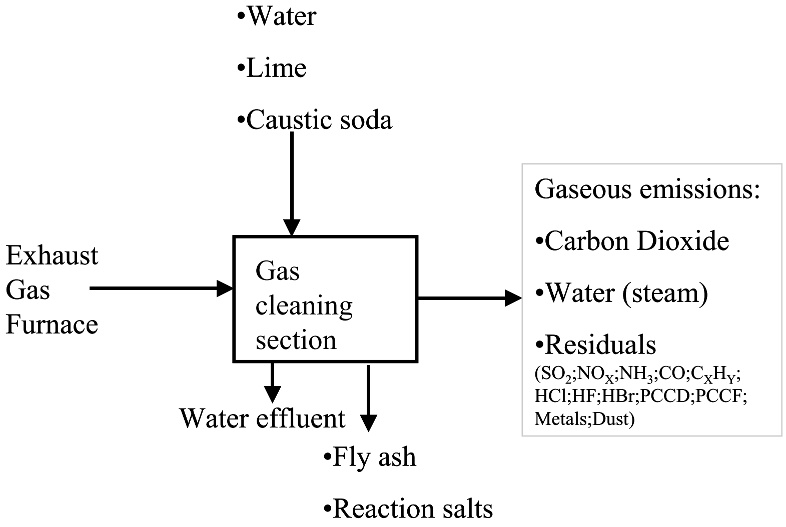
The conceptual process design will focus mainly on the flue gas treating section. The combustion region will not be considered. The composition and conditions of the flue gas stream entering the flue gas cleaning train is based on the current process. Exit conditions are determined by legislation (BLA). The important equipment inside the battery limit is shown in figure 3.3.

Figure 3.3: The important equipment inside the battery limit



A chimney is already present at the location and has sufficient capacity for the extension.

Figure 3.4: The battery limit



3.3 Financial margin

3.3.1 Existing process

The economic assessment of the process will consist of comparing the current flue gas section with the newly designed flue gas installation.

Table 3.3: Investment for the current AVI Amsterdam installation

Costs	Million Guilders (Million Euro)
Preparatory costs	50 (22.7)
Land price	35 (15.9)
Building costs:	
-Mechanical engineering, main process	380 (172.4)
-Mechanical engineering, auxiliary installations	100 (45.4)
-E & I installations	90 (40.8)
-Construction/ civil engineering	180 (81.7)
Additional Costs	95 (43.1)
Start-up costs	20 (9.1)
Total	950 (431.1)

These investments have resulted in exploitation costs amounting to DFL.200 per ton of refuse.

3.3.2 About the new process

The cost of the High Temperature (HT) dust removal system is difficult to calculate and therefore has a large error margin, because there is no cost data available in use in this application field. The SCR system requires a relatively high investment in capital costs. However compared to the current process the O&M costs are lower: the reagent consumption (ammonia) is reduced substantially. The catalysts lifetime is about 3 years. The SCR system needs a larger capital investment that can be 3-5 times as high as for a SNCR system. The operating and maintenance costs, however, are a factor of about two lower. The Bag Filter system has a relatively high capital cost and power consumption due to the pressure drop. The new system with two incineration and flue gas cleaning lines, with a capacity of 250,000 ktons/a each. Roughly, the total capital investment will be about 270 Million Euro.

Chapter 4

Thermodynamic properties

See for thermodynamic properties appendix V

Chapter 5

Process structure and description

5.1 High temperature dust filter

The use of hot gas filter media is currently under development. Filters based on ceramic sintered granules and fibers are already commercially available and successfully used for several years. ([13] [14]) Fields where hot gas filtration is applied succesfully is in Integrated Gasification Combined Cycle (IGCC), Pressurised Fluidised Bed Combustion (PFBC) and Fluidesed Catalytic Cracking (FCC) units. Advantages of high temperature particulate removal in waste incineration are:

- Less ash deposition on the heat exchanging tubes in the convection zone of the boiler section, hence improving the thermal efficiency.
- Prevention of dioxin and furan formation during the cooling stage of the flue gases.
- After filtration possibility for Selective Catalytic Reduction of NO_x at high temperatures without pre-heating.
- High particulate removal efficiency

The disadvantages are:

- New technology for municipal waste incinerators hence little practical experience.
- Larger pressure drop then the alternative existing cold particulate removal with ElectroStatic Precipitators.
- No condensation of volatile components on the fly ash at lower temperature (i.e. SO_3,$HgCl_2$) so these substances must be removed downstream.

5.1.1 Candle filters

The scope of this paragraph is on rigid ceramic filter media formed from sintered granules, the so called candle filters. Depending on the chemical composition of the gas, they can be used up to $1000°C$ applications in process industry. Candle filters are hollow, porous walled cylindrical tubes. A typical filter element may have a outside diameter of around 60 mm, a wall thickness of 10-20 mm and an overall length of 1-1.5 m. (Thambimuthu, 1993 [13]) The filtration velocity and the surface area of each candle determine the number of candles needed. The dust particles are collected on the outer wall of the candle surface, so called surface filtration.

Operating charactarisctics

The dust particles are collected on the outer wall of the candle surface (surface filtration). Because the filter would plug as the filter cake grows, a blowback system is installed to regenerate the filter. The filter regeneration is performed in cycles of reversed high pressure air pulses (Thambimuthu, 1993 [13]). Important operating features for candle filters are filtration velocity, filter regeneration and the cake formation and removal charactaristics which depend on the surface properties of the dust. Depth filtration must be prevented because it plugs the filter irreversible, the filtration velocity must therefore be low.

Ideal filter pressure drop modeling

The simulation is done with the aid of the computer program MATLAB release 12. All scripts are included in Appendix C. The net, measured pressure drop is a combination of the pressure drop across the filter and the filter cake.

Filter

The pressure drop in a fresh filter is given by the following relation:

$$\Delta p = \frac{k_1 \mu U_0 b}{2} \, ln(\frac{b}{a}) \tag{5.1}$$

for the derivation of this equation, the reader is referred to appendix A. Hence a relation can be obtained between pressure drop (Δp) and the filtration velocity (U_0) for different filter porosities. The result of the simulation in Matlab is plotted in figure 5.1:

cake formation and release

After a while a permeable cake will form on the surface of the candle which has to be dislodged at a predetermined pressure drop by initiating a reverse air flow. This pressure drop is a function of cake thickness and compressibility. The dislodged particulates (fly-ash) are collected in a hopper and stored in a silo awaiting transportation for further use. The filter is then returned to forward flow until the pressure drop rises to the chosen setpoint and the air flow reverses again. This cycle is repeated throughout the filters lifetime. After a certain period of time a permanent cake is formed on the candles surface due to undesired depth filtration. The pressure drop over the permanent cake and

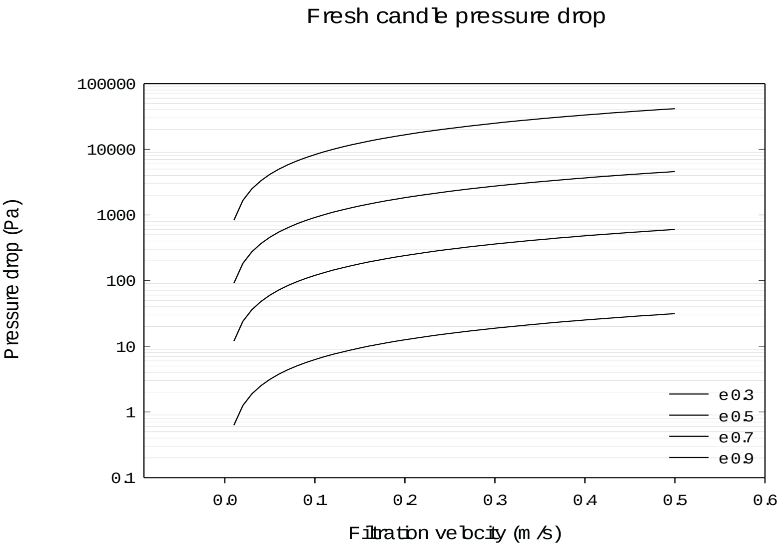


Figure 5.1: simulated pressure drop over a clean candle filter; e represents the porosity (ϵ) of the filter; e 0.3 corresponds with the top line of the graph and so on.

the filter should, after regeneration, be as constant as possible. A schematic representation of the cleaning cycle is given in figure 5.2:

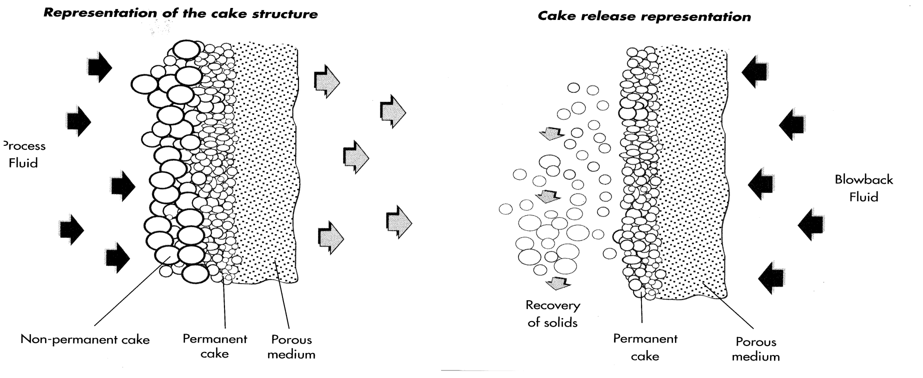


Figure 5.2: pressure drop during filtration

Because no experimental data of characteristics of municipal waste incinerator (MWI) fly-ashes are available, the cake permeability cannot be determined. A rough calculation based on estimations would offer no advantage. To get insight in the filter behavior over time the effect of the change in pressure drop by permanent cake formation is shown in the following graph, taken from the information folder of the Pall filtration corporation [15]:

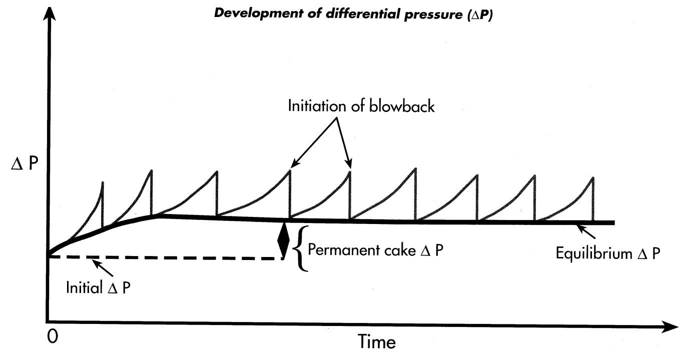


Figure 5.3: pressure drop including permanent cake vs. time. from: Pall filtration corporation[15]

5.1.2 Equipment

Candles used in a waste incineration process are exposed to rather extreme conditions like high temperatures, corrosive gases, thermoshock during the regeneration cycle and varying dust loads. These extreme conditions must be handled during long periods of time without critical failure of the candles. These conditions ask for reliable robust candles, this robustness is at the expense of the porosity. As shown in figure 5.1, stronger candles translate into a larger pressure drop. Because of the high temperature and corrosive process conditions the use of ceramic candles is more favorable then of metal candles. Two suppliers of candle filters sent technical data for these process conditions suitable filters. Relevant technical data are summarised below:

Table 5.1: Physical properties of candle filters

Manufacturer	Pall	USF Schumacher
Type	Vitropore C-23-60	Dia-Schumalith-10
efficiency (%)	99.99	99.995
max. temp. (°C)	1000	1000
porosity (-)	0.46	0.50
material	SiC	$Al_2O_3 : SiO_2$ + SiC
length (m)	1.5	1.5
outer diam. (m)	0.06	0.06
inner diam. (m)	0.04	0.04

Filter size

All calculations and data used are given in appendix B. For a fresh filter a initial pressure drop of 2000 Pa (20 mbar) is chosen as acceptable. Since the pressure drop is dependent of the porosity and the filtration velocity, as shown in figure 5.1, the filtration velocity is 0.21 m/s. The filtration velocity yields the total filtration surface needed for a given gas throughput as shown in figure

8.1. The total filtration surface determines the total cost of the filtration unit.

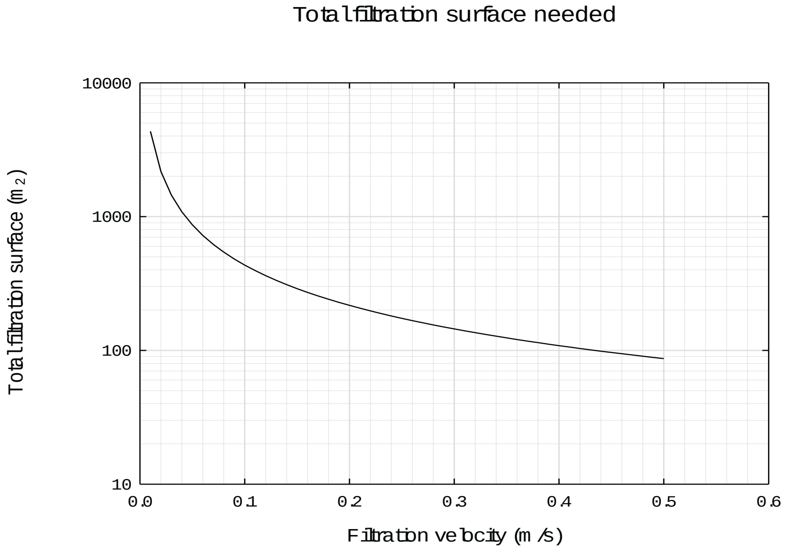


Figure 5.4: Total filtration surface as function of the filtration velocity

With the throughput of the raw gas known (43.40 Nm^3/s) this yields the total required filtration surface (206.67m^2). With an individual surface of 0.29m^2 the number of required candles is 713. The candles are combined in sets of 33 candles often refered as candle bundles. The diameter of a bundle is 0.66 m and the number of bundles (spare bundles included) is 23. The diameter of the required vessel for the filtration unit is 4.42 m. The total volume of the vessel is set to 50 m^3. The hot gas filter system is estimated to last at least 4 years, since it is successfully applied for longer periods in other processes (with a higher dust load and higher operating pressures) (scheibner[16].)

5.2 Selective Catalytic Reduction

5.2.1 Process arangement of the SCR-unit

Because of the advantages mentioned in the BOD we will use a SCR. The next question is then the placement of the reactor. There are basically two options.

1. straight after the high temperature dust removal
2. the end of the gas cleaning section

The following table gives an overview of the two different placenments of the SCR(Soung *et al.*, 1994 [17]):

Table 5.2: Two SCR process arangements

	Option (1)	Option (2)
catalyst life time	low	high
energetic returns	high	low
formation of ammonium sulfates	yes	less
final gas quality	better	good

With option (2) energy is needed to re-heat the flue gas stream from the exit temperature of the wet scrubbers (±70°C) to the desired SCR entrance temperature (300-400 °C), valuable energy is wasted here which is not the case for option (1). Another advantage of option (1) is that the devices that are situated downstream the SCR have cleaner entrance flue gas eg., SCR units operating at higher temperatures (300-350°C) oxidise metallic mercury (Hg°) to Hg(II). (Sloss, 1995 [18]) reports 80% Hg° oxidation to Hg(II). Since Hg(II) is removed far more easily than Hg° in wet scrubbers, SCR benefits the mercury and other heavy metal removal efficiency.

5.2.2 Catalyst selection

The placement of the SCR unit after the high temperature dust removal demands a high performance catalytic material. The presence of especially HCl, HF and the heavy metals can cause fast deactivation of the catalyst. There are three main categories of materials that can be used for SCR(Porsgrunn, 2001 [19]):

- base oxides
- metal loaded zeolites
- noble metals

The perfect catalyst would have to meet the following demands (Moulijn *et al.* [20]):

- low SO_2 oxidation activity
- high activity

- low pressure drop
- minimum pore diffusion resistance
- high mechanical strength
- high selectivity
- high conversion
- low costs
- insensitive for poisoning, fouling and thermal degradation (sintering)

Different companies that manufacture catalytic material have been contacted in search of a catalytic material/system that will meet the demands. Most SCR-units are currently placed at the end of the gas cleaning system because they do not meet the demands. Positioning the SCR after the dust removal is more progressive, and therefor finding a suitable catalyst was more difficult. The different companies that have been contacted are shown in appendix F.
Finally a company was found in Zurich, Von Roll Environmental Technology. They offer a complete system for the removal of NO_X including ceramic high temperature dust removal. Unfortunatelly this company was not willing to give any detailed information about the catalyst that they use. For this reason we decided to design our SCR unit based on a V_2O_5-monolith, in order to determine the reactor size. We did not take the poisioning components into account. It can be expected that the calculation based on V_2O_5 will not differ significantly from the VonRoll system.

5.3 Spray Absorber

5.3.1 Introduction

Spray absorbing is by definition the passing of gaseous pollutants to the liquid state. After which absorption through chemical reaction. Subsequently transformation of the fluid state to a dried form, and at the end separation of the dried product from the gas stream. In the case of a flue gas cleaning section of a municipal waste incinerator, the pollutants are HCl, HF, HBr, and SO_2. The liquid feed can be either a solution, suspension, dispersion, or emulsion. The dried product can be in the form of powders, granules, or agglomerates depending upon the physical and chemical properties of the feed, and the dryer design. In this case the form of the dried product does not matter, it is the composition of the gas leaving the spray absorber that is important. The advantages and disadvantages of the spray absorber are tabulated below. [21]

Table 5.3: Advantages and disadvantages of the spray absorber

Advantages	Disadvantages
Relatively low pressure drop	Particulates deposition can cause plugging
Capable of achieving high mass transfer efficiencies	Relatively high maintenance costs
Increasing height improves mass transfer without requiring the purchase of new equipment	
Relatively low capital cost	
Relatively small space requirements	
Ability to collect particulates as well as gases	

5.3.2 Spray absorber processes

Spray absorbing consists of five process stages:[22]

1. Atomization of liquid feed into a spray
2. Spray-gas contact (mixing and flow)
3. Absorption of gaseous pollutants
4. Drying of the spray (moisture evaporation)
5. Separation of the dried product from the gas stream

All of these processes are highly developed and are a science on their own. A rotary atomizer disc, powered by an electro motor, is used for the formation of a spray (atomization). Liquid feed is introduced to a wheel or disc rotating at a high velocity. The liquid flows outward, accellerating to the periphery; on leaving it, the liquid disintegrates to a spray of droplets. Rotary atomizers are

low pressure drop systems. A wide variety of sprays can be obtained, dependant on atomizer design, liquid viscosity, wheel velocity, etc.
Spray-gas contact is an important factor in spray absorber design. An important item in spray-gas contact is the position of the atomizer in relation to the gas inlet. Many positions are available. In this process the atomizer is situated at the top of the spray chamber, operating in co-current mode. This setup creates the most uniform temperature distribution throughout the chamber.The spray absorber liquid flow is regulated on the exit temperature of the gas. Absorption of the gas is dependant on the liquid to gas surface and the mass transfer coefficient. Drying of the spray takes place in two stages. The first stage is the straight evaporation of a part of the droplet, the second stage starts when the critical droplet diameter is reached. This is the diameter at which some of the slurry forms initial solid. The second stage of drying takes more time than the first stage, because the moisture will have to evaporate through a crust of solids. During their time in the absorber, the feed droplets lose their moisture to the hot gas and are converted into dry powder particles. Hot gas absorbs this moisture, so its absolute humidity increases while its temperature is reduced. The dry powder falling on to the conical portion of drying chamber slides down to the bottom of drying chamber with the assistance of vibrators/knockers and is collected in a collection bag. The gas leaving the drying chamber entrains some of the dry powder, which is recovered in, and collected from the bag filter.
The following chemical reactions take place in the spray absorber, the last reaction however doesn't occur in the spray absorber however, sulphur dioxide does not absorb well in acidic conditions:

$$\begin{aligned}
Ca(OH)_2\text{(aq)} + 2HCl &\longrightarrow CaCl_2\text{(s)} + 2H_2O\text{(l)} \\
Ca(OH)_2\text{(aq)} + 2HF &\longrightarrow CaF_2\text{(s)} + 2H_2O\text{(l)} \\
Ca(OH)_2\text{(aq)} + SO_2 &\longrightarrow CaSO_3\text{(s)} + H_2O\text{(l)}
\end{aligned}$$

5.4 Fabric Filter

Downstream the spray absorber a fabric filter is placed. The dust formed in the spray absorber is collected in the fabric filter. The separated dust is a mixture of unreacted lime and salts (e.g. CaF_2, $CaCl_2$, $CaSO_4$). Fabric filters have a very high collection efficiency towards particles. Another advantage is the additional effective contact time between the flue gas and a layer of absorbent (lime) on the filter surface. Hence a larger conversion is estabished then with a spray-absorber and ESP.

5.4.1 Operation

Fabric filters consist of various compartments, in each of which a number of dust bags is installed. The flue gas has to pass through the fabric material of the bags, including the filter cake on the bag filter material, which itself also acts as a filter. If the dust layer on the bags in a compartment is too thick, operation for this compartment is interrupted and the bags are cleaned. Cleaning methods include mechanical shaking, reverse flow and pulsed jet cleaning. These three cleaning techniques are discussed below. With bag filters, very low dust emission concentrations can be reached (<5 mg/m^3). The two fundamental parameters in sizing and operating bag houses are the air to cloth (A/C) ratio (in m/s) and the pressure drop (in Pa) (Soud, 1995[23]). Other important factors which affect the performance of the fabric filter include the flue gas temperature, dew point and moisture content, particle size distribution and chemical composition of the fly ash. The air to cloth ration is a measure of fabric required to filter the flue gas in a given baghouse. Pressure drop is

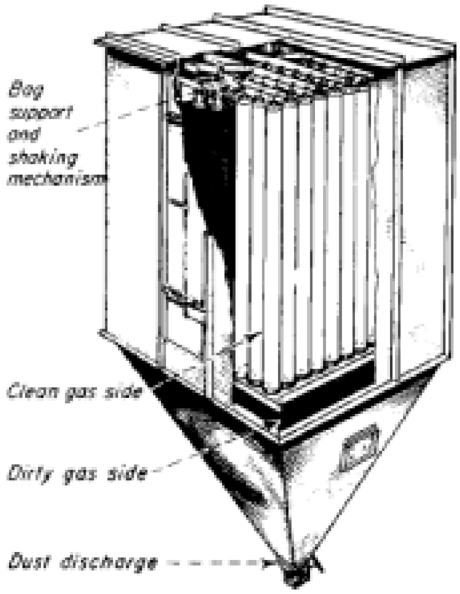


Figure 5.5: Fabric Filter with shake system

the measure of the energy required to move the flue gas through the baghouse stucture and bags. Factors to be considered with the air to cloth ratio include type of filtration fabric, dust properties, the inlet dust loading, the cleaning method and the interaction of these factors and others with the selected fabric. The air to cloth ratio is the most important parameter in baghouse design as it determines the size of the device and hence the capital cost. Factors affecting the pressure drop are particle size distribution, cake porosity, filtration media and particle properties/flue gas composition. The pressure drop increases as the particle size decreases for a given flue gas throughput. Dust is collected on the surface of the fabric. Fabric filtration technology can be divided into three types depending on the bag cleaning mechanism

- reverse gas (sending a stream (of i.e. cleaned flue gas) or air in a reverse direction through the filter compartment causing the bags to collapse inwards partially and dislodge the fly ash cake);
- pulse-jet (sending pulses of compressed air into and through the filter bags);
- shake/deflate (mechanical shaking of the bags)

Reverse gas systems

Reverse gas systems generally operate at low air to cloth ratio of 0.008-0.011 m/s. Fly ash collection is on the inside of the fabric. Reverse gas systems are off-line bag cleaning methods. A variation in the reverse gas bag cleaning mechanism is the introduction of low frequency sound (sonic horns), simultaneously with the normal flow of the reverse flue gas. This is to add energy to the removal of the fly ash layer (Bustard et al, 1988 [24])

Pulse jet systems

Pulse jet technology was first applied to collect fly ash from coal combustion in the mid-1970s. In general, they operate at an air to cloth ratio of 0.015-0.02 m/s. Fly ash collection takes place on the outside surface of the fabric. A pulse of air is used to dislodge the fly ash off the fabric. Bag cleaning can be performed on-line by pulsing selected bags while the remaining bags continue to filter the flue gas. Three cleaning methods have evolved for the pulse-jet systems. These are (Belba et al, 1992 [25])

- high pressure/low volume pulse (HP/LV) (276-690 kPa) used mainly in the USA;
- intermediate pressure and volume pulse (IP/IV) (103.5-207 kPa);
- low pressure/high volume pulse (LP/HV) (51.8-69 kPa).

Longer filter bags are used in pulse-jet systems so that fewer bags reduces area. Their compactness translates as reduced capital cost compared to the other conventional baghouses.

Shake/deflate systems

Shake/deflate systems are off-line bag cleaning methods. Their design in many ways is similar to that of reverse gas baghouses. For bag cleaning, a shaking force is applied, at the top of the bags, at a frequency of several cycles per second causing the bags to sway. In general, shake/deflate units operate at a higher air to cloth ratio compared to reverse systems due to the more efficient bag cleaning mechanism. The air to cloth ratio corresponding to a particular pressure drop is typically in the range of 0.03-0.04 m/s. The choice of fabric depends on the characteristics of the particles to be collected, the composition and the temperature of the flue gas and the operating temperature of the baghouse. A primary fly ash layer is usually necessary to achieve high performance in conventional fabrics. Plugging in the fabric caused by small particles or water droplets in the flue gas can cause excessive pressure drop, hence reducing collection efficiency with a possible consequential reduction in plant output. Wear and tear of the fabric, ripping or pin-holes, can also reduce the fabric effectiveness as a filter. Filter drag (resistance to flue gas flow) is an indicator of baghouse operating stability and performance. It is the ratio of tubesheet pressure drop to air to cloth ratio. Tubesheet pressure drop is the difference measured across the tubesheet, from which the filters are suspended, in a single compartment. This is the sum of pressure drops through the cage (which is holding the bag), the bag fabric and the filter cake. It is dependent on air to cloth ratio, baghouse cleaning frequency, cleaning pressure and boiler load. Filter drag should remain constant while cleaning frequency and boiler load remain constant. When the gas pressure drop rises to a chosen upper limit as the result of dust accumulation, the gas flow is stopped and the shaker is operated, giving a whipping motion to the bags. The dislodged dust falls into the dust hopper located below the tube sheet. If the filter to be operated continuously, it must be constructed with multiple compartments, so that the individual compartments can be sequentially taken off line for cleaning while the other compartments continue in operation.

5.5 Wet Scrubbers

5.5.1 Introduction

Wet scrubbers are very commonly used as gaseous pollutant control devices. Wet scrubbers create large liquid-to-gas surfaces so that gaseous pollutants may be absorbed by the scrubbing liquid. A large ratio of liquid surface area to gas volume is created by a spray of droplets. The surface is maximized when the greatest number of the smallest sized droplets is created per unit volume of scrubber. In the scrubber gaseous pollutants first dissolve physically in the scrubber's washing liquid. Consequently, the physically dissolved pollutants may react chemically with components in the liquid phase. Since the pollutants have thus been transferred from the gaseous phase to the liquid phase, it is necessary to remove the 'dirty' scrubber liquid from the scrubber and clean it. This is done by a downstream device that separates the pollutants from the washing liquid. Typical downstream devices of this type are -settling tanks, cyclones, or in this process design a bag filter [26] [27]. The chief advantages and disadvantages are mentioned in table 5.5.1.

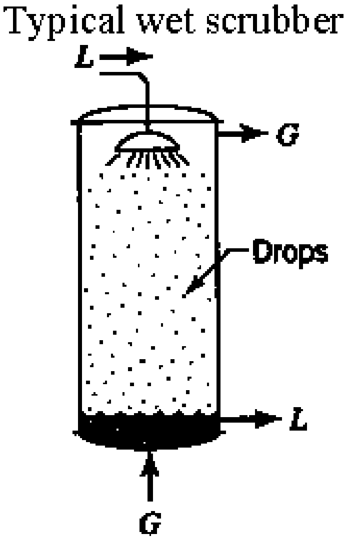


Figure 5.6: Typical Wet Scrubber (counter current)

Table 5.4: Table 1; Advantages and disadvantages of wet spray scrubbers

Advantages	Disadvantages
Relatively low pressure drop	Waste product collected wet
Can handle flammable and explosive dusts with little risk	May create water (or other liquid) disposal problem
Fiber glass-reinforced plastic (FRP) construction permits operation in highly corrosive atmospheres	When FRP construction is used, it is sensitive to temperature
Ability to collect particulate matter as well as gases	Relatively inefficient at removing fine particulate matter
Increasing height improves mass transfer without requiring purchasing of new equipment	Relatively high operating and maintenance costs
Relatively low capital cost	
Relatively free from plugging	
Relatively small space requirements	

Main processes in the first wet scrubber (first 3); the last reaction in the second wet scrubber :

HCl(g) + H_2O(l) $\longrightarrow$ H^+(aq) + Cl^-(aq) + H_2O(l)
HF(g) + H_2O(l) $\longrightarrow$ H^+(aq) + F^-(aq) + H_2O(l)
Heavy Metals + water(pH$\approx$ 1) $\longrightarrow$ dissolved Heavy Metals
SO_2(g) + $2NaOH$(l) $\longrightarrow$ Na_2SO_3(s) + H_2O(l)

5.5.2 Wet scrubber processes

In order for the absorption process to occur, several criteria must be met. First, a driving force; second, sufficient contacting area between gaseous and liquid phase (often called solvent phase); third a sufficient contact time to ensure that the gas and solvent can reach equilibrium. There are two basic mechanisms of absorption: chemical and physical.

Physical absorption

Physical absorption is the process by which a gas (e.g. a gaseous pollutant) physically dissolves into a liquid phase without any change in chemical composition occurring. A common example is the absorption of HCl into water. HCl is very soluble in water; HCl physically dissolves into water forming dissolved HCl. Given sufficient time in a closed system, physical absorption eventually leads to an equilibrium state being reached between the liquid and the gaseous phase; that is, no net mass transfer occurs with time. The main factors driving the rate of physical absorption are:

1. The difference between the molar concentration of the gas prior to absorption, and the equilibrium concentration of the gas in the liquid phase. The greater this difference in concentration, the greater the rate of absorption.

2. The contacting area of the liquid phase per unit of scrubber volume ($m^2/m^3_{Reactor}$). The greater the contacting surface area, the greater the

rate of absorption.

Chemical absorption

In chemical absorption, the gaseous pollutant first dissolves physically into the liquid phase and subsequently reacts chemically with components in the liquid phase to form one or more new compounds.
Although chemical absorption does not alter the mechanisms of physical absorption (i.e. mass transfer from the gaseous to the liquid phase), it usually strongly affects the equilibrium state. As described above, the rate of absorption is directly related to the difference between the concentration of the pollutant within the bulk of the gaseous phase and the concentration of the pollutant in the bulk of the liquid phase. Again, given sufficient time in a closed system, physical absorption eventually leads to an equilibrium state being reached between the liquid and the gaseous phase, at which no net mass transfer occurs between the liquid and the gaseous phase. The concentrations in the gaseous and the liquid phase corresponding to this equilibrium are called the equilibria concentrations. By chemical reaction, a new equilibrium state is created, the concentration of the pollutant in the liquid phase can be reduced to zero. Thus, through chemical reaction, the liquid phase (the solvent) can absorb much greater quantities of gaseous pollutant than it could have without chemical reaction. This phenomenon often drastically increases the rate of gas absorption. In general, the chemical reactions used in absorption (e.g. neutrilization) are relatively fast compared to the time required for mass transfer. These reaction rates are therefore usually assumed to be instantaneous.
In figure 2, a graphical representation is given of the differences for straight physical absorption, and physical absorption followed by instantaneous chemical reaction.

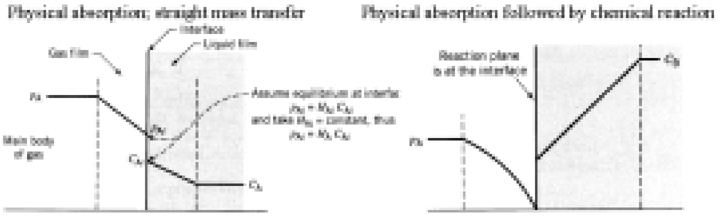


Figure 5.7: Difference of concentration profile between straight physical absorption, and physical absorption followed chemical reaction

Chapter 6

Process control

In order to prevent emissions due to eventual pressure build up, the main flue gas stream is free of valves. All pumps shown in the Process flow scheme are dual implemented in order to insure safe process continuity.

6.1 Control for the High Temperature filter

The pressure drop over the ceramic candles is constantly monitored, when this pressure drop exceeds a normal value, air is used to clean the filters by means of an air blow (from V101). The air tank (V101) is filled up under pressure, when the pressure in the air tank recheases is high enough, the entrance valve is closed. The fly ash is dislodged into the fly ash storage tank (V102).

6.2 Control for the SCR reactor

Controls are installed for the following purposes:

1. ammonia quantity injection control
2. monitoring gas side pressure drop
3. reactor temperature. The inlet especially is used for the injection of ammonia only above a minimum allowed operating temperature

The amount of ammonia that has to be injected is related to the flue gas flow entering the reactor, it is assumed that the NO_X content remains constant. The reactor temperature is measured, when this temperature reaches values below 280 ° the amount of ammonia that is added is reduced in order to diminish ammonia slip. The reactor temperature is kept at a constant temperature by adjusting the flow through the heatexchanger 1 (R101). By monitoring the pressure drop, the fouling of the catalyst can be followed.

6.3 Control for the spray absorber

The spray absorber lime feed flow is controlled on the acidity of the gas. The lower the pH of the gas, more lime will be introduced in the spray absorber. The spray scrubber liquid feed flow is controlled on the exit temperature of the gas. The inlet temperature of the gas is 210 °C and the exit temperature is 150°C. The higher the outlet temperature of the gas, more liquid will be introduced. This liquid feed consists of a part coming from the wet scrubbers, and a part coming from the lime pre-mixing tank.

6.4 Control for the Fabric filter

The pressure drop over the fabric filter is measured, when the pressure drop becomes to high, the bag is cleaned by means of a mechanical shaking mechanism. The fabric filter consists of 6 compartments that can shake seperately

6.5 Control for the wet scrubbers

The first scrubber liquid feed is regulated by the pH in the scrubber, which should be ≤ 1. When the pH becomes higher than one, the liquid feed will be regulated to a lower flow, thus lowering the pH. If the pH in the scrubber becomes too low, the gas contains more acids, which are also transported to the liquid; and thus the liquid feed will be increased to increase the pH.
The quench of the first scrubber regulates the temperature in the scrubber to 74°C. The temperature may not be higher than 80°C, otherwise the rubber lining of the column may catch on fire. If the temperature of the gas increases suddenly, the liquid flow to the quench will be increased to prevent temperatures higher than 80°C.
The second scrubber liquid feed is regulated by the pH in the scrubber, which should be $\cong 6$. If the pH is too low, the gas contains more sulphur dioxide, which is also transported to the liquid. Thus more caustic soda solution will be added to neutralize the environment in the second scrubber.

Chapter 7

Mass balances

See Appendix U for the stream summary

Chapter 8

Process equipment and design

8.1 High Temperature dust filter

8.2 Filter size

All calculations and data used are given in appendix B. For a fresh filter a initial pressure drop of 2000 Pa (20 mbar) is chosen as acceptable. Since the pressure drop is dependent of the porosity and the filtration velocity, as shown in figure 5.1, the filtration velocity is 0.21 m/s. The filtration velocity yields the total filtration surface needed for a given gas throughput as shown in figure 8.1. The total filtration surface determines the total cost of the filtration unit.

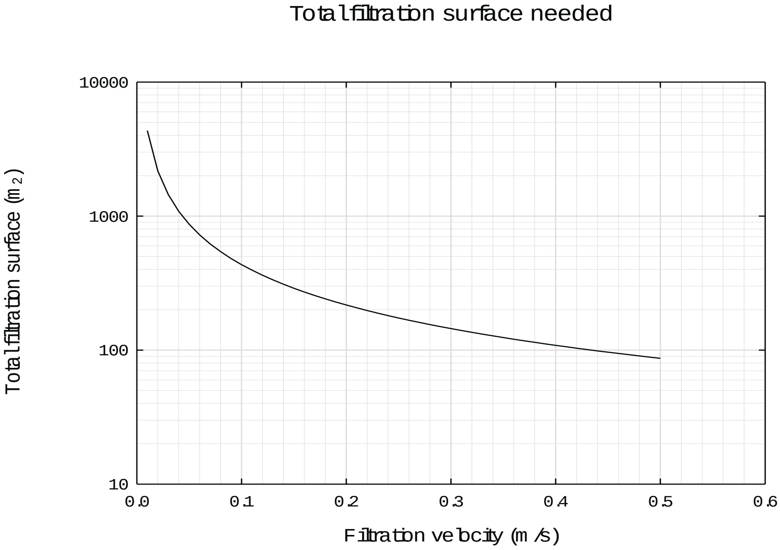


Figure 8.1: Total filtration surface as function of the filtration velocity

With the throughput of the raw gas known (43.40 Nm^3/s) this yields the total required filtration surface (206.67m^2). With an individual surface of 0.29m^2 the number of required candles is 713. The candles are combined in sets of 33 candles often refered as candle bundles. The diameter of a bundle is 0.66 m and the number of bundles (spare bundles included) is 23. The diameter of the required vessel for the filtration unit is 4.42 m. The total volume of the vessel is set to 50 m^3. The hot gas filter system is estimated to last at least 4 years, since it is successfully applied for longer periods in other processes (with a higher dust load and higher operating pressures) (scheibner[16].)

8.3 Selective Catalytic Reduction

8.3.1 Monolith-shaped SCR catalyst

The use of a monolith system have the main advantage that is has a low pressure drop. Figure 8.2 shows an schematic picture of a monolith SCR reactor.

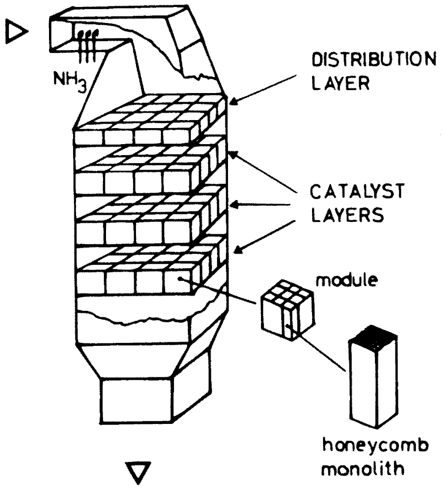


Figure 8.2: Schematic representation of a monolithic SCR reactor

8.3.2 Kinetics of the DeNOx reaction

The rate of the DeNOx reaction is first order in respect to NO concentration and essentially independent of NH_3 concentration when ammonia is in excess. The substoichiometric feed ratio ($\alpha = NH_3/NO < 1$) is employed in most of the SCR indutrial applications in order to minimize slip of unconverted ammonia when NH_3 becomes the limiting reactant. Beekman and Hegedus (Beeckman *et al.*, 1991 [28]) have proposed and fitted to experimental data obtained over commercial SCR catalysts the following kinetic expression based on Eley-Rideal kinetics, which reduces to first order in respect either to NO or to NH_3 in the limiting cases of $K_{NH_3}C_{NH_3} >> 1$ and $K_{NH_3}C_{NH_3} >> 1$, respectively.

$$r_{NO_X} = k_{NO_X} C_{NO_X} \frac{K_{NH_3}C_{NH_3}}{1 + K_{NH_3}C_{NH_3}} \tag{8.1}$$

With:

$$k_{NO_x} = k_0 \exp^{-\frac{E_a}{RT}} \tag{8.2}$$

The derivation of this kinetic expression is shown in appendix E.
With $k_0 = 3.51 \cdot 10^4$ m/s and E_a=79800 J/mol (Beeckman *et al.*, 1991 [29]). Equation (8.1) neglects the influence of oxygen and water concentrations, this simplification is correct in our design because the concentrations of O_2 >2% and $H_2O > 5\%v/v$ The derivation of this kinetic expression is shown in appendix E. Because the adsorption of NH_3 on the catalytic surface is a much faster

process then the desorption, K_{NH_3} has a high value so equation 8.1 combined with equation 8.2 is reduced to equation 8.3.

$$r_{NO_X} = k_0 \exp^{-\frac{E_a}{RT}} C_{NO_X} \tag{8.3}$$

With the use of equation 8.3 catalyst surface of 37689 m^2 is calculated (see appendix D.1) in order to remove 99.8 % of the NO_X from the flue gas stream. (see appendix D.1). In order to determine if external mass transfer limitations are present, equation D.3 was used. Because the adsorption to the catalyst surface is very fast, the concentration at the bulk and at the surface are almost equal (Lydia, 1992 [30]). So the rate is not influenced more then 5% by transport limitations (see appendix D.3) The monolith volume needed for this system is 48 m^3 (with the use of the specific surface (see tabel 8.1))

8.3.3 Pressure drop

Engineering correlations for pipes are readily available in literature. These can be used for monoliths if the feed of each channel is the same. The monolith can the be regarded as a large number of (parallel) tube reactors. The Fanning equation was used to calculate the pressure drop in the pipes.

$$\Delta P = \frac{L}{d}\left(\frac{1}{2}\rho v^2\right)4f \tag{8.4}$$

$$f = \frac{16}{Re}\text{laminar flow circular channels} \tag{8.5}$$

According to the calculation shown in appendix D.4 the pressure drop is approximatelly 200 Pa (2 mbar).

8.3.4 Monolith properties

Table 8.1: Monolith properties (BASF catalyst O 4-85, type 784/G/060)

Properties	value
dimensions of catalyst elements [mm]	150 * 150 * 1100
no. of openings	35 * 35
size of openings [mm]	3.60
internal wall thickness [mm]	0.62
opening ratio	0.71
specific surface [m^2/m^3]	784
density [kg/m^3]	529.92
weight of one element [kg]	13.12
thermal capacity [kJ/kg K]	0.80

8.4 Spray Absorber

8.4.1 Design

Liquid Flow The spray absorber liquid flow is regulated on the exit temperature of the gas. See appendix 8.5 for the determination of the liquid flow. This calculation is based on an energy balance over the spray absorber:[31]

$$Q_{w,leavingthegas} = \phi_{v,gas,in} \cdot \rho_{gas,in} \cdot C_{p,gas} \cdot (T_{gas,in} - T_{gas.out}) \quad (8.6)$$

With:

$Q_{w,leaving\ the\ gas}$ = *Heat flow from gas to liquid* (J/s)

$\phi_{v,gas,in}$ = *Volumetric flow of the gas* (m^3/s)

$\rho_{gas,in}$ = *Density of the gas* (kg/m^3)

$C_{p,gas}$ = *Heat capacity of the gas* $(J/(mol \cdot K))$

$T_{gas,in}$ = *Temperature of the gas at the inlet* (K)

$T_{gas.out}$ = *Temperature of the gas at the outlet* (K)

This heat needs to be transferred from the gas stream to the liquid water stream. This liquid is assumed to have a constant feed temperature of 298 K. The liquid is heated until the boiling point and then it is evaporated. The liquid is assumed to have the same properties as water, because the largest part of the liquid is water. The outlet temperature of the gas is 150°C by demand. The temperature may not be lower, because of possible condensation of water in the bag filter.

At steady state operation an average water flow of 35.75 m^3/hr is required.

Evaporation time The evaporation time of a droplet is determined by its evaporation rate. Amongst other factors, the droplet diameter is the most important factor. The diameter of the droplets is by no means constant. In literature many droplet size ranges are mentioned, from as low as 10 μm. to as high as 800 μm.[22][32][33][34]. In order to keep the size of the apparatus within limits, the evaporation time may not be too high. Based on the mean droplet diameter, 350μm., the evaporation time is calculated, namely 15 seconds. A typical diameter for a spray absorber is 5 m. The gas velocity now becomes 0.55 m/s. The droplets will have the same velocity as the gas flow due to drag. After 8.25 meter there is no more liquid spray in the in the spray absorber. From this moment the conversion will drop. To be sure that all of the liquid is evaporated, because of larger droplets for instance, the drying time is doubled to 30 seconds. The height of the spray absorber is taken 16.5 m, hence the volume of the spray absorber is 324 m^3.

Reaction model The reaction rate can be calculated using the two film theory and the stagnant film model. The mass transfer is limited by gas film mass transfer. Please look in appendix G for a complete derivation of the model. The reaction rate is given by:

$$-r_A = \frac{1}{\frac{1}{k_{Ag}a}} \cdot p_A = k_{Ag}a \cdot p_A \quad (8.7)$$

Table 8.2: Dimensions and characteristics spray absorber

Diameter	Height	Volume	Conversion	Conversion	Conversion	liquid	liquid
(m)	(m)	(m^3)	HCl	HF	SO_2	feed(m^3/hr)	outlet(m^3/hr)
5	16.5	324	62.5%	58%	-	35.75	-

With:
$-r_A$ = $[(moles\ A\ reacted)/(volume\ of\ reactor\ \cdot\ time)]$
k_{Ag} = mass transfer coefficient of the gas film $[(mol)/(m^2 \cdot s)]$
a = interfacial area per unit volume of the tower $(m^2/m^3{}_{reactor})$
p_A = partial pressure of reactant A (bar)

The main acid component absorbed in the spay absorber of the gas, is HCl. The minor component is HF. The dimensions and characteristics of the spray absorber are tabulated in table 8.4.1. See appendix G for detailed calculation. No adequate design equation was found to describe the pressure drop over the spray absorber. Through communication, however, it was found that a typical pressure drop of about 0.8-1.2 mbar is common for spray absorbers.

8.4.2 Process control

The spray absorber lime feed flow is controlled on the acidity of the gas. The lower the pH of the gas, more lime will be introduced in the spray absorber. The spray scrubber liquid feed flow is controlled on the exit temperature of the gas. The inlet temperature of the gas is 210°C and the exit temperature is 150°C. The higher the outlet temperature of the gas, more liquid will be introduced. This liquid feed consists of a part coming from the wet scrubbers, and a part coming from the lime pre-mixing tank.

8.5 Determination of water flow to spray absorber

The following Matlab script was used to determine the water flow to the spray absorber: The flow of water was determined to be 35.75 m^3/hr.

Figure 8.3: Heat flow calculation from gas to water in spray absorber

8.6 Evaporation time of a droplet

The evaporation time of a droplet is dependent on a great number of variables[22]. It is nearly impossible to accurately estimate the evaporation time of a droplet. In the evaporation of a droplet, two stages are identified. In the first period of drying, the evaporation rate is constant. At the beginning of the second period of drying, the first solids begin to form. The diameter of the droplet at this point, is called the critical diameter. The moisture content of the droplet at this point, is called the critical moisture content. The temperature of the droplet will have risen from its initial temperature (T_0) to its temperature at critical diameter (T_{cd}). The temperature of the gas that dries the droplet has lowered from its inlet temperature ($T_{gas,in}$) to the temperature of the gas after the first drying period ($T_{gas,cd}$).
Starting at the second period of drying of the droplet, the moisture in the droplet will not evaporate as quickly as in the first period of drying, because of a forming crust on the outside of the droplet. This resistance will increase by the solid phase becoming more extensive. From this point on, sub surface evaporation occurs. The formed vapor will diffuse through the crust to the gas. The temperature of the gas will drop again from the temperature of the gas at critical droplet diameter ($T_{gas,cd}$) to the outlet temperature of the gas ($T_{gas,out}$). The droplet temperature will rise from its temperature at critical diameter (T_{cd}) to the outlet temperature of the dried particle (T_{out}).
The moisture content of the dried particle is usually defined by specifications of the dried particle. In this estimation of the drying time, the moisture content of the dried particle is assumed to be zero. The generally accepted equation to describe the drying time of a droplet containing (dissolved) solids, is:

$$t_{evaporation} = \frac{\lambda \rho_{liq}(D_0^2 - D_{cd}^2)}{8K_d(\Delta T_{LN1})} + \frac{\lambda D_{cd}^2 \rho_{solid}(W_{cd} - W2)}{12K_d(\Delta T_{LN2})} \tag{8.8}$$

with:

$$(\Delta T_{LN1}) = \frac{(T_{gas,in} - T_0) - (T_{gas,cd} - T_{cd})}{ln(\frac{(T_{gas,in} - T_0)}{(T_{gas,cd} - T_{cd})})} \tag{8.9}$$

and:

$$(\Delta T_{LN2}) = \frac{(T_{gas,cd} - T_{cd}) - (T_{gas,out} - T_{out})}{ln(\frac{(T_{gas,cd} - T_{cd})}{(T_{gas,out} - T_{out})})} \tag{8.10}$$

with:
In the equations above, there are a lot of unknowns. However, the values marked with a (*) are typical values in a spray absorber [22]. The actual, real values of these parameters are usually determined through experiments, and differ from case to case. The calculated drying time for droplets of 350 μm is 15 seconds.

λ = 2268 Latent heat of evaporation (kJ/kg)
ρ_{liq} = 1000 density of liquid (kg/m^3)
D_0 = 350E-6* diameter of droplet at inlet (m)
D_{cd} = 290E-6* critical diameter droplet (m)
K_d = 0.084* mean thermal conductivity of gaseous film around droplet $(\frac{kJ\ m^3}{hr\ ^\circ\mathrm{C}})$
ρ_{solid} = 800* density dried solid (kg/m^3)
W_{cd} = 0.7* critical moisture content $(kg_{liq}/kg_{drysolid})$
W_2 = 0 moisure content in dried solid $(kg_{liq}/kg_{drysolid})$
$T_{gas,in}$ = 210 inlet temperature of the gas (°C)
T_0 = 20* inlet temperature of the droplet (°C)
$T_{gas,cd}$ = 175* temperature of the gas at end of first drying period (°C)
T_{cd} = 65* temperature of droplet at end of first drying period (°C)
$T_{gas,out}$ = 150 outlet temperature of the gas (°C)
T_{out} = 100* outlet temperature of the dries particle (°C)

8.7 Fabric Filter

8.7.1 Design

Information needed relative to specifying bag filters is listed in table 8.4. The filters must be protected from dew points (both acid and moisture) to prevent plugging. The key characteristics of fabrics for use in gas filtration include maximum operational temperature and resistance to acids, alkalis and flexing (due to bag cleaning). Also gas humidity can affect the strength and dimensional stability of the fabrics, due to hydrolysis. Several basic fibre properties are summarised in table 8.3. On basis of this information a bag filter is designed.

Table 8.3: Fabric Filter Characteristics

Generic Name	Aramid	Glass	PTFE	Polyphenylenesulphide	Polybezi Midazole
Trade name	Nomex	Fibreglass	Teflon	Ryton	PBI
Recommended continous operation temperature(dry heat)	204°C	260°C	260°C	190°C	260°C
Water vapour saturated condition (moist heat)	177°C	260°C	260°C	190°C	260°C
Maximum (short time) operation temperature (dry heat)	232°C	290°C	290°C	232°C	343°C
Specific density	1.38	2.54	2.30	1.38	1.43
Resistance to alkalis	Good	Fair	Excellent	Excellent	Good
Resistance to mineral acids	Fair	Very good	Excellent	Excellent	Excellent
Resistance to organic acids	Fair	Very good	Excellent	Excellent	Excellent
Resistance to oxidising agents	Poor	Excellent	Excellent	Attacked by strong oxidising agents	Fair
Resistance to organic solvents	Very good	Very good	Excellent	Excellent	Excellent

Table 8.4: Information needed for the design of the bag filter)

Material of construction	Stainless steel
A/C	0.035 $m \cdot s^{-1}$
Cloth type	Teflon
Filter type and configuration	Shake
Cleaning cycle time	n.a. because no cake data was available

The temperature of the gas that is entering the bag house is about 160 °C. The material for construction of the baghouse is Stainless Steal. The Air to Cloth is set to: 0.035 $m \cdot s^{-1}$. This is a normal A/C ratio of the chosen fabric filter. The Cloth Type chosen is Teflon. This cloth type is widely used and has an excellent resistance against acids and alkali gases and furthermore it has a high durability. The shake system is the configuration of the fabric filter. Because the baghouse has to be operated continously the number of compartments is set to six. Each compartment can be switched off when cleaning is necessary. Each compartement is fitted with 56 bags to comply with the A/C ratio of 0.035 m/s. When one compartment is switched off the pressure drop over the other five isn't influenced much. The cleaning cycle time is not determined because not cake data was available. The bag has the dimension of 5 meters in length and a diameter of 0.25 m. The surface area of a filter is then 3.93 m^2. In the compartment the filter bags have a spacing of 0.1 m. The dimensions of a compartment to fit the filter bags is 2.7x2.35x6 meters (width x length x height). The total housing for this filter is approximately 6 times bigger. A manometer connected across the filter is useful in determining when the filter should be shaken.

8.8 Wet Scrubbers

The models for absorption

The most widely used theory for designing mass transfer devices is the two-film theory [35] [36]. Of all derivatives of this model, the stagnant film model is the most commonly model for modern gas absorption equipment design. The stagnant film model states that in physical absorption, there are three kinds of mass transfer resistance: the gas film resistance, the liquid film resistance, and the liquid bulk resistance. However, due to physical absorption followed by chemical reaction, the liquid film- and the liquid bulk resistance are negligible. The gas film resistance is the only resistance concerning mass transfer that remains in this case. The reaction rate is given by:

$$-r_A \;=\; \frac{1}{\frac{1}{k_{Ag}a}} \cdot p_A \;=\; k_{Ag}a \cdot p_A \tag{8.11}$$

With:

$-r_A$ = $(moles\ A\ reacted)/(m^3_{reactor}\ \cdot\ s)$
k_{Ag} = mass transfer coefficient of the gas film $(mol)/(m^2 \cdot bar \cdot s)$
a = interfacial area per unit volume of the tower $(m^2/m^3{}_{reactor})$
p_A = partial pressure of reactant A (bar)

For a complete derivation and calculation, see appendix G. The typical diameter of a wet scrubber is 3 to 5 meters [37]. The wet scrubber diameter used here is given a diameter of 4 m. The typical wet scrubber consists of cylindrical vessel that can be approximated by a tube. This is not entirely true, because some back mixing and axial dispersion will occur,; these effects will be negligible. Despite of this, the general design equation of a plug flow reactor (PFR) is used to approach the conversion of each substances.

$$\tau_{pfr} \;=\; C_{A,0} \int_0^{X_A} \frac{dX_A}{-r_A} \tag{8.12}$$

With

X_A = conversion of pollutant A (-)
τ_{pfr} = residence time of the PFR (s)
$C_{A,0}$ = inlet concentration of pollutant A (mol/m^3)

The design equation, where conversion of pollutant A is described as a function of the length of the reactor, is given by:

$$X_A \;=\; 1 - e^{-\tau\cdot(\frac{k_{Ag}\cdot a\cdot p_{A,0}}{C_{A,0}})} \;=\; 1 - e^{-(\frac{0.25\cdot\pi\cdot D^2_{pfr}\cdot H}{\phi_V})\cdot(\frac{k_{Ag}\cdot a\cdot p_{A,0}}{C_{A,0}})} \tag{8.13}$$

With:

This equation has the form of a common plug flow reactor design equation. That means that the conversion increases with increasing length of the reactor.

V_{pfr} = volume of PFR (m^3)
ϕ_v = volumetric gas flow (m^3/s)
D_{pfr} = diamter of PFR (m)(= 3.5 m)
$P_{A,0}$ = initial partial pressure pollutant A (bar)
H = height of the scrubber (m)

The partial pressure of the pollutant is calculated by combining the initial concentration of the pollutant, and the initial total molar flow of the gas.

See figure 3, for a typical conversion versus length of reactor graph. At a certain point in the reactor the conversion has the desired value. The bigger part of the pollutants have been absorbed into the liquid and has reacted (possibly with other components) in the liquid phase. The conversion of the gaseous pollutant per height unit of the wet scrubber is known. By combination of the conversion curve and emission regulations, and thus a maximum release of pollutants per cubic meter, the volume of the reactor is determined.

Emission regulations in the Netherlands demand that the HCl release to the atmosphere from waste incinerators, is maximal 10 mg/m^3. At the inlet the concentration is 450 mg/m^3, thus the conversion (X_A) must be at least ((450-10)/444) = 0.978. It has been taken that in the first scrubber all acid gases absorb, except for sulphur dioxide (SO_2), which absorbs much better in less sour environment. The scrubber height is designed on the conversion of HCl throughout the scrubber.

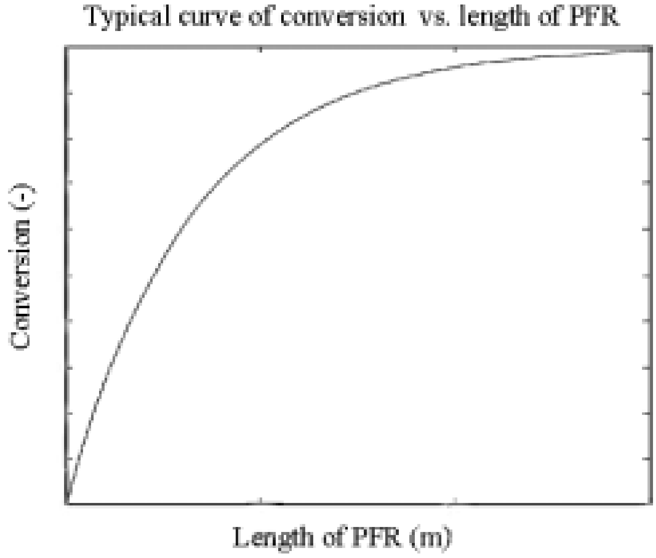


Figure 8.4: Typical conversion vs. length of PFR curve

The k_{Ag} of HCl in the first scrubber is 0.6 $(mol)/(m^2 \cdot bar \cdot s)$ [38]. Wet scrubbers have a typical a of 60 (m^2/M^3) [35]. The initial partial pressure of HCl is 3.58E-4 bar. The required conversion reaches the desired level of 97.8% at the height of 13.0 m. The conversion of HF is also satisfactory at this point in the scrubber. Emission regulations state a maximal release of 1 mg/m^3 of

Pollutant	a (m^2/m^3)	k_{Ag} $(mol)/(m^2 \cdot bar \cdot s)$	$P_{A,0}(bar)$	Conversion (%)
HCl	60	0.9	3.58E-4	97.8
HF	60	0.8	0.22E-4	96.2

Table 8.5: Dimensions and characteristics wet scrubber 1 and 2

Diameter (m)	Height (m)	Volume (m^3)	Conversion HCl	Conversion HF	Conversion SO_2
4	13	163.4	97.8%	96.2%	-
4	19	238.8	-	-	90%

HF, the release from the first wet scrubber is 0.24 mg/m^3.
The height of the first wet scrubber is 13.0 m., the diameter is 4 m. The volume of the first wet scrubber is 163.4 m^3.

The volume of the second wet scrubber is determined in the same manner. In the second scrubber, the main gaseous component that is to be removed is sulphur dioxide (SO_2). The volume of the second wet scrubber is 238.8 m^3. For the detailed calculation, see appendix G.

8.8.1 Water balance

Maximal addition of water to the process

In this section, the evaporation rate in the spray absorber and wet scrubber 1 is calculated. As well as the condensation rate in the wet scrubber 2.
In the AVI Amsterdam, no waste water stream is generated. This means that the amount of water that goes into the flue gas cleaning section, also comes out again. There are three locations where water enters the system: in the gas from the furnace, the quench water for the spray absorber, and the liquid feed of the second wet scrubber. The outlet of water is the gas flow from the second scrubber. Consider the spray absorber and the two wet scrubbers as a black box.
From steam tables, the humidity of the outlet of the second wet scrubber is determined. At 70°C, the absolute humidity of a gas stream is approximately $0.28(kg_{H_2O}/kg_{dry\ gas})$. The dry gas mass stream is 48.6 (kg/s). From these two values, the outlet water vapor stream is calculated: $0.28 \cdot 48.6 = 13.61$ (kg/s) water vapor. The inlet flow of water vapor is 7.18 (kg/s).
An overall water balance over the spray absorber and wet scrubbers, shows that an amount of 6.43 (kg/s) of liquid water is added to the system. With respect to the density of water (ρ=1000kg/m^3) and the fact that one hour is

Table 8.6: Black box over the spray absorber and the wet scrubbers

Water vapor outlet = 13.61 (kg/s)
Water vapor inlet = 7.18 (kg/s)
Water supplied = 6.43 (kg/s)

3600 seconds, the hourly volumetric flow rate is: 23.15 (m^3/hr).

Gaseous phase, amount of evaporation/condensation

Spray absorber In the spray absorber, an amount of 35.75 (m^3/hr) is evaporated. With respect to the density of water and with respect to time (1 hr=3600 s), the evaporated water mass flow is 9.931 (kg/s). So after the spray absorber, the water vapor flow is the sum of the inlet water vapor flow plus the evaporated water flow: 7.18 + 9.931 = 17.1 (kg/s). The absolute humidity is (17.1/48.6) = 0.35.

Wet scrubber 1 This is also the inlet water vapor flow of the first wet scrubber. The inlet temperature of the first wet scrubber is 140°C. The gas is immediately quenched to a temperature $\leq$80°C for the protection of the rubber lining. This quench will have an effect on the mass flows: water will be evaporated. Let us assume the gas is quenched to 74°C. After the first wet scrubber, the gas is fully saturated with water. With the help of Mollier diagrams [39], a rough estimation can be made of the outlet conditions of the first wet scrubber. See appendix H for a typical Mollier diagram. At 74°C, the humidity at the outlet is approximately 0.36. From the difference in humidity (e.g 0.36-0.35=0.01), the water flow that is evaporated in the first wet scrubber can be determined; this flow is approximately 0.486 (kg/s) (e.g. 48.6$\cdot$ 0.01=0.486). Thus, the water vapor flow from the first to the second scrubber is: 17.1+0.486=17.6 (kg/s).

Wet scrubber 2 In the second wet scrubber, part of the water vapor condenses, because the temperature is lowered to 70°C. The water vapor outlet flow from the second scrubber to the chimney is 13.61 (kg/s). The water vapor inlet flow is 17.6 (kg/s). The difference between these values is the amount of water that condenses per second in the second wet scrubber: 17.6-13.61=4(kg/s). With respect to the density of water and with respect to time, this flow is 14.4(m^3/hr).

Liquid phase

The required flow of caustic soda can be calculated from the removal of sulphur dioxide. The amount of sulphur dioxide that is removed is 56.2 (kg/hr). This means that 140.4 (kg/hr) of 50% $Na(OH)_2$ solution is required. This is equal to a volumetric flow of 0.0937 (m^3/hr). Let's assume that the required caustic soda solution is diluted by a factor 50. The volumetric feed flow rate to the second wet scrubber is 4.7(m^3/hr). With respect to density ($\rho \approx$1000(kg/m^3)) and time, the mass flow is 1.31(kg/s).

The liquid flow from the second wet scrubber to the first wet scrubber, is the sum of the feed of the second wet scrubber, plus the amount that condenses in the second scrubber: 4+1.31=5.31(kg/s).

Table 8.7: Summarized results

Flow phase	Flow from	Flow to	Amount (kg/s)	Amount (m^3/hr)
liquid	lime pre-mix tank	spray absorber	5.12	18.4
liquid	caustic soda pre-mixer	wet scrubber 2	1.31	4.7
liquid	wet scrubber 2	wet scrubber 1	5.31	19.1
liquid	wet scrubber 1	spray absorber	4.81	17.3
gaseous	furnace	spray absorber	7.18	
gaseous	spray absorber	wet scrubber 1	17.1	
gaseous	wet scrubber 1	wet scrubber 2	17.6	
gaseous	wet scrubber 2	chimney	13.6	
liq.to gas	inside	spray aborber	9.931	35.75
liq.to gas	inside	wet scrubber 1	0.486	1.75
gas to liq.	inside	wet scrubber 2	4.0	

The liquid flow from the first scrubber, via the settling tank, to the spray absorber, is the liquid flow to the first wet scrubber minus the flow of water that evaporates in the first scrubber: 5.31-0.486=4.82(kg/s).
The total liquid flow to the spray absorber is 9.931(kg/s). The lime milk solution flow is the total liquid flow to the spray absorber minus the liquid flow coming from the first wet scrubber: 9.931-4.82=5.1(kg/s).

Summarized

In table 4 the results of the calculations are shown.

From contact with Mr.Lohe from Lurgi in Germany, a liquid recycle rate was determined [40]. A typical recycle rate ($\phi_{V,rec}$ in (m^3/hr)) to maintain enough liquid to gas surface, should be about five times the volume of the reactor. For wet scrubber I, the recycle rate is $\phi_{V,rec}$=800 m^3/hr. For wet scrubber II, the recycle rate is ϕ_V, rec=1200 m^3/hr. No adequate design equation was found to describe the pressure drop over the wet scrubbers. Through communication, however, it was found that a typical pressure drop of about 0.8-1.2 mbar is common for wet scrubbers.

Nomenclature

a, b	inside and outside diameter of the cilindrical candle	(m)
C_{NO_X}	NO_X concentration	$(mol/(m^3s))$
C_{NH_3}	NH_3 concentration	$(mol/(m^3s))$
d	Monolith channel diameter	(mm)
E_a	Activation energy	(J/mol)
f	Fanning friction factor	(-)
k_1	Resistance corresponding to viscous effects	(m^{-2})
k_{NO_X}	Reaction constant	(m/s)
k_0	Pre exponential factor	(m/s)
L	Length monolith channel	(m)
r_{NO_X}	NO_X reaction rate	$(mol/(m_{cat}^2s))$
R	Gasconstant	(J/mol K)
T	Temperature	(K)
U_0	Face velocity through outside surface of filter	$(m \cdot s^{-1})$
v	Velocity	(m/s)
Δp	Pressure drop over filter	(Pa)
μ	gas viscosity	$(Pa \cdot s)$
ρ	Density	(kg/m^3)

Chapter 9

Waste streams

The waste streams produced in the flue gas cleaning system are respectively the flue gas, waste water and solid residues. The flue gas leaves the chimney and satisfies strict Dutch and future European legislation. The lisence of AVI-Amsterdam prohibits waste water drain off.

9.1 Flue gas cleaning residue

The waste water produced in the wet scrubbers is first neutralised, flocculated and sedimentated to remove mainly heavy metals. The sedimentated solid is separated from the water by a room filter press. The obtained filter cake is discharged as described in paragraph 9.4. The partially cleaned water is evaporated in the spray absorbers. The solid salty residue of the evaporated waste water is collected together with the solid reaction residues of the flue gas in the downstream fabric filter and is collected as flue gas cleaning residue. From the fabric filter it is transported pneumaticly to the silos. The salts can either be further processed to produce saleable salts or transported by lorries to a special dumping area.

9.2 Fly-ash

The fly ashes from the high temperature dust removal section are transported to a silo. These fly ashes can either be treated with acid water from the wet scrubbers to leach out heavy metals (not included in this design) or directly loaded onto lorries for further use. A useful application for fly ash is in the asphalt industry as filling material.

9.3 SCR catalyst

After the three years life span of the catalyst, the catalyst is returned to the supplier for regeneration.

9.4 Filter cake

The filter cake from the water treatment section consists mainly of heavy metal containing salts and are therefor stored in containers¡106¿. The containers are transported to a special dump area.

Chapter 10

Process safety, Health and Environment

10.1 Process Safety

In order to operate the refuse incineration plant safely, a risk analysis needs to be assessed. This conceptual process design only contains the flue gas cleaning section of the factory, therefore items such as the high pressure steam drum and pipes that are used for electricity generation are not assessed. Still, several risks are present in this section of the plant. They can be divided into chemical and mechanical risks; subsequently their possible influence on people, property, and environment has to be assessed. The mechanical risks imply risks from moving parts of the equipment, or from failure of equipment for instance, such as:

- Movement of raction salt removal conveyer belt
- rupture of a conduit
- Plugging of a nozzle

The chemical risks imply handling of the side stream chemicals, such as ammonia, lime, and caustic soda. Other chemicals are those that could be released from process streams in the case of failure, or from the chemical waste streams. Examples of chemical risks are:

- Leakage of ammonia feed
- Leakage of flue gas

This is why a unit per unit HAZOP (Hazard and Operability) analysis and a DOW's F&EI assessement is needed.
First, a part of the refuse incineration plant that is not part of the flue gas cleaning system has to be mentioned, because of its possible impact on people and the environment, and because it will be excluded from further analysis. This unit is the refuse bunker. This part of the plant is a sultry place that contains large quantities of refuse that could catch fire. Therefore a fire extinguishing

system is needed in the bunker. Also, a biological risk is attendant here: next to a variety of wildlife, such as rats and other vermin, bacteria and possible viruses are present in the bunker. The spreading of bacteria and viruses is only possible through physical contact or through air. Direct contact with the refuse after it has been dumped into the bunker is impossible, it is forbidden to enter the bunker. Spreading through the air is compromised, because the air for the incineration process is extracted from the refuse bunker. All bacteria and viruses present in the air will be incinerated. The risk of rats and other vermin is contained inside the bunker, they too are incinerated. Another risk is involved with the big refuse crane. Obviously, this could inflict serious harm to people. However, entering the bunker is forbidden.

10.2 HAZOP

In the Netherlands the ARBO legislation (Factories Act) lays down strict working conditions for employees. Strict regulations concerning mechanical and chemical risk are established. In the order of appearance in the flue gas cleaning section, possible unit failure is assessed in table 1.

More chemical risks lie in the handling of the side streams of chemicals, such as lime milk and caustic soda, and in handling of the waste streams. All molecular standard and hazard properties and characteristics are tabulated in appendix I The waste product from the HT-filter is fly ash, which contains some toxic substances, such as condensed sulphur dioxide (SO_2), hydrochloric acid (HCl), hydrofluoric acid (HF), heavy metals, and more. The fly ash will be transported mechanically; if, however human intervention is required, protective clothing, gloves, and goggles are obligatory.
The side stream to the SCR consists of ammonia. Direct contact with ammonia is a burning and painfull exprience, it is also toxic. Ammonia can catch on fire, although difficult. More important is that it is explosive within the vlometric percentage of 15-30.5 v%. Complete physical protection is needed, as well as very good ventilation.
The side stream to the spray absorber is the lime milk ($Ca(OH)_2$)) stream. Lime can react violently with human tissue. Therefore, complete physical protection, as in handling the fly ash, is needed. The waste stream consists of reactions salts, which are transported pneumatically. If human intervention is required, it shoud be handled with full physical protection.
The waste stream from the bag filter is the same as from the spray absorber.
The liquid waste streams from the wet scrubbers are realeased to the waste water treatment plant, after which it is evaporated in the spray absorber. Although the waste water treatment plant lies outside of the battery limit, it should be mentioned. The waste from the water treatment plant consists of a filter cake that contains flocculated heavy metals and some reaction salts. Again, if human action is needed, next to automated transport, full physical protection is required. The fly ash is used for asphalt filling. The reaction salts and the filter cake are dumped in a landfill.

Table 10.1: Table 1; HAZOP per process unit

Unit	Problem	Possible Cause	Consequence[1]	Action
High Temperature Dust Removal	filter rupture	wear and tear/ sudden enormous presure drop	high dust load downstream / plugging of equipment/ exceeding emission regulation norms	bag filter and wet scrubbers as dust collector & repair HT filter
Selective Catalytic Reduction (SCR)	disintegration/ rupture of ammonia feed conduit	external disaster / ammonia explosion	formation of explosive ammonia cloud / fire/ exceeding emission regulation norms	use emergency ammonia conduit/ ventilate/ fire extinguisher
Spray Absorber	disintegration/ no water feed/ no lime milk feed	external disaster/ stuck valve/ conduit rupture	temperature of gas too high for downstream operations/ acidity of gas too high/ exceeding emission regulation norms	commence emergency water feed/ use wet scrubbers as acid gas absorber
Bag Filter	filter rupture/ melting of filter	wear and tear/ failure of spray absorber	sudden dust load in wet scrubbers/ temperature too high for downstream operation/ exceeding emission regulation norms	bypass filter and repair instantly
Wet Scrubbers	fire/ no water for quench/ no water supply/ no caustic soda supply	failure spray absorber/ plugging or rupture of conduit	destruction rubber inner coating of scrubber/ no acid gas removal/ exceeding emission regulation norms	fire extinguisher and increase liquid flow to quench/ use emergency water conduit/ use emergency caustic soda conduit

[1] A possible consequence of desintegration for all equipment, is the release of the toxic gases that need to be cleaned. In this case, intensive ventilation is needed and containment procedures should be invoked.

10.3 DOW Fire & Explosion Index

There are not many substances in the flue gas treatment section that are hazardous concerning fire and explosion. Actually, only ammonia can explode or burn. On site there are only two locations where ammonia is pesent in excess: the ammonia storage tank and the SCR unit. In order to find out what impact an ammonia explosion might have, the DOW Fire and Explosion Index will be determined. The higher the DOW F&EI, the more hazardous the process is. The determination of this index depends on the material factor, the general process hazard factor, and the special process hazard factor.

The material factor is determined by the stability/detonatability of the material. The general hazard factor is determined by the kind and design of the process. The special hazard factor is determined by toxicity, operating conditions, quantity, and process control.

In appendix J the calculation and specification of this index is shown. The value of the F&EIndex is 2.63 ; this value lies in the range of 1 - 60, which, according to DOW's Fire and Explosion Index Hazard Classification Guide, this value represents a light degree of hazard.

10.4 Dioxins

10.4.1 Introduction

Dioxins are a class of persistent polyhalogenated aromatic hydrocarbons that induce a wide spectrum of toxic responses in experimental animals including reproductive, developmental, and immunologic toxicities as well as carcinogenicity. Dioxin is the generic name for polychlorinated dibenzo-p-dioxins (PCDD) and Furans are polychlorinated dibenzofurans (PCDF), which are abbreviated as PCDD/F. The history of the PCDD/F problem goes back to the late seventies. In 1977 the presence of PCDD and PCDF in fly ash of municipal waste incinerators were discovered (Olie, 1977 [41]). Shortly thereafter it was reported that these compounds were also present on particulates emitted from a municipal waste incinerator. It was already known by that time that PCDDs are extremely toxic for some animal species, and that 2,3,7,8-Tetrachlordibenzo-p-dioxin (also abbreviated as TCDD) is probably the most toxic substance made by man (Reggiani,1982 [42]) (see appendix K). These two discoveries caused considerable discussion on the issue of PCDD formation by thermal treatment of chlorine containing wastes and fuels. Some factors affecting dioxins emissions are:

- Presence of dioxins in the feed,
- Presence of dioxin precursors in the feed,
- Chlorine in the feed,
- Combustion conditions (temperature, oxygen level, turbulence),
- Feed processing.

10.4.2 Health & Toxicity

Contamination of the environment with TCDD or related compounds is commonplace. Most human exposure to these compounds is through food. An estimate by the U.S. Environmental Protection Agency (EPA) in 1994 placed average daily human exposure at 119 pg I-TEQ. A more recent estimate from EPA is 1 pg/kg/day for adults, or 60 to 70 pg/day I-TEQ for an average adult woman. Environmental contamination with dioxin-like compounds can result in small amounts of these compounds in almost any consumer product, including those manufactured from cotton or from unbleached wood pulp (Scialli, 2001 [43]).

The majority of the effects of TCDD and other dioxinlike chemicals appear to be mediated by their binding to a cellular protein called the aryl hydrocarbon (Ah) receptor (Poland et al.,1982 [44]). For many toxic endpoints, the relative potency (in comparison to TCDD) of an individual dioxin congener correlates closely with its affinity for the Ah receptor [6]. Moreover, they accumulate and biomagnify in the food chain due to their fat solubility and pronounced resistance to metabolic degradation. One of the most acute effect of dioxin exposure to man is chloracne, a severe skin disease.

Risk assessments for exposures to dioxins are now typically done using a toxic equivalency factor approach. The toxicity of a mixture of dioxins and furans is expressed in the toxicity of the most toxic compound using weight factors. These weight factors are known as TEF (Toxic Equivalent Factors). The most toxic congener is 2,3,7,8-tetracloricdibenzo-p-dioxine or 2,3,7,8-TCDD and has an TEF of 1. Only the congeners that have chlorine atoms substituted at the 2nd, 3rd, 7th and 8th place have significance toxicity. By multiplying the content of a 2,3,7,8-PCDD/F congener with the concerning TEF the TEQ (Toxic Equivalency Quotient) for this particular congener is obtained. By adding up all TEQ's of the congeners the toxicity of the mixture is expressed as an amount of 2,3,7,8-TCDD.

While a number of toxicity rating schemes have been developed on a national basis, as shown by table M on appendix M, the scheme that has been internationally adopted is that of NATCO/CCMS, under which the TEFs are termed international toxic equivalent factors, or I-TEFs (McKay, 2001[45]). The I-TEFs for the seventeen 2,3,7,8-positional congeners of PCDDs and PCDFs are presented in table N on appendix N. All other congeners that may be present in a sample are assigned a TEF value of 0.0. By using the I-TEFs the corresponding I-TEQs of the compounds can be found by using the method mentioned above. In the Netherlands the maximum emission of PCDD/F in flue gas is 0.1 ng $I-TEQ/m^3$ (11% O2, dry).

A revision of the TEF scheme was undertaken by the World Health Organisation (WHO). The proposed scheme includes coplanar congeners of PCBs within the overall TEQ scheme, by defining TEFs for 12 coplanar PCBs on the basis that their mode of action and the responses elicited in biological systems parallel those of the 2,3,7,8-positional PCDD/Fs. These are also listed in table N on appendix N together with their proposed TEFs.

All European regulatory agencies regard PCDDs and PCDFs as carcinogenic promoters and have defined a tolerable daily intake (TDI) based on a no observed adverse effect level (NOAEL) derived from animal studies. The World Health Organisation (WHO, 1997 [46]) classed 2,3,7,8-TCDD as a known human carcinogen, but continues to regard other PCDDs/PCDFs as not classifiable despite a similar mode of action to 2,3,7,8-TCDD.

Dose responses and tolerable daily intake levels

The USEPA recently reappraised their toxicity rating of PCDDs/PCDFs for 2,3,7,8-TCDD from the slope factor of 156,000 (mg $kg-1$ per day) to 100,000 (mg $kg-1$ per day)[45](McKay, 2001[45]). The approach adopted by the European regulatory agencies has been to assess chronic and acute animal studies for a full range of carcinogenic and acute animal studies for a full range of carcinogenic and non-carcinogenic effects based on NOAEL. European governments have developed a range of TDI, dosage levels. In 1996, the Health Council of The Netherlands reduced their TDI level from 4 pg, I-TEQ kg_{bw}^{-1} per day to 1 pg I-TEQ kg_{bw}^{-1} per day [47]. In Germany, safety factors of 1.10 pg I-TEQ kg_{bw}^{-1} per day with the lower range considered as a precautionary TDI and the higher levels as a preventative TDI. UK, France and Belguim adopted the WHO guideline of 1989, which made a recommendation of 10 pg I-TEQ kg_{bw}^{-1} per day. Sweden, Norway and Finland have adopted a TDI level of 5 pg I-TEQ kg_{bw}^{-1} per day based on using a NOAEL of 1000 pg I-TEQ kg_{bw}^{-1} per day and a safety factor of 200. In the UK, the Committee on Toxicology of Chemicals in Food, Consumer Products and the Environment re-examined the existing UK TDI of 10 in relation to the USEPA report (McKay, 2001[45]). The UK COT considered the existing TDI was sufficient.

Dioxins emission limits

Based on the EEC dioxin directive of 1989, many central European countries [82] have adopted a permissible limit for PCDD/PCDF emissions from MWI plants. In Germany, the emission limit for PCDD/PCDF in stack gas of waste incinerators was set to 0.1 ng $I\text{-}TEQ/Nm^3$ by the 17th BimSchV. For industrial incinerators and thermal processes, a general minimisation rule was released with a guide value of 0.1 ng $I\text{-}TEQ/Nm^3$ for large-scale plants. On the European level a few other countries, among them Sweden, Austria and The Netherlands, have also regulated the PCDD/PCDF emissions to 0.1 ng $I\text{-}TEQ/Nm^3$ for waste incinerators. In the US, a PCDD/PCDF emission limit for waste incinerators has only been released recently with the sum of tetra-through octachlorinated PCDD/PCDF set to 30 ng/Nm^3 ; the US emission limit is about five times higher than the valid Dutch limit.

10.4.3 Dioxins from incineration procesees

Emissions from incinerators are e.g. the flue gases, the fly ash and the slag. Technology advances in the past 15 years has decreased the levels of PCDDs and PCDFs in the fly ash and slag so dramatically, that they are difficult to measure. Recent studies (Abe et al. 1997[48]; Calaminus et al. 1997[49]) have shown that secondary treatment of incinerator residues can reduce the dioxin levels by more than 99%. A new technique in this field is a pre-treatment of the fly-ash with supercritical CO_2 (Kawajiri [50]). In order to design MSW incineration systems to eliminate or minimise dioxin formation, it is important to understand how PCDD and PCDF formation takes place.

10.4.4 Formation of PCDD/PCDF in waste incinerators

General

This section will discuss the thermal degradation of dioxin in incineration systems and then review the PCDD/F formation theories and factors affecting PCDD/F emissions. Particular attention will be given to precursors and also formation and reformation theory mechanisms downstream of the actual incinerator.

- Incomplete combustion of organic wastes in the combustion chamber leads to the formation of precursors which can act as precursor for the dioxin/dibenzofuran molecule.
- The MSW waste containts chlorine and metals. The metals are incorporated into fly ash which passes the heat exchanger and so the cooling stage between 400 and 200°C.
- The precursors reacts on the fly ash to dioxin/dibenzofuran catalysed by metals (mainly copper). Other chlorinated trace organics can be formed as well.

Destruction of dioxins and precursors in incinerators

Combustion of dioxins is known to proceed very rapidly at temperatures which occurs in the flame zone of the incinerator. In practice it is generally agreed that combustion temperatures of 850°C and a gas residence time of 2 seconds are necessary for total destruction. It is also generally agreed that at a temperature of 1000°C and a residence time of 1 second the dioxins are oxidised. Attempts to correlate incineration temperature, CO concentrations and other indicators of combustion conditions, with dioxin emission concentrations have been only partially successful. Poor, low-temperature combustion has been shown to result in relatively high emissions of dioxin formation. In an incineration chamber, non-homogeneous conditions may produce localised zones where low temperatures and lower oxygen concentration can cause dioxin formation. Three possibilities for the origin of PCDD/PCDF found in incinerator waste (bottom-ash, fly-ash and fluegas cleaning residue) and the effluent gas have been considered. Firstly, the PCDD and PCDF are already present in the waste burned. Secondly, it is well documented that chlorinated aromatic precursors such as polychlorinated-phenols, benzenes and bi-phenyls act as "precursors" for dioxin formation in the cooling stage of 400-200°C. Thirdly, the presence of active carbon provides the organic material and/or catalytic surface for dioxin formation. The homogeneous gas-phase reaction is also being discussed. To minimise these possibilities for dioxin formation, the optimum design of an incinerator must pay attention to the next four conditions for high destruction efficiency of dioxins

1. Temperature
2. Time
3. Turbulence
4. Excess oxygen

10.4.5 PCDD/F formation and factors affecting emissions

Major factors affecting emissions of dioxins/dibenzofurans from combustion of MSW are:

1. Dioxins/dibenzofurans in the feed
2. Precursors in the feed
3. Chlorine in the feed
4. Combustion temperature
5. Residence time
6. Oxygen available

Dioxins/dibenzofurans in the feed

Dioxins enter the environment as part of a chemical product, such as prestícides. These products are burned as waste in incinerators or as sludge which is contaminated with pesticides. The burning of any organic material containing organochlorine compounds or even inorganic chlorides, such as sodium chloride (Wikstrom, 1998[51]) can form dioxins.

Precursors in the feed

A lot of studies have been done on the formation of dioxins/dibenzofurans from precursors. Three classes of precursors can be distinguished:

1. Polyhalogenated phenols with a halogen-ortho to the hydroxyl group, with a high probability of dioxin formation (Ballschmiter et al. [52], Luijk et al. [53])
2. Ortho-halogenated phenols, primarily with a halogen-ortho to the hydroxyl group, with a high probability of CDD formation (Weber et al.[54],[55])
3. Other chemicals having the possibility, but less likelihood, of PCDD/F formation. These include chlorinated aromatic compounds (Luijk et al. [53])

The majority of the experimental work to date has centred on three classes of precursors: chlorinated phenols, chlorinated benzenes, and PCBs. PCDD formation from the combustion of chlorinated phenols has been tested extensively. It has been shown that these precursors form the highly TCDD and congeners.

Chlorine in feed

The chlorine content of fuel is obviously an important parameter affecting the formation of PCDDs or PCDFs. Shin and Chang (Shin et al.[56]) developed a list of combustion systems emitting polycyclic organic matter including PCDD/F. Other authors have demonstrated the effect of chlorine on PCDD emissions and it has been shown (Moche et al. [57]) that PCDDs were emitted from coal combustion only when chlorine was added and PCDD formation occurred during the combustion of pine in the presence of HCl, but no PCDDs were detected during the combustion of pine alone. The precursor theory has been widely accepted but these inorganic chlorine studies show that the mechanisms involved for dioxins/dibenzofurans formation are complex. However it can be generally stated that chlorine has to be present for the formation of dioxins. Also can be stated that increased chlorine content of the waste shows an increased dioxin emission. The dioxin formation is influenced by such an amount of factors that the role of chlorine is still uncertain. Furhter studies also have shown that the presence of sulphur dioxide reduces the dioxin concentration during incineration (Raghunathan et al, 1996[58], Lindbauer et al, 1992[59]).

Combustion temperature

Experimental evidence suggests that temperatures of 500-800 °C promote dioxin formation, while temperatures greater than 900 °C destroy PCDD/Fs. Municipal waste incinerators are considered a major combustion source of dioxins. The large mass burn units are characterised by low combustion temperatures. In comparison, many hazardous waste incinerators and high efficiency boilers are designed for efficient combustion. For example, no PCDDs were detected in the emissions of the Vulcanus incinerator ship during the combustion of PCDD contaminated herbicide orange. The combustion temperature during this study was 1600 °C.

Residence time

The residence time necessary to destroy PCDDs and the combustion temperature are inversely related. The higher the combustion temperature, the shorter the required residence time for PCDD destruction.

Oxygen availability

Oxygen availability is a function of both the air/fuel ratio and air/fuel mixing efficiency, both of which are of concern when burning solid waste. An insufficient supply of oxygen or poor air/fuel mixing will promote poor combustion conditions and PCDD formation. Municipal waste incinerators are usually fired with excess air. However they may have poor air/fuel mixing due to the great amount of waste or poorly designed air distribution system.

10.4.6 Formation and reformation mechanisms

The presence of dioxins in the flue gases and on particulates in combustion systems can be attributed to two possible formation mechanisms based on heterogeneous catalysed reactions:

- Dioxins are formed from precursors which are present within the fuel or waste, or which are formed during the combustion processes,
- De novo synthesis from non-chlorinated hydrocarbons, carbon, oxygen, chlorine and other atoms present in the combustion products.
- Some work is being carried out on possible contributions to PCDD/PCDF formation from homogeneous reactions (Taylor, 1999[60]).

Dioxin formation occurs on particles entrained in the flue gas during the brief time they pass the 300°C region or from reactions on particles deposited on surfaces where the temperature of 300o°C prevail. Estimates of the activation energy for desorption of dioxin molecules from a particle surface suggest that, at temperatures below 400 °C, the rate of desorption of dioxin molecules from a particle surface is too slow for the observed dioxin concentrations to be produced during the transit time of the flue gas. If this is the case, then it may only be reactions on deposited particles that make a significant contribution to observed fluegas dioxin concentrations. Another theory, apart from possible gas-phase reactions, is the formation of dioxins in air from partculate organic carbon, by gas-solid reactions with oxygen and halides catalysed by copper(II) (Lujk et al, 1994[61]). It is claimed that the resulst from laboratory experiments clearly prove that particulate carbon is the primary source for dioxins. The optimum temperature for formation is 300-400°C.

De novo synthesis of dioxins from particulate carbon is supported by experimental work (Dickson, 1989[62]). This work shows that the catalysed formation of dioxins from pentachlorophenol(PCP) results in concentration magnitudes higher than the de Novo systhesis from particulate carbon, inorganic chlorides and copper(II). These reactions were tested under identical conditions of temperature, air flow rate and heating time. This research did conclude, however, that particulate carbon can catalyse the formation of dioxins from PCP, and promote the dechlorination of highly chlorinated dioxins to lower congeners. There is no consesus about which of the mechanisms dominates, or whether both can participate. In the de novo synthesis the PCDDs/PCDFs form from a variety of carbon species, condensed to a polymeric network referred to as particulate carbon (Heev et al, 1995[63], Stieglitz et al, 1997[64]). The precursor theory predicts PCDD/PCDF formation from chemical similar species such as chlorobenzens and chlorophenols (Lipper et al,1991[65], Born et al, 1993[66]). Other studies have extended studies of the precurser theory to two carbon chain length compounds such as ethylene and acetylene (Froese et al, 1997[67],Wehrmeier et al, 1998[68]). A detailed analysis of the de novo and precursor theory has been presented by (Lenoir et al, 1991 [69]) and these authors propose that the precursor theory is likely to be the dominant mechanism in MSW incineration.

The relationship between the HCl concentration and the general dioxin concentration under fixed combustion conditions appears to be exponential. In the reported tests dioxin formation was found over a temperature range from 900 to 240°C. Recently, it has been demonstrated (Iino et al, 1999[70], Gullett et al, 2000[71]) that polycyclic aromatic hydrocarbons also chlorinate and decouple to form PCDD/Fs. Since HCl is a combustion product of all organochlorine compounds, it follows that any of these compounds is a potential dioxin precursor on combustion. Laboratory studies on the effect of oxygen, carbon monoxide and hydrogen chloride show a weak correlation with PCDD/PCDF formation levels in MSW incineration systems (Shin et al, 1999[56], Addink et al, 1995[72], Kairmann et al, 1992[73]). It has been shown that chlorine was more reactive to chlorinate organic materials then hydrogen chloride (Gullett et al, 1993, 1994 [74],[75]).

Influence of the flue gas temperature on dioxin formation

The optimum formation temperature of de Novo synthesis is still a point of dicussion. There is, however, agreement that the temperature is the most influential parameter in dioxin formation (Stieglitz et al, 1997 [64], Born et al, 1993[66], Addink et al, 1991[76]). Data from three research groups were analysed by Shin and Chang (Shin et al, 1999[56]) and plotted as shown in based on chlorophenol as a precursor. They did not concern gas-phase precursors and PCDD/F and analysed only the solid residue after the formation reaction. According to others the most PCDD/F is evaporated rather than it stays in the solid form above 350°C. This is why the optimum temperature in their experiments is around 300°C (Altwicker, 1991[77], Milligan and Altwicker[78]). They also showed that de novo synthesis synthesis in the existence of a chlorine source in the gas stream had a peak rate at 373°C and 398°C for PCDDs and PCDFs, respectively

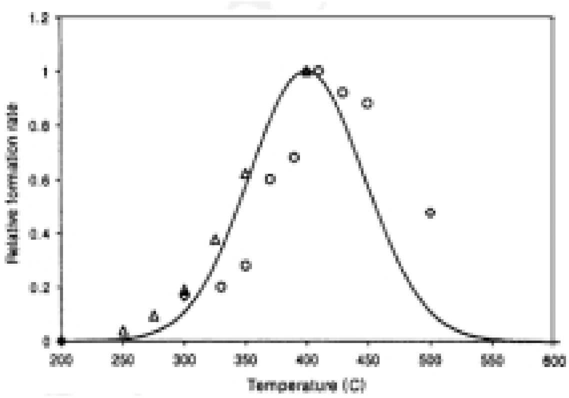


Figure 10.1: Relative formation rate of PCDD/F vs Temperature with chlorophenol as precursor(Shin et al, 1999[56]).

Chapter 11

Economy

In this section an evaluation of the chosen design will be given. This is important for deciding to build the design or not. The following economic information is presented: the investment, the operating costs, income and cash flow. The economic criteria used here are the Rate of Return (ROR), Pay out Time (POT) and the Discounted Cash Flow Rate On Return or earning power (DCFROR).

11.1 Total investment costs

The total investment cost is the sum of the fixed capital costs (FCC), working capital and license costs. The fixed capital is the total cost of the plant ready for start-up. It is the cost paid to the contractors, which includes:

1. Design costs,
2. Equipment and installation,
3. Piping, instrumentation and control systems,
4. Building and structures,
5. All other facilities, such as utilities, land and civil engineering work.

The working capital is the additional investment needed, over and above the fixed capital, to start the plant up and operate it to the point when income is earned. These costs can be divided in:

1. Start-up,
2. Initial catalyst charges,
3. Raw materials and intermediates in the process,
4. Finished product inventories,
5. Funds to cover outstanding accounts from customers.

The difference between fixed capital and working capital is that the latter is recovered at the end of the project and the first one, which are once-only costs, have only the value of scrap at the end. The fixed capital costs are calculated using the Lang factorial method. The fixed capital costs are 91% of the total investment cost. The working capital can vary form 5% for a simple, single product process to 30% for a process producing diverse products. The working capital is fixed at 10% of the FCC.

11.2 Fixed capital Costs

The fixed capital Costs is calculated using the Lang factorial method (see equation 11.1)

$$C_f = f_L \cdot C_e \tag{11.1}$$

in which

C_f Fixed capital costs
C_e Total equipment costs
f_L Lang factor [79]

The calculations of the fixed capital costs can be found in table R.1 & R.2 on appendix R. The cost of the designed units There are no exact data known on the furnace, bunker, heat exchanger and pumps and therefore these costs are estimated.

11.3 Operating costs

Costs for producing the product are operating costs. These cost can be divided in two groups:

1. Fixed operating costs: costs that do not vary with production rate,
2. Variable operating costs: costs that are dependent on the amount of product produced.

Fixed costs

- Maintenance
- Operating labour
- Laboratory costs
- Supervision
- Plant overheads
- Capital charges
- Rates (and other local taxes)
- Insurance

- License fees and royalty payments

Variable costs

- Raw materials
- Miscellaneous operating materials
- Utilities
- Shipping and packaging

Utilities like electricity and steam are a product and not a costs for a waste incinerator. The income on electricity are therefore 'netto'. The calculation of the production costs can be found on appendix S.

11.4 Income and Cash flow

The main product of an waste incinerator is electricity. The income, however, is determined mainly by the income of waste that is collected. The calculation of the income and cash flow can be found in table 11.1.

11.5 Economic Criteria

Economic Criteria is the link between Once-Off investment and annual income and costs. The Economic Criteria used here are the Rate on Return (ROR), the Pay Out Time (POT) or pay-back time and the DCFROR (=earning power). The income tax is set to 45% and the economic plant life is estimated at 15 years and 2 years for construction.
The ROR is is the ration of the annual profit to investment. It is an index of the performance of the money invested. The ROR before tax is simply calculated by dividing the net cash flow by the total investment by equation 11.2.

$$ROR = \frac{Cumulative\ net\ cash\ flow\ of\ the\ project}{Life\ of\ the\ project \cdot original\ investment} \cdot 100\% \tag{11.2}$$

The POT is the time required after the start of the project to pay off the initial investment. This criterion does not consider the performance of the project after the pay-back time and is normally used for judgement of small improvement projects. The POT is normally between two and five years and can be calculated with equation 11.3

$$POT = \frac{Total\ Investment\ Costs}{Net\ Cash\ Flow} \tag{11.3}$$

The DCFROR or earning power is used to calculate the present value of future earnings. The Net Present Value (NPV) has to be calculated for various interest rates. The rate at which the NPV is zero is called the DCFROR. The next equation is used for calculating the DCFROR:

$$\sum_{n=1}^{n=t} \frac{NFV}{(1+r')^n} = 0$$

In which:

r'	Discounted Cash Flow Rate Of Return [-]
NFV	Net Future Value [-]
t	Life of the project [year]
n	Time passed after start of construction [year]

The calculation of the DCFROR is a trial-on-error process and with the aid of a spreadsheet program this value can be found easily. The calculation can be found on appendix T. All important economic numbers are listed in table 11.1.

Table 11.1: Gross Income, net cash flow, economic criteria

Item	Unit	Value	€(x1000)/a	Remarks
Gross Income			68,956	
Production Costs			51,045	
Net Cash Flow, Before Tax			17,911	= (A)
Economical Plant Life & Depreciation				Excl. 23th year salvage
- **Total Investment**	€(x1000)	334,752		= (B)
- Econ. Plant Life, years	Years	22	1	Incl. 2 yrs Des. & Con.
- Annual Depreciation over 22 years			15,216	
Net Cash Flow, After Depreciation			2,695	
- Income Tax @ 45%			1,213	
Net Cash Flow, After Tax			1,482	
Pay-Out Time, Before Tax	Years	18.7		= (B) / (A)
Rate of Return, Before Tax	5.4 %			= (A) / (B)
DCF Rate of Return, Before Tax	%		nil	DCFRoR, IRR, EP
Net Present Value, Before Tax	%	0.2%	-18	From DCF Calc.
Net Future Value, Before Tax			5,565	Interest = 0

Nomenclature

C_e	Total equipment costs	(€)
C_f	fixed capital costs	(€)
DCFROR	Earning power	(-)
f_l	Lang factor	(-)
t	Life of the project	(year)
n	Time passed after start of construction	(year)
NFV	Net future value	(-)
NPV	Net Present Value	(-)
POT	Pay out time	(years)
r'	Discount cash flow rate of return	(-)
ROR	Rate of return	(%)

Chapter 12

Conclusions & Recommendations

12.1 Conclusions

1. High temperature dust removal, with ceramic candle filters is a promising technique. This technique has already applied succesfully in other industries (e.g. Coal combustion)

2. The use of HT-Dust filter prevents precursors of dioxins to form, because the catalyst, copper(II) on fly-ash that supports the formation reaction of dioxins, is removed. Also other reactions that form dioxins are prevented when fly-ash is collected at high temperatures.

3. Catalytic removal of NO_x has the big advantage that also dioxins are destroyed. Dioxins/dibenzofurans and precursors are destroyed by the catalyst. Less ammonia is needed in comparison to SNCR.

4. In the SCR-unit elemental heavy-metals vapors are converted to ionic vapors.

5. The use of a fabric filter instead of a ESP after the spray absorber has the advantage of a longer contact time between lime and the flue gas. The lime is collected on the bag filter and functions as a filter as well which lengthens the time of contact with the flue gas.

6. Minimal waste water is emitted when a wet scrubber is combined with a spray absorber.

12.2 Recommendations

1. Install a cylcone prior to the ceramic candle filters. The majority of the fly ash is then trapped (>90% especially the coarse particulates. The regeneration cycle time can then be extended.

2. Use acidic wash water from the wet-scrubbers to leach the heavy metals out of the fly ash particles yields a more valuable product. Afterwards the acidic water can be cleaned in the described way.
3. The reaction salts of the spray absorbers should be further processed to saleable salts. In this design the salts are free of active carbon and hence heavy-metals and dioxins
4. More research has to be done on catalytic material that can withstand the relative high concentrations of heavy metals and halogenated acids.
5. Combine the SCR-catalyst with the ceramic filter to obtain a intesified catalytic filter. This is also reffered as "process intensification". Process intensification is technically possible and saves a lot of capital cost because only one device is needed instead of two. It is also likely that a lot of energy loss is prevented and space is saved. More research is needed and new ground has to be broken to come to commercial succesful design.
6. Combine the spray absorber with the fabric filter in a new chemical absorbtion filter. The lime droplets are then directly sprayed on the filters surface to form a solid lime cake where the acids react to the corresponding salts. This is another oppertunity the authors see to intensify the flue gas treatment section. This also reduces the number of apparatus needed.
7. Ultimatly one could think of combining the catalytic (SCR) filter with the chemical absorbtion filter to a filter that removes acids, NO_x and fly-ash simultaneously. This of course has the disadvantage that no pure residues are obtained so reuse as useful products is difficult.

Bibliography

[1] http:
www.vvav.nl.

[2] Gemeentelijke dienst afvalverwerking. Avi-amsterdam refuse incineration plant.

[3] http://www.vrom.nl.

[4] M. van Berlo; Jorn Wandschneider. Hr-avi concept voor uitbreiding avi-amsterdam. internal report AVI-Amsterdam.

[5] Cor de Vries. Procestechnoloog avi amsterdam. Personal contact, november 2001.

[6] Koning. Vermindering van microverontreiningen in verbrandingsemissie.

[7] IEA Coal research. Developments in nox debatement and control. *IEA Coal research*, 89:62–69, 1996.

[8] VIP International. Vip international offers sulfuric acid industry no-nox scrubber system. http://www.vipinc.com/nox.asp, 2001.

[9] Thermal energy. Thermal thermalonox tm competitive advantages. http://www.thermalenergy.com/solutions/environment/sol-lownox3.html, 2000.

[10] Prins W.L.; Ham van J., editor. *Industrieele luchtverontreiniging, technieken voor bestrijding en preventie*, Rotterdam, 1994. Vereniging lucht, Samsom H.D. Tjeenk Willink.

[11] Personal communication with R. Holste. bb-power.

[12] Sloss L L. *mercury emission and effects-the role of coal.* IEA coal research, 1995.

[13] Kelly V Thambimuthu. Gas cleaning for advanced coal-based power generation. *IEA coal research*, IEACR/53:73–82, 1993.

[14] D.H. Smith; Victor Powell; Goodarz Ahmadi; Essam Ibrahim. Analysis of operational filtration data, part i. ideal candle filter behaviour. *Powder Technology*, 94:15–21, 1997.

[15] Pall Filtration company. Hot gas filtration. Corporate infomation folder.

[16] Bernd Schneibner. Scumacher hot gas filtration technology. information folder.

[17] Dr.Soung M. Cho; Foster Wheeler Development Corporation. Properly apply scr-reduction for nox removal. *Chemical Engineering Progress*, manuary 1994.

[18] Lesley L. Sloss. Mercury emission and effects-the role of coal. *IEA coal research*, 19, 1995.

[19] Oil and research centre porsgrunn. Nox, survey of nox abatement technology. 2001.

[20] Moulijn J.A.; Kapteijn F. ;Diepen van A.E.; Jansen J.C. Catalysis engineering. Lecture Notes University of Technology Delft, march 1996.

[21] Green D. Perry R H. *Perry's Chemical Engineers Handbook*, volume 18. 6 edition, 1984.

[22] K Masters. Spray drying handbook, fourth edition. 1985.

[23] Soud H. N. Developments in particulate control for coal combustion. *IEA Coal Research*, IEACR 78, 1995.

[24] Bustard C J; Cushing K M; Pontius D H; Smith W B; Carr R C. Fabric filters for the electric utility industry: volume 1: general concepts. *Electric Power Research Institute*, EPRI-CS-5161-4 volumes, 1988.

[25] Belba V H; Grubb T; Chang R. A worldwide survey of pulse-jet baghouse performance on coal-fired boilers. In *Proceedings of the ninth particulate control symposium: volume 2: baghouses and advanced particulate control technologies*, volume 2 of *ERPI-TR-100471*, pages 1.1–1.17, Williamsburg, VA, USA, 15-18 Oct 1991. Electric Power Research Institute.

[26] A. Theodore, L. & Buonicore. Air pollution control equipment; selection, design, operation, and maintenance. 1994.

[27] N de. Nevers. Air pollution control engineering; second edition. 2000.

[28] BRANCH ENVIRONMENTAL CORP. Nox removal... http://www.branchenv.com/nox.htm, 2001.

[29] Beeckman J.W.; Hegedus L.L. Design of monolith catalysts for power plant nox emission comtrol. *Industrial Engineering Chemical research*, 30:969–978, 1991.

[30] Lydia Singoredjo. *Low temperature SCR of nitric oxide with ammonia.* PhD thesis, University of Amsterdam.

[31] A. Gerritsen. Chemical reactor engineering syllabus. 2000.

[32] Unknown. http://www.dynafog.com/a10ulv.html. 2002.

[33] Unknown. http://www.impexequip.com/equip-drying.html. 2002.

[34] Unknown. http://home.iag.net/ para/specific.htm. 2002.

[35] O. Levenspiel. Chemical reaction engineering. 1999.

[36] J.C McCabe, W.L & Smith. Unit operations of chemical engineering. 1967.

[37] H.E. Schifftner, K.C. & Hesketh. Wet scrubbers. 1983.

[38] Personal communication with employees kramer's laboratory, delft university of technology.

[39] D.C Shallcross. Handbook of psychrometric charts. 1997.

[40] Personal communication with employees of lurgi-allee germany.

[41] Olie K.; Vermeulen P.L.and Hutzinger O. Chlorodibenzo-p-dioxins and chlorobenzofurans are trace components of fly ash andflue gas of some municipal incinerators in the netherlands. *Chemosphere*, 6:445–459, 1977.

[42] G. Reggiani. Chlorinated dioxins and related compunds. *Pergamon Press*, 1982. page 463-493.

[43] Scialli A.R. Tampons, dioxins, and endometriosis. *Reproductive Toxicology*, 15:231–238, 2001.

[44] Poland A.; Knutson J. 2,3,7,8-tetrachlorodibenzo-p-dioxin and related halogenated aromatic hydrocarbons: examiniation of the mechanism of toxicity. *AnnRev Pharmacol Toxicol*, 13(3):387–406, 1982.

[45] McKay G. Dioxin characterisation, formation and minimisation during municipal solid waste (msw) incineration: review. *Chemical Engineering Journal*, 3907(2001):1–26.

[46] WHO. Health criteria for polychlorinated dibenzo-para-dioxins and dibenzofurans. *IPCS International Programme on Chemical Safety*, Geneva, 1997.

[47] Health Council of The Netherlands. *Dioxins*. Health Council of The Netherlands, (1994) Committee on Risk Evaluation of Substances, Rijswijk,, report no. 1996/10e, edition, 1996.

[48] Kimura T; Kokado M Abe S; Kanbayashi F. Decomposition of dioxin and related compounds in msw ash melting process. *Organohalogen Compounds*, 31:348–353, 1997.

[49] Calaminus R; Fiedler H;Stahlberg R. Technological measures to prevent formation of chloroorganics in thermal waste disposal. *Organohalogen Compounds*, 31:354–359, 1997.

[50] Hirose T Kawajiri S; Goto M, Kodama A. Extraction of toxic-organo halogenated compounds from fly ash with scco2.

[51] Wikstrm E; Lfvenius G; Rapp C; Marklund S. Influence of level and form of chlorine on the formation of chlorinated dioxins, debenzofurans, and benzenes during combustion of an artificial fuel in a laboratory reactor. *Environmental Science and Technology*, 30:1637–1644, 1996.

[52] Ballschmiter K; Braunmiller I; Niemczyk R; Swerev M. Reaction pathways for the formation of polychloro-dibenzodioxins (pcdd) and polychloro-dibenzofurans (pcdf) in combustion processes. 2. chlorobenzenes and chlorophenols as precursors in the formation of polychloro-dibenzodioxins and polychloro-dibenzofurans in flame chemistry. *Chemosphere*, 17:995–1005, 1998.

[53] Smith P Govers H Luijk R, Dorland K. The halogenation of dibenzo-p-dioxin and dibenzofuran in a model fly ash system. *Organohalogen Compounds*, 8:273–276, 1992.

[54] Weber R; Hagenmaier H. On the mechanism of the formation of polychlorinated dibenzofurans from chlorophenols. *Organohalogen compounds*, 31:480–485, 1997.

[55] Weber R; Hagenmaier H. Pcdd/pcdf formation in fluidized bed incineration. *Chemosphere*, 48:2643–2654, 1999.

[56] Shin K.J; Chang Y. Characterization of polychlorinateddibenzo-p-dioxins, dibenzofurans, biphenyls, and heavy metals in fly ash produced from korean municipal solid waste incinerators. *Chemosphere*, 38:2655–2666, 1999.

[57] Rotard W; Thanner G. Pcdd/f-emissions from coal combustion in small residential plants. *Organohalogen Compounds*, 36:329–332, 1998.

[58] Raghunathan K; Gullett B.K. Role of sulphur in reducing pcdd and pcdf formation. *Environmental Science and Technology*, 30:1827–1834, 1996.

[59] Lindbauer R.L; Wurst F; Prey T. Combustion dioxin suppression in municipal solid watse incineration with sulfur additives. *25*, pages 1409–1414, 1992.

[60] Taylor P.H; Sidhu S.S.; Rubey W.A.; Dellinger B.; Wehrmeier A.; Lenoir D. Evidence for a unifed pathway of dioxin formation from aliphatic hydrocarbons. In *Proceedings of the Twenty Sevent International Combustion Symposium*, pages 1769–1782. The Combustion Institute, 1999.

[61] Luijk D; Akkerman D.H; Slot P; Olie K; Kapteijn F. Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the catalyzed combustion of carbon. *Environmental Science and Technology*, 28:312–321, 1994.

[62] Dickson L; Lenoir D; Hutzinger O. Surface-catalyzed formation of chlorinated dibenzodioxins and dibenzofurans during incineration. *Chemosphere*, 19:277–282, 1989.

[63] Heev N; Dolezal I; Buhrer T; Mattrel P; Wolfsenber M. Distribution of halogenated phenols including mixed brominated and chlorinated phenols in municipal incineration flue-gas. *Chemosphere*, 31:3033–3041, 1995.

[64] Stieglitz L; Bautz H; Roth W. Investigation of precursor reactions in the de novo-synthesis of pcdd/pcdf on fly ash. *Chemosphere*, 34:1083–1090, 1997.

[65] Lipper T; Wokaun A; Lenoir D. Surface-reactions of brominated areanes a smodel for the formation of chlorinated dibenzodioxins and dibenzofurans in incineration inhibition by ethanolamine. *Environmental Science and Technology*, 25, 1991.

[66] Born J; Mulder P; Louw R. Fly ash mediated reactions of phenol and monochlorophenols; oxychlorination, deep oxidation and condensation. *Environmental Science and Technology*, 27:1847–1863, 1993.

[67] Froese K; Hutzinger O. Mechanisms of the formation of polychlorinated benzenes and phenols by heterogeneous reactions of c-2 aliphatics. *Environmental Science and Technology*, 31:542–547, 1997.

[68] Wehrmeier A; Lenoir D; Sidhu S. Role of copper species in chlorination and condensation reactions of acetylene. *Environmental Science and Technology*, 32:2741–2748, 1998.

[69] Lenoir D; Kaune A; Hutzinger O; Mutzenich G; Horch K. Influence of operating parameters and fuel type on pcdd/f emissions from a fluidized bed incinerator. *Chemosphere*, 23:1491–1500, 1991.

[70] Iino F; Imagawi T; Takeuchi M; Sadakata M. De novo sysnthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristics isomers of poltchlorinated naphthalones. *Environmental Science and Technology*, 33:1038–1042, 1999.

[71] Gullett B; Sarofim A; Smith K; Procaccini C. The role of chlorine in dioxin formation. *Trans Inst Chem Eng B*, 78, 2000.

[72] Addink R; Bakker W; Olie K. Influence if hcl and cl_2 on the formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in a carbon/fly ash mixture. *Environmental Science and Technology*, 29:2055–2058, 1995.

[73] Kairmann B; Kluwe M; Kocker H; Lorber K. Correlation between co- and pic-emissions. *Chemosphere*, 25:1403–1407, 1992.

[74] Gullett B; Bruce K; Beach L; Drago A. Mechanisitic steps in the production of pcdd and pcdf during waste combustion. *Chemosphere*, 25:1387–1392, 1993.

[75] Gullett B; Lemieux P; Dunn J. Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran formation during waste combustion. *Environmental Science and Technology*, 28:107–118, 1994.

[76] Addink R; Drijver D; Olie K. Formation of polychlorinated dibenzo-p-diozins/dibenzofurans in the carbon/fly ash system. *Chemosphere*, 23:1205–1211, 1991.

[77] Altwicker E. Some laboratory experimental designs for obtaining dynamic property data on dioxins. *Science of Total Environment*, 104:47–72, 1991.

[78] Milligan M; Altwicker E. Mechanistic aspects of the de novo synthesis of polychlorinated dibenzo-p-dioxins and furans in fly-ash from experiments using isotopically labelled reagents. *Environmental Science and Technology*, 29:1353–1358, 1995.

[79] Sinnott R.K. *C&R Volume 6. Chemical Engineering Design.* Butterworth Heinemann, 1996.

[80] S. Ergun. *Chemical Engineering Progress*, 48, 1951.

[81] J. P. K. Seville;R. Clift; C.J.Wither;W. Keidel. Ridgid ceramic media for filtering hot gases. *Filtr. Sep.*, 26:265–271, 1989.

[82] R.K. Sinnott. *Coulson & Richardson's Chemical engineering*, volume 6 : Chemical engineering design. Butterworth Heinemann, Linacre house, Jordan Hill, Oxfort, revised second edition edition, 1996.

[83] Dutch Association of Cost Engineers. *Prijzenboekje.* H.J.M. Gunnewiek, 21 edition, december 2000.

[84] Prins W.L.; Nuninga Z.L. Design and experience with catalytic reactors or scr-denox. *Catalysis today*, 16:187–205, 1993.

[85] DOW chemical corporation. Dows fire and explosion index hazard classification guide. 2001.

[86] R.L. Rawls. Dioxin's human toxicity is most difficult problem. *Chem. Eng. News.*, pages 37–48, 1983.

[87] Zevenhoven R.; Kilpinen R. *Control of pollutants in flue gases and fuel gases.* http://www.hut.fi/ rzevenho/gasbook, 2001.

Appendix A

Pressure drop trough a thick walled candle filter

The general equation for flow trough packed beds is given by:

$$\frac{-dp}{dz} = k_1 \mu U + k_2 \rho U^2 \tag{A.1}$$

Where (-dp/dz) is the pressure gradient in the direction of flow and U is the superficial velocity, ie. the actual flow rate per unit area. Equation A.1 is used for flow through porous media in general. The equation consists of two terms: resistance arising from gas viscosity effects and resistance arising from gas density. The gas flow rate U depends on which of these two effects dominates. The two resistance terms depend on the structure of the filter. The Ergun equation (Ergun, 1951 [80]) describes flow trough a granular packed bed and can be distinguished into two regimes, a laminar and a turbulent one. It can be written in the form:

$$k_1 = 150(1-\epsilon)^2 \epsilon^{-3} (\phi \cdot d)^{-2} \tag{A.2}$$

$$k_2 = 1.75(1-\epsilon) \epsilon^{-3} (\phi \cdot d)^{-1} \tag{A.3}$$

where ϵ is the porosity of the medium, d is the diameter and ϕ is the sphericity of the granules. A typical ceramic candle filter has a porosity ϵ of 0.3-0.9 and granules with diameter 40 μ m and $\phi \approx 1$. With the aid of the Reynolds number the flow regime can be determined. In gas filteration the reynolds number $U\rho d/\mu \ll 1$ thus the turbulent term k_2 in the Ergun equation can be neglected. That means that the density term in equation A.1 can be neglected, and hence only the viscosity term is dominant (at low Reynolds). Equation A.1 reduces to:

$$\frac{-dp}{dz} = k_1 \mu U \tag{A.4}$$

This equation where the pressure drop is proportional to the flow rate is known as Darcy's law (Seville, 1989 [81]). In a thick walled candle filter with inside diameter a and outside diameter b the raw flue gas flows radially inwards. The filtration velocity ie. superficial velocity is U_0. The density change over the filter is neglected. The superficial velocity at any R is given by:

$$U = \frac{U_0 b}{2R} \tag{A.5}$$

Hence if Darcy's law applies as in A.4

$$\frac{dp}{dR} = -k_1 \mu U = -\frac{k_1 \mu U_0 b}{2R} \tag{A.6}$$

The total pressure drop over the candle can be derived as:

$$\Delta p = \int_{\frac{a}{2}}^{\frac{b}{2}} \frac{k_1 \mu U_0 b}{2R}\, dR \; = \; \frac{k_1 \mu U_0 D_0}{2} \int_{\frac{a}{2}}^{\frac{b}{2}} \frac{dR}{R} \; = \; \frac{k_1 \mu U_0 b}{2}\, ln(\frac{b}{a}) \tag{A.7}$$

Nomenclature

a, b	inside and outside diameter of the cilindrical candle	(m)
d	mean diameter of a individual granule of the candle filter	(m)
k_1	Resistance corresponding to viscous effects	(m^{-2})
k_2	Resistance corresponding to density change effects	(m^{-1})
p	Gas pressure	(Pa)
R	intermediate radius between a and b	(m)
U	superficial gas velocity	$(m \cdot s^{-1})$
U_0	Face velocity through outside surface of filter	$(m \cdot s^{-1})$
z	Distance in direction of gas flow	(m)
Δp	Pressure drop over filter	(Pa)
ϵ	porosity of filter medium	(-)
μ	gas viscosity	$(Pa \cdot s)$
ρ	gas density	$(m^3 \cdot s^{-1})$
ϕ	Sphericity of granules in filter medium	(-)

Appendix B

Filter size & cost calculation

B.1 Size

For a fresh filter a initial pressure drop of 2000 Pa (20 mbar) is chosen as acceptable. Since the pressure drop is dependent on the porosity (≈ 0.5) and the filtration velocity, as shown in figure 5.1, the filtration velocity is 0.21 m/s. The filtration velocity yields the total filtration surface needed for a given gas throughput as shown in figure 8.1. The total filtration surface determines the total cost of the filtration unit.

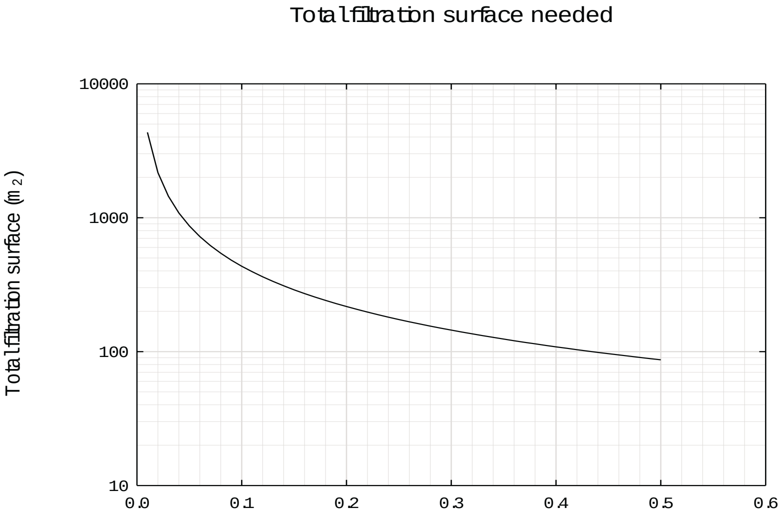


Figure B.1: Total filtration surface as function of the filtration velocity

With the throughput of the raw gas known (43.40 Nm^3/s) this yields the total required filtration surface (206.67m^2). With an individual surface of 0.29m^2 the number of required candles is 713. The candles are combined in sets of 33 candles often refered as candle bundles. The diameter of a bundle is 0.66 m and the number of bundles (spare bundles included) is 23. The diameter of the required vessel for the filtration unit is 4.42 m. The total volume of the vessel is set to 50 m^3.

B.2 Cost

All cost data are retrieved from Coulson & Richardson [82]. The vessel should be constructed of monel because of the corrosion resistance of the material against the process conditions. There are no cost data available for the use of a vessel above 300°C since the operating temperature is 700°C, the vessel cost is multiplied by an estimated factor of 1.5.

Table B.1: Vessel cost data

Equipment	size (S (m^3))	Constant C (£)	n
vertical process tank	50	1250	0.6

The constants can be substituted in equation:

$$C_e = C \cdot S^n \tag{B.1}$$

Including the penalty for the usage of monel and for the high operating temperature the total cost is summarised below:

Table B.2: Vessel cost data

C_e	material factor (MF)	temperature factor (TF)	Total equipment cost (in 1992)
£ 13,070	3.4	1.5	£ 66,659
€ 21,080	3.4	1.5	€ 107,515

The cost of a candle is estimated at €600 each. Therefor with 759 candles the total costs is €455,400 per incineration line. The extra equipment needed for blowback system of the filtration unit consists of a compressor and a pressurised air tank, and accounts for €100,000 (cost retrieved from DACE prijzenboekje [83]). Summarised the total cost are given in the table hereunder:

Table B.3: summarised total cost of the high temperature filter

equipment	cost (€)	Year of cost data	current cost (€, interest =7 %)
Vessel	107,515	1992	197,661
Candles	455,400	2002	455,400
Blowback system	100,000	2001	107,000
Total cost in 2002			760,061

The hot gas filter system is estimated to last at least 4 years, since it is successfully applied for longer periods in other processes (with a higher dust load and higher operating pressures) [16].

Nomenclature

C_e	Total equipment costs	(€)
C	Cost constant factor	(-)
S	characteristic size parameter	(-)
n	index for cost calculation	(-)
MF	Material factor	(-)
TF	Temperature factor	(-)

Appendix C

MATLAB scripts for HT-Dust calculations

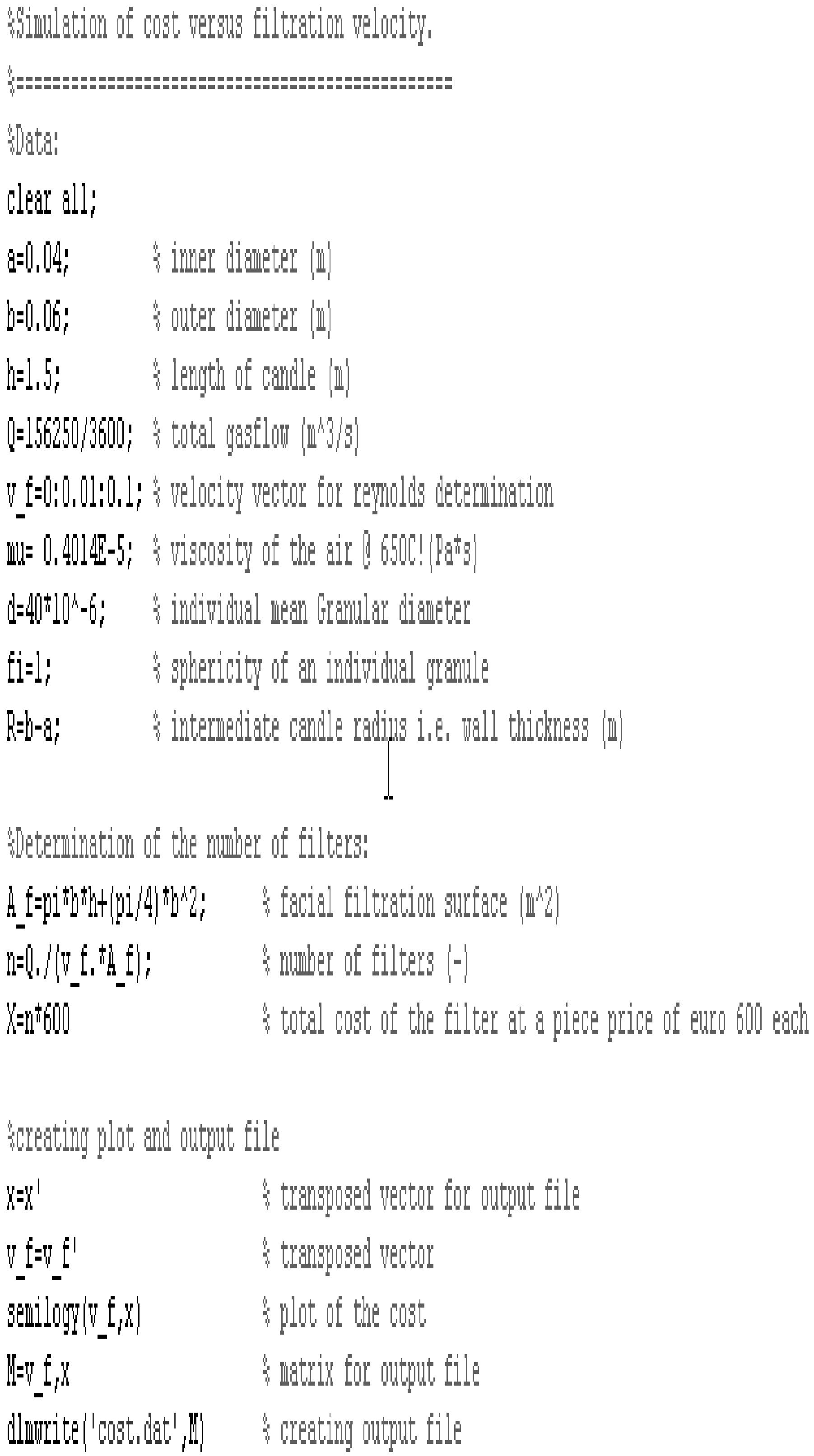
```
%Simulation of pressure drop over a cilindrical candle filter.
%=================================================================
%Data:
clear all;
a=0.04;          % inner diameter (m)
b=0.06;          % outer diameter (m)
h=1.5;           % length of candle (m)
Q=156250/3600;   % total gasflow (m^3/s)
v_f=0:0.01:0.1;  % velocity vector for reynolds determination
mu= 0.4014E-5;   % viscosity of the air @ 650C!(Pa*s)
d=40*10^-6;      % individual mean Granular diameter
fi=1;            % sphericity of an individual granule
R=b-a;           % intermediate candle radius i.e. wall thickness (m)

%Flow characterisation
U=v_f.*b/(2*R);  % superficial velocity (m/s)
Re=U*d/mu        % reynolds

%Determination of the number of filters:
A_f=pi*b*h+(pi/4)*b^2;       % facial filtration surface (m^2)
n=Q./(v_f.*A_f);             % number of filters (-)

%Pressure drop over the filter:
for i=1:1:7
    epsilon(i)=0.1*i+0.2;                                  %vector of filter porosity (-) varies from 0.03 to 0.09
    k_1(i)=150*(1-epsilon(i))^2*epsilon(i)^(-3)*(d*fi)^-2;  %
    for j=1:1:11
        v_f(j)=0.01*j-0.01;                                %vector of ideal filtration velocity (m/s)
        dP_f(i,j)=(k_1(i)*mu*v_f(j)*b/2)*log(b/a);         %
    end
end

dP_f=dP_f'                   %Transposed matrix
%creating plot and output file
semilogy(v_f,dP_f);          %Matlab plot y in log scale
v_f=v_f';                    %transed vector
M=[v_f,dP_f];                %Matrix for output file
dlmwrite('candle.dat',M);    %Creating output file
```



```
%Simulation of cost versus filtration velocity.
%==============================================
%Data:
clear all;
a=0.04;        % inner diameter (m)
b=0.06;        % outer diameter (m)
h=1.5;         % length of candle (m)
Q=156250/3600; % total gasflow (m^3/s)
v_f=0:0.01:0.1; % velocity vector for reynolds determination
mu= 0.4014E-5; % viscosity of the air @ 650C!(Pa*s)
d=40*10^-6;    % individual mean Granular diameter
fi=1;          % sphericity of an individual granule
R=b-a;         % intermediate candle radius i.e. wall thickness (m)

%Determination of the number of filters:
A_f=pi*b*h+(pi/4)*b^2;    % facial filtration surface (m^2)
n=Q./(v_f.*A_f);          % number of filters (-)
X=n*600                   % total cost of the filter at a piece price of euro 600 each

%creating plot and output file
x=x'                      % transposed vector for output file
v_f=v_f'                  % transposed vector
semilogy(v_f,x)           % plot of the cost
M=v_f,x                   % matrix for output file
dlmwrite('cost.dat',M)    % creating output file
```

Appendix D

SCR Design

D.1 Calculation of the catalyst volume

Table D.1: Specifications needed to calculate the catalyst volume

Properties	units	explanation	value
F_{in}	(m^3/s)	Flow into the SCR	43.40
$C_{NOx,in}$	(mg/m^3)	NO_X concentration in	350
$C_{NO,in}$	(mg/m^3)	NO concentration in (NO_X=90% NO)	315
$C_{NO,in}$	(mol/m^3)	NO concentration in (NO_X=90% NO)	0.0105
T_{in}	(K)	Entrance temperature	623
k_0	(m/s)	Pre exponential factor	35100
E_a	(J/mol)	Activation energy	79800
R	(J/[mol K])	Gas constant	8.314472
X_{NO}	(-)	Conversion	99.8
W_h	(h/year)	Working hours/year	8400

Equation D.1 is used to calculate the catalyst surface

$$r_{NO_X} = k_0 \exp^{-\frac{E_a}{RT}} C_{NO_X} \tag{D.1}$$

With

- r_{NO_X} (mol/m^2 s)
- k_0 (m/s)
- E_a (J/mol)
- T (K)
- C_{NO_X} (mol/m^3)

D.2 SCR, reactor design

Equation D.1 can be rewritten in the following form (D.2).

$$-\ln(X_{NO}) = \frac{A}{F} k_0 \exp^{-\frac{E_a}{RT}} \tag{D.2}$$

With : A as the catalyst area (m^2). The conversion that is wanted is 99.8 % This results in an catalytic surface of 37689 m^2, the specific surface of the monolith is 784 m^2/m^3, so the monolith volume finally is 48 m^3

D.3 Mass transfer limitations

Extraparticle mass transfer can be determined from when you know the bulk concentration (c_b) and the concentration at the surface (c_s). Because adsorption is fast and the reaction is slow, the concentration at surface will not differ significantly from the bulk concentration. This means that the dimension less Carberry number (see equation D.3) is low.

$$Ca = \frac{c_b - c_s}{c_b} \tag{D.3}$$

A criteria for the absence of extraparticle gradients in the rate data can be derived from the definition of an effectiveness factor for a particle. This should not deviate more then 5% from unity as criterion:

$$\eta_e = (1 - Ca)^n = 1 \pm 0.05 \tag{D.4}$$

For an isothermal, n-th order irreversible reaction this results in the following criterion:

$$Ca < \frac{0.05}{|n|} \tag{D.5}$$

There is no extraparticle transfer present because the effectiveness factor does not deviate from 1, see figure D.1

D.4 Calculation of the pressure drop over the monolith

With the use of the Fanning equation for pressure drop in pipes (equation D.6 and D.7) the pressure drop can be calculated.

$$\Delta P = \frac{L}{d}\left(\frac{1}{2}\rho v^2\right) 4f \tag{D.6}$$

$$f = \frac{16}{Re} \text{laminar flow circular channels} \tag{D.7}$$

This results in a pressure drop of 1.96 mbar.

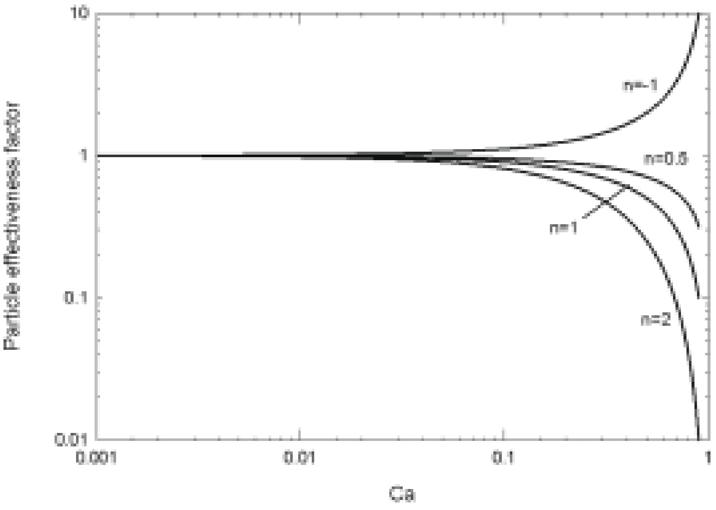


Figure D.1: particle effectiveness factor versus Carberry number for various reaction orders

D.5 Calculation of the SCR costs

D.5.1 Costs of the reactor vessel

The installation costs of the SCR reactor are calculated according to the following equation D.8(C&R 258)

$$Ce = C * S^n \tag{D.8}$$

With :

- S (characteristic size parameter, m^3) = 60 m^3
- C (Cost constant factor from C&R) = 2339
- n (index) = 0.6
- Ce (Purchased equipment costs, €)

This results in a purchased equipment cost of €27,281, this factor has to be multiplied by 3.4 (C&R) for Monel (higher quality, corrosion resistant). So the final costs are €92,757.

D.5.2 Catalyst costs

The catalyst costs €10,700 $1/m^3$, this muliplied by the catalyst volume makes : €514,397 (guarantied for 3 years)

D.5.3 Chemicals costs

Nomenclature

Table D.2: Specifications needed to calculate the pressure drop

Properties	units	explanation	value
L	(m)	Length monolith channel	1.1
d	(m)	inner diameter monolith channel	0.0036
ρ	(kg/m^3)	density gas	1.29
v	(m/s)	velocity in the channel	4.03
μ	(kg/[m s])	viscosity	1.81E-05
Re	(-)	Reynolds Number	1.03E+03
f	(-)	(16/Re)	1.55E-02
F	(m^3/s)	total flow	43.40
A_{mon}	(m^2)	inlet area of a monolith channel	1.017E-05
n_{mon}	(-)	number of openings	1058400
A_{tot}	(m^2)	total inlet area	10.76

Table D.3: Specifications needed to calculate the amount of ammonia

Properties	units	explanation	value
ρ_{NH3}	(kg/m^3)	Density of NH_3 (25%)	916
F_{NH3}	(m^3/s)	Flow NH3 (25%) NH_3:NO (1:1)	3.38E-05
F_{NH3}	$(m^3/year)$	usage of NH_3 $m^3/year$	1023
$F-NHr(m)$	(ton/year)	usage of NH_3 tons/year	937
$NH3_{Price}$	(EURO/ton)	Max. Price NH_3 at DSM	140
$NH3_{price,tot}$	(EURO/year)	NH_3 costs per year	131197

A	Catalyst area	(m^2)
A_{mon}	inlet area of monolith channel	(m^2)
C	Cost constant factor	(-)
$C_{NOx,in}$	(mg/m^3)	NO_X concentration in
$C_{NO,in}$	(mg/m^3)	NO concentration in (NO_X=90% NO)
$C_{NO,in}$	(mol/m^3)	NO concentration in (NO_X=90% NO)
Ca	Carberry number	(-)
c_b	Bulk concentration	(mol/m^3)
C_e	Total equipment costs	(€)
c_s	Surface concentration	(mol/m^3)
d	monolith channel diameter	(m)
E_a	(J/mol)	Activation energy
F_{in}	(m^3/s)	Flow into the SCR
f	Fanning factor	(-)
k_0	(m/s)	Pre exponential factor
L	Monolith channel length	(m)
n	index for cost calculation	(-)
n_{mon}	Number of monolith channels	(-)
R	$(J/[molK])$	Gas constant
Re	Renolds number	(-)
S	characteristic size parameter	(-)
T_{in}	(K)	Entrance temperature
v	velocity in the monolith channel	(m/s)
W_h	(h/year)	Working hours/year
X_{NO}	(-)	Conversion
ΔP	Pressure drop over SCR	(Pa)
η_e particle effectiveness factor	(-)	
μ	viscosity	(Pa s)
ρ	Density	(kg/m^3)

Appendix E

Derivation of the reaction rate

The following section describes how the reaction rate equation is derived(Prins *et al.*, 1993 [84]). In the Eley-Rideal mechanism one compound (NH_3) which is adsorbed on the catalyst surface reacts with the other compound (NO) in the gas phase, this mechanism is shown in figure E.1. For the Eley-Rideal mechanism the equations for steady state (Θ is constant) are :

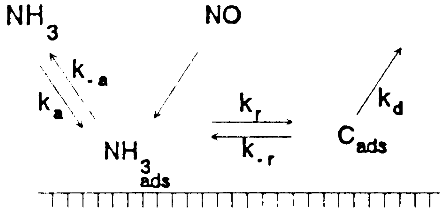


Figure E.1: caption text

$$R_a - R_{-a} - R_r + R_{-r} = v \tag{E.1}$$

$$R_r - R_{-r} - R_d = 0 \tag{E.2}$$

$$R_r - R_{-r} - R_d = 0 \tag{E.3}$$

The reactionrate r = $R_r - R_{-r}$

$$k_a P_{NH_3} \left(1 - \Theta_{NH_3} - \Theta_{N_2}\right) - k_a \Theta_{NH_3} - k_r P_{NO} \Theta_{NH_3} + k_{-r} \Theta_{N_2} = 0 \tag{E.4}$$

$$k_r P_{NO} - k_{-r} \Theta_{N_2} - k_d \Theta_{N_2} = 0 \tag{E.5}$$

$$r = \frac{k_r \frac{k_a}{k_{-a}} P_{NH_3} P_{NO}}{\frac{k_a}{k_{-a}} \frac{k_r}{k_d} P_{NH_3} P_{NO} + \frac{k_a}{k_{-a}} \left(1 + \frac{k_r}{k_d}\right) P_{NH_3} + \frac{k_r}{k_{-a}} P_{NO} + \left(1 + \frac{k_{-r}}{k_d}\right)} \tag{E.6}$$

Now, if the reaction is not fast relative to adsorption and desorption equation E.6 reduces to E.7

$$r = \frac{k_r b_{NH_3} P_{NH_3} P_{NO}}{b_{NH_3} P_{NH_3} + 1}, \text{with } b_{NH_3} = \frac{k_a}{k_{-a}} \tag{E.7}$$

Appendix F

Companies that have been contacted

Table F.1: Contacts

Companies	Business	Reason for contact	Contact person	Tel Nr./email address
BASF AG	Chemicals	Catalyst Price	Mr. Regenauer	+49 6216043140
Haldor Topsoe	Catalysts	DENOX systems	Mr. A.B. Jensen	+45 45272000
BB-Power	Technology	Denox systems	Mr. R. Holste	+49 2261852735
Siemens	Catalysts	SinNOX systems	Mr. M. Joisten	+49 957481510
DSM-agro	Chemicals	NH_3 price	Mr. B. Vissers	Ben.Vissers@dsm.com
VonROll	Ceramic materials	4-D Filter	Mrs. H. Gablinger	+41 12771229
AVR	Waste incinerator	General information	Mr. J. Luteijn	+31 181275840
Huisvuilcentrale NH	Waste incinerator	General information	Mr. R. Sleijster	+31 725411311
SITA ReEnergy	Waste incinerator	General information	Mr. C. Stuart	+31 165534492
USF Schumacher	Hot gas filtration	Ceramic filter specs	Mr. B. Schneider	
Pall filtration group	Hot gas filtration	Ceramic filter specs	Mr. A. Sweers	

Appendix G

The design equation for Wet Scrubbers

The most widely used theory for designing mass transfer devices is the two-film theory. The rate at which the solute gases are taken into the solvent is a function of the potential energy divided by the resistance. In the two film theory, the potential energy is caused by the difference in partial pressure resulting from the difference in concentration of a given solute between the two phases (gas and solvent). The resistance that is offered by the two films is due to the rates of diffusion and the solubility of the solute into the solvent.

Many models have been presented to describe the phenomenon of mass transfer along the boundary of the process gas. The best known models are:

1. The stagnant film model
2. The penetration model
3. The surface renewal model

The stagnant film model is the most common model used for modern absorption equipment design. This theory states that mass transfer is represented by a concentration gradient on the gas side Y, as well as on the solvent side X, which occur on across the gas and solvent films. In most cases of absorption the slope of the equilibrium line is not constant. In some situations however, such as in the case where there is chemical reaction between the solute and a solvent, the slope of the equilibrium line is constant. This means that nearly no partial pressure exists in the solvent film at the interface. The absence of this partial pressure reduces the solvent's resistance to zero, which means that the slope is nearly zero and the overall mass transfer coefficients are equal to the gas film mass transfer coefficient. This effect is also observed when the gas is infinitely, or nearly so, soluble in the solvent. Therefore:

$$\frac{1}{k_{og}} = \frac{1}{k_{Ag}} \quad or \quad k_{og} = k_{Ag} \tag{G.1}$$

Although the stagnant film model has its limitations, it reveals the essential features of real systems. The concept of the equilibrium line controlling the

k_{og} = mass transfer coefficient of overall gas $(mol)/(s \cdot bar \cdot m^2)$
k_{Ag} = mass transfer gas film coefficient $(mol)/(s \cdot bar \cdot m^2)$

rates of mass transfer demonstrates the real problem of resistances that can dramatically effect the design of a mass transfer device. The results of the use of this model are in many cases identical, or nearly identical, to the predictions of more sophisticated models. Its value lies in its simplicity, and that is why it is the most widely accepted model for developing design correlations.

The concept of the penetration model is that the physical elements of the solvent are replaced at intervals of time by other elements from the bulk of the solvent, which have the mean bulk composition. The rate of mass transfer is then described to be a function of the time of exposure for both the gas and solvent films. This exposure time is rarely known. The value of the penetration model lies in describing change in the rate of mass transfer when changing some parameters, while keeping all the other parameters constant.

The surface renewal theory is an extension of the penetration theory. The penetration theory assumes the exposure time to be the same for all exposed elements, the surface renewal theory assumes a wide spectrum of exposure times and then averages the varying degrees of penetration. The practical application is limited, because the fraction of the interface area that is replaced in an interval of time is usually not known. The value of this model also lies in predicting the effect of change.

The overall rate expression for the reactions will have to account for the mass transfer resistance and the resistance of the chemical reaction step. The magnitude of these resistances can vary greatly, so a whole spectrum of possibilities is to be considered. The general chemical reaction rate equation is [35]:

$$-r_A = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_Bf_l}} p_A \qquad \text{(G.2)}$$

With:
$-r_A$ = $(moles\ A\ reacted)/(volume\ of\ reactor\ \cdot\ time)$
k_{Ag} = mass transfer coefficient of the gas film $(mol)/(m^2 \cdot bar \cdot s)$
a = interfacial area per unit volume of the tower $(m^2/m^3{}_{reactor})$
H_A = Henry's law constant $((m^3 \cdot bar)/mol)$
k_{Al} = mass transfer coefficient of the liquid film $((m^3/(m^2) \cdot s)$
E = the enhancement factor an infinitely fast reaction
k = reaction rate constant $((mol^2/m^6)/s)$
C_B = concentration of reactant B in the liquid bulk (mol/m^3)
f_l = volume fraction of liquid phase (-)
p_A = initial partial pressure of reactant A (bar)

The three terms in the denominator respectively represent the resistance of 1) the gas film; 2) the liquid film; and 3) the liquid bulk. In special cases, such as in the case of infinite solubility or chemical reaction, this equation can be simplified because the overall resistance will be represented by the mass transfer coefficient of the gas.

$$-r_A = \frac{1}{\frac{1}{k_{Ag}a}p_A} = k_{Ag}a \cdot p_A \qquad \text{(G.3)}$$

The general design equation of a plug flow reactor (PFR) is used to approach the conversion of each substances.

$$\tau_{pfr} \; = \; C_{A,0} \int_0^{X_A} \frac{dX_A}{-r_A} \tag{G.4}$$

With Combine equation (1) and equation (2) to:

X_A = conversion of pollutant A (-)
τ_{pfr} = residence time of the PFR (s)
$C_{A,0}$ = inlet concentration of pollutant A (mol/m^3)

$$\tau_{pfr} \; = \; C_{A,0} \int_0^{X_A} \frac{dX_A}{k_{Ag}a \cdot p_A} \tag{G.5}$$

The partial pressure of A (p_A) can be written as;

$$p_A = p_{A,0} \cdot (1 - X_A) \tag{G.6}$$

Combination equations G.5 and G.6 yields:

$$\tau_{pfr} \; = \; \frac{-C_{A,0}}{k_{Ag}a \cdot p_{A,0}} \int_0^{X_A} \frac{1}{(1-X_A)} dX_A \; = \; \frac{-C_{A,0}}{k_{Ag}a \cdot p_{A,0}} \cdot ln(1 - X_A) \tag{G.7}$$

$$\tau_{pfr} \; = \; \frac{V_{pfr}}{\phi_v} \; = \; \frac{\pi \cdot D^2_{pfr} \cdot L}{\phi_v} \tag{G.8}$$

With:

V_{pfr} = volume of PFR (m^3)
ϕ_v = volumetric gas flow (m^3/s)
D_{pfr} = diamter of PFR (m)(= 3.5 m)

The design equation, where conversion of pollutant A is described as a function of the height of the reactor, is given by:

$$X_A \; = \; 1 - e^{-\tau \cdot (\frac{k_{Ag} \cdot a \cdot p_{A,0}}{C_{A,0}})} \; = \; 1 - e^{-(\frac{\pi \cdot D^2_{pfr} \cdot L}{\phi_V}) \cdot (\frac{k_{Ag} \cdot a \cdot p_{A,0}}{C_{A,0}})} \tag{G.9}$$

This equation is a derivative of the standard solution for a plug flow reactor, which has the design equation:

$$X_A \; = \; 1 - e^{-k \cdot \tau} \tag{G.10}$$

The terms in the exponential power are readily determined. The mass transfer coefficients (k_{Ag}) for each of the pollutants are tabulated below. Amongst many other factors, the mass transfer coefficients are dependent on the driving force (e.g. the difference in concentration between the gaseous and the liquid phase), this is the reason that the mass transfer coefficient can differ from the different types of equipment. These values were provided by the 'Kramers Laboratorium' of the Delft University of Technology, department of Chemical Engineering.

The interfacial area per unit volume of the tower a ($m^2/m^3{}_{reactor}$) is typically 60 for wet scrubbers [35]. For spray absorber ,however, it is corrected

Pollutant	Equipment	k_{Ag} $((mol)/(m^2 \cdot s))$
HCl	Spray Absorber	0.9
HCl	Wet Scrubber I	0.6
HF	Spray Absorber	0.8
HF	Wet Scrubber I	0.5
SO_2	Wet Scrubber II	0.25

[38]

Equipment	pollutant	$inletconcentration$ (mg/m^3)	conversion %	$outletconcentration$ (mg/m^3)
spray absorber	HCl	1200	62.5	450
spray absorber	HF	15	58.0	6.3
wet scrubber 1	HCl	1200	97.8	10
wet scrubber 1	HF	6.3	96.2 0.24	
wet scrubber 2	SO_2	400	90	40

for the fact that the liquid evaporates. In spray absorbers, the interfacial area per unit volume of the tower is typically 4-5 [40]. The partial pressure is calculated from the composition of the stream. Partial pressure is deduced from the mole flow of the pollutant divided by the total mole flow. $C_{A,0}$ is readily calculated by dividing the inlet concentration in (mg/m^3) by the molecular weight of the pollutant (g/mol), which provides a concentration in (mol/m^3). All of the terms, except the length of the reactor, are known. Solving the design equation, graphs and tables are generated that describe the conversion of the pollutant as a function of the length, and thus the volume of the reactor.

The Spray Absorber: The following Matlab scripts were used to determine the conversion of HCl and HF at H=8.25 m. The conversion per apparatus is tabulated below.

The wet scrubbers: The following Matlab scripts were used to determine the conversion of HCl and HF in the first scrubber, and the conversion of SO_2 in the second scrubber as a function of the height of the scrubber.

Figure G.1: Matlab script for HCl conversion in spray absorber

The first wet scrubber:

The second wet scrubber:

Figure G.2: Matlab script for HF conversion in spray absorber

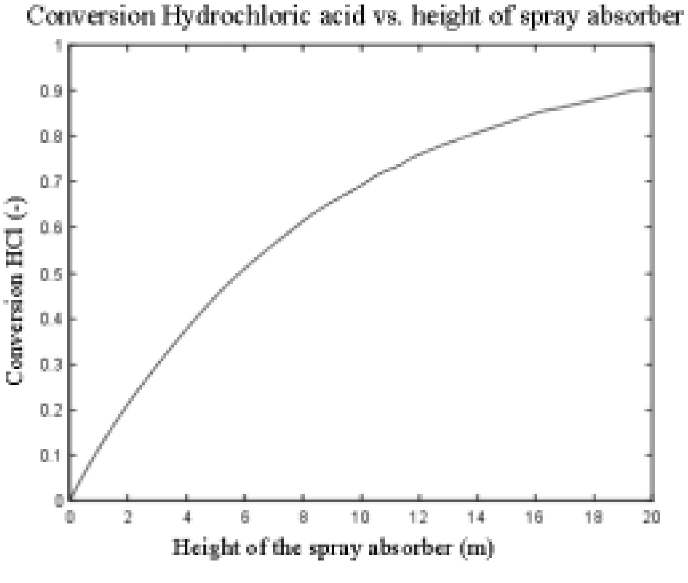


Figure G.3: Conversion of HCl vs.length spray absorber

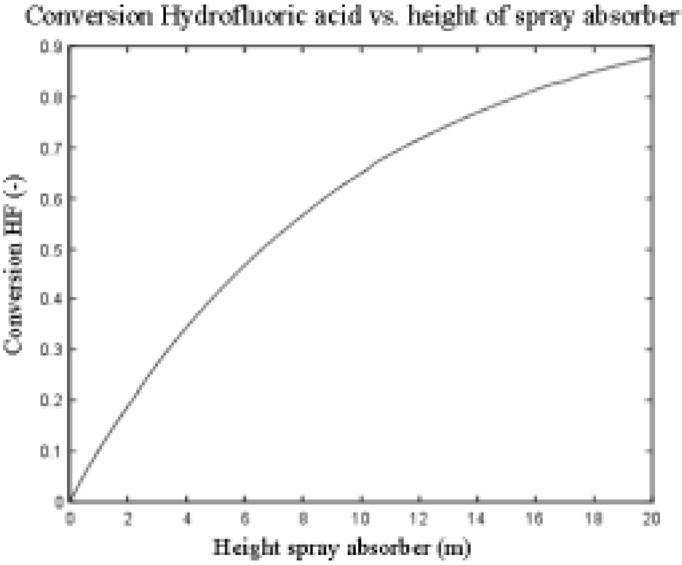


Figure G.4: Conversion of HF vs.length spray absorber

Figure G.5: Matlab script for HCl conversion in first wet scrubber

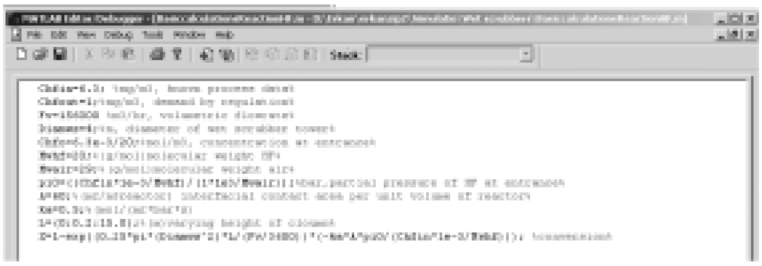


Figure G.6: Matlab script for HF conversion in first wet scrubber

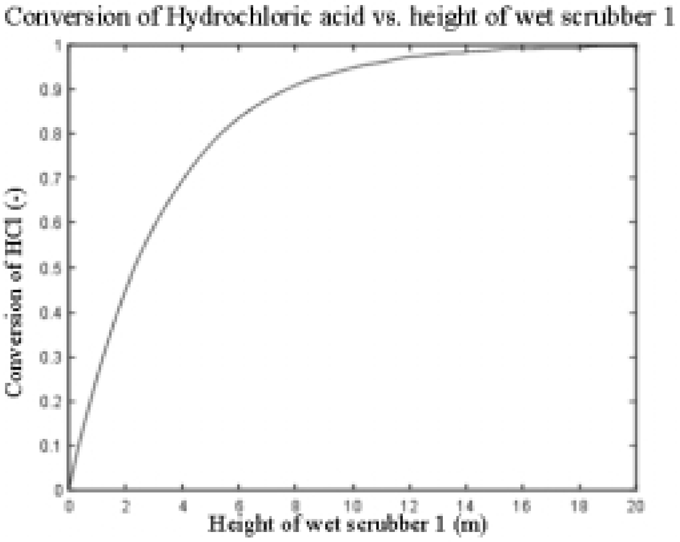


Figure G.7: Conversion of HCl vs. height first wet scrubber

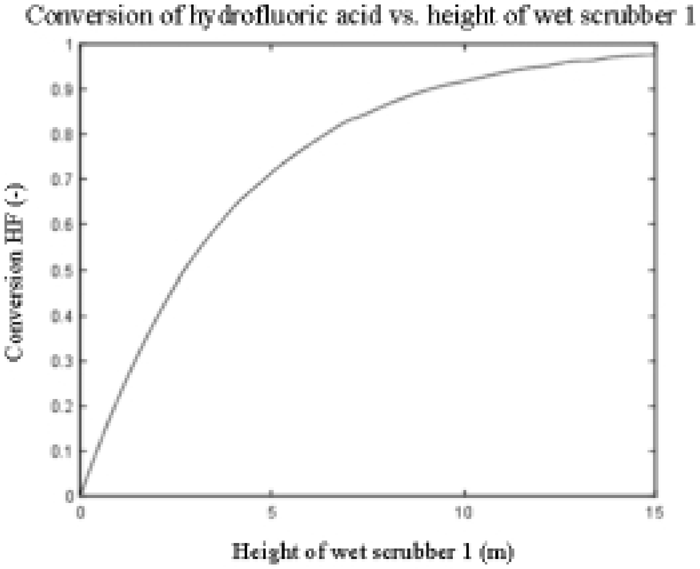


Figure G.8: Conversion of HF vs. height first wet scrubber

Figure G.9: Matlab script for SO_2 conversion in second wet scrubber

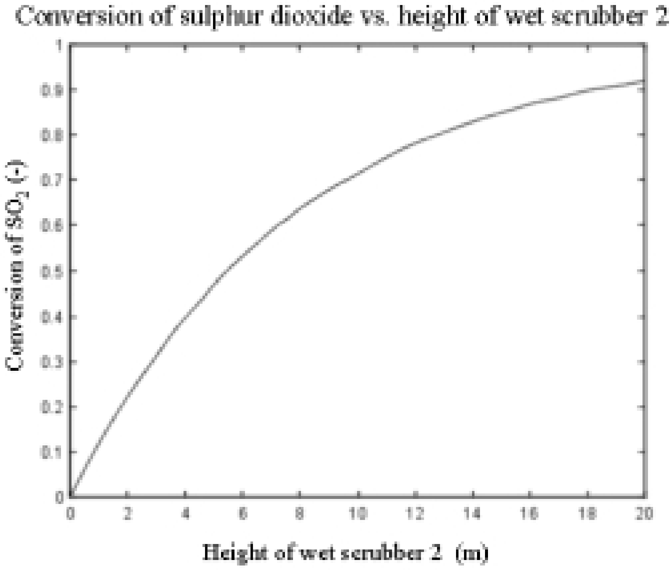


Figure G.10: Conversion of SO_2 vs. height second wet scrubber

Appendix H

A typical Mollier diagram

A typical Mollier diagram or psychrometric chart is shown below.

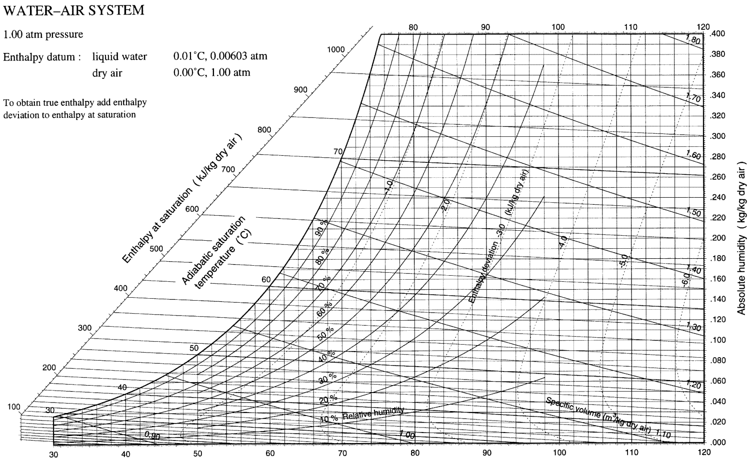


Figure H.1: Typical phychrometric chart for air-water mixture

Appendix I

Pure component properties

PURE COMPONENT PROPE						
Component Name			**Tecnological Data**			
Trivial	System	Design	Structural Formula	MW g/mole	BP °C	MP °C
ammonia	ammonia	ammonia	NH3	17.00	-33.0	-78.0
Unslaked lime	calciumoxide	calciumoxide	CaO	56.00	2850.0	2570.0
Slaked/hydrated lime	calcium dihydroxide	calciumhydroxide	Ca(OH)2	74.10	n.a.	580.0
Caustic soda	odiumhydroxide	caustic soda	NaOH (50%)	40.00	145.0	12.0
Hydrochloric acid	hydogen chloride	hydogen chloride	HCl	36.50	-85.0	-114.0
Hydrofluoric acid	hydrogen fluoride	hydrogen fluoride	HF	20.00	20.0	-83.0
Hydrobromic acid	hydrogen bromide	hydrogen bromide	HBr	80.90	-67.0	-87.0
Sulfur dioxide	sulfur dioxide	sulfur dioxide	SO2	64.00	-10.0	-76.0
Ammonium	ammonium	ammonium	NH4OH	35.10	38.0	-58.0
Calcium chloride	calcium dichloride	calcium chloride	CaCl2	111.00	1600.0	772.0
Calcium fluoride	calcium difluoride	calcium fluoride	CaF2	79.00	n.a	n.a
Calcium bromide	calcium dibromide	calcium bromide	CaBr2	200.80	n.a	n.a
Calcium sulfite	calcium sulfite	calcium sulfite	CaSO3	121.00	n.a	n.a.
Sodium chloride	sodium chloride	sodium chloride	NaCl	58.80	1413.0	801.0
Sodium fluoride	sodium fluoride	sodium fluoride	NaF	42.00	1700.0	990.0
Sodium sulfite	disodium trisulfite	sodium sulfite	Na2SO3	126.10	n.a	600.0
Mercury	Mercury	Mercury	Hg	200.60	357.0	-39.0
Dioxin	Dioxin	2,3,7,8-terta-chloro-dibenzo-p-dioxin	C12H4Cl4O2	322	-4	305
Mercury chloride	Mercury chloride	Mercury (II) dichloride	Cl2Hg	271.5	303	277
Carbon dioxide	Carbon dioxide	Carbon dioxide	CO2	44	-79	n.a.
Carbon monoxide	Carbon monoxide	Carbon monoxide	CO	28	-191	-205
Nitrogen monoxide	Nitrogen monoxide	Nitrogen monoxide	NO	30	-152	-164
Nitrogen dioxide	Nitrogen dioxide	Nitrogen dioxide	NO2	46	21	-11
Oxygen	Oxygen	Oxygen	O2	32	-183	-218
Cadmium	Cadmium	Cadmium	Cd	112.4	765	321

Notes:

Appendix J

Dow Fire and Explosion Index

As described earlier the DOW F&E Index depends on the material factor, the general process hazard factor, and the special process hazard factor [85]. Only ammonia (NH_3) is explosive between certain volume percentages.
The material factor(MF) is dependent on the flammability and the reactivity of NH_3, the MF is 4. The general process hazard factor is dependant on process characteristics. The total DOW's F&E index is calculated with the equation below:

Table J.1: DOW's F&EI calculation

Material factor (MF)		4
General process hazard factor (F_1)	Cracking by catalyst	0.40
Indoor process unit	Dust filters/ collectors present	0.50
	Quantity present is more than 3.5 m^3	0.45
	mechanical ventilation present	-0.475
Special process hazards (F_2)	Toxic material	0.60
Operation in or near flammable range	in case of equipment failure	0.30

$$F\&EI = F_1 \cdot F_2 \cdot MF \tag{J.1}$$

The F&EI = $0.675 \cdot 0.90 \cdot 4.0 = 2.43$

$$\begin{aligned} F_1 &= 0.20 + 0.475 = 0.675 \\ F_2 &= 0.60 + 0.30 = 0.90 \\ MF &= 4.0 \end{aligned}$$

This vale lies between zero and sixty; according to the classification in the fire and explosion index hazard classification guide [85], the overall process hazard is light. Although the overall process hazard is light, ammonia should be handled with great care.

Appendix K

Minimal lethality of several toxins

Minimal lethality of several natural toxins (Rawls, 1983 [86])

Substance	Animal	minimal lethal dose ($mol \cdot kg_{b.w.}^{-1}$)
Botulinum toxin A	Mouse	$3.3 \cdot 10^{-17}$
Tetanus toxin	Mouse	$1.0 \cdot 10^{-15}$
Diphteria toxin	Mouse	$4.2 \cdot 10^{-12}$
2,3,7,8-TCDD	Guinea Pig	$3.1 \cdot 10^{-9}$
Bufotoxin	Cat	$5.2 \cdot 10^{-7}$
Curare	Mouse	$7.2 \cdot 10^{-7}$
Strychnine	Mouse	$1.5 \cdot 10^{-6}$
Muscarin	Cat	$5.2 \cdot 10^{-6}$
Diisopropylfluorophoshate	Mouse	$1.6 \cdot 10^{-5}$
Sodium cyanide	Mouse	$2.0 \cdot 10^{-4}$

Appendix L

I-TEF of the 2,3,7,8-PCDD/F congeners

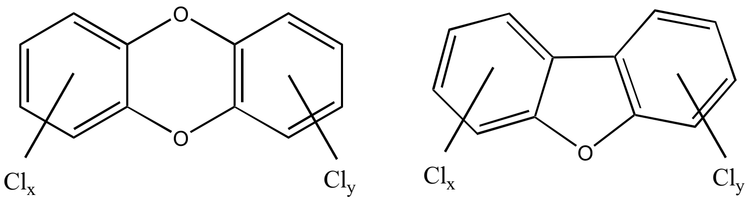


Figure L.1: Dioxin (left) and Furan (right) molecule

Dioxin	I-TEF	Furan	I-TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PCDD	0.5	1,2,3,7,8-PCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,7,8,9-HpCDD	0.01	2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8,9-OCDD	0.001	1,2,3,7,8,9-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		1,2,3,4,6,7,8,9-OCDF	0.001

Ref: (Zevenhoven,2001 [87])

Appendix M

Equivalence factors for four standard models

Model name	NORDIC	USEPA	FRG UBA	EADON
2,3,7,8-Tetra CDF	0.1	0.1	0.1	0.33
Non 2,3,7,8-tetra CDF	0	0.001	0.01	0
2,3,7,8-Tetra CDD	1.0	1.0	1.0	1.0
Non 2,3,7,8-tetra CDD	0	0.001	0.01	0
1,2,3,7,8-Penta CDF	0.01	0.1	0.1	0.33
2,3,4,7,8-Penta CDF	0.5	0.1	0.1	0.33
Non 1,2,3,7,8-penta CDF	0	0.001	0.01	0
1,2,3,7,8-Penta CDD	0.5	0.5	0.1	1.0
Non 2,3,7,8-penta CDD	0	0.005	0.01	0
2,3,7,8-Hexa CDF	0.1	0.01	0.1	0.01
Non 2,3,7,8-hexa CDF	0	0.0001	0.01	0
2,3,7,8-Hexa CDD	0.1	0.04	0.1	0.03
Non 2,3,7,8-hexa CDD	0	0.0004	0.01	0
2,3,7,8-Hepta CDF	0.01	0.001	0.01	0
Non 2,3,7,8-hepta CDF	0	0.00001	0.001	0
1,2,3,4,6,8-Hepta CDD	0.01	0.001	0.01	0
Non 2,3,7,8-hepta CDD	0	0.00001	0.0001	0
OCDF	0.001	0	0.001	0
OCDD	0.001	0	0.001	0

Ref: McKay, 2001[45]

Appendix N

Toxic equivalent factors (I-TEFs)

Congener	I-TEFs	WHO TEFs
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0001
2,3,7,8-TCDF	0.1	0.1
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,7,8-PeCDF	0.05	0.05
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0001
Coplanar PCBs		
3,4,4,4,5-TrCB	.	0.0001
3,3,4,4-TrCB	.	0.0001
3,3,4,4,5-PeCB	.	0.1
3,3,4,4,5,5-HxCB	.	0.01
2,3,3,4,4-PeCB		0.0001
2,3,4,4,5-PeCB	.	0.0005
2,3,4,4,5-PeCB	.	0.0001
2,3,4,4,5-PeCB	.	0.0001
2,3,3,4,4,5-HxCB	.	0.0005
2,3,3,4,4,5-HxCB	.	0.0005
2,3,4,4,5,5-HxCB	.	0.00001
2,3,3,4,4,5,5-HpCB	.	0.0001

Ref: McKay,2001 [45]

Appendix O

Homologues and congeners of PCDD/F

Homologue abbreviation	Number of congeners	
	PCDDs	PCDFs
Monochloro (M)	2	4
Dichloro (D)	10	16
Trichloro (Tr)	14	28
Tetrachloro (T)	22	38
Pentachloro (Pe)	14	28
Hexachloro (Hx)	10	16
Heptachloro (Hp)	2	4
Octachloro (O)	1	1
Total	75	135

Ref: (McKay, 2001 [45])

Appendix P

Physical properties of PCDD/Fs

Homologue	Vapour pressure (mmHg at 25 °C)	log Kow	Solubility ($mg \cdot l^{-1}$ at 25 °C)	Henrys constant
TCDD	$8.1 \cdot 10^{-7}$	6.4	$3.5 \cdot 10^{-4}$	$1.35 \cdot 10^{-3}$
PeCDD	$7.3 \cdot 10^{-10}$	6.6	$1.2 \cdot 10^{-4}$	$1.07 \cdot 10^{-4}$
HxCDD	$5.9 \cdot 10^{-11}$	7.3	$4.4 \cdot 10^{-6}$	$41.83 \cdot 10^{-3}$
HpCDD	$3.2 \cdot 10^{-11}$	8.0	$2.4 \cdot 10^{-6}$	$5.14 \cdot 10^{-4}$
OCDD	$8.3 \cdot 10^{-13}$	8.2	$7.4 \cdot 10^{-8}$	$2.76 \cdot 10^{-4}$
TCDF	$2.5 \cdot 10^{-8}$	6.2	$4.2 \cdot 10^{-4}$	$6.06 \cdot 10^{-4}$
PeCDF	$2.7 \cdot 10^{-9}$	6.4	$2.4 \cdot 10^{-4}$	$2.04 \cdot 10^{-4}$
HxCDF	$2.8 \cdot 10^{-10}$	7.0	$1.3 \cdot 10^{-5}$	$5.87 \cdot 10^{-4}$
HpCDF	$9.9 \cdot 10^{-11}$	7.9	$1.4 \cdot 10^{-6}$	$5.76 \cdot 10^{-4}$
OCDF	$3.8 \cdot 10^{-12}$	8.8	$1.4 \cdot 10^{-6}$	$4.04 \cdot 10^{-5}$

Appendix Q

Capital Costs calculation per unit

In this appendix the capital cost for each unit is calculated.

Q.1 HT-Dust

The cost of a candle is estimated at €600 each. Therefor with 759 candles the total costs is €455,400 per incineration line. The extra equipment needed for blowback system of the filtration unit consists of a compressor and a pressurised air tank, and accounts for €100,000 (cost retrieved from DACE prijzenboekje [83]). Summarised the total cost are given in the table hereunder:

Table Q.1: summarised total cost of the high temperature filter

equipment	cost (€)	Year of cost data	current cost (€, interest =7 %)
Vessel	107,515	1992	197,661
Candles	455,400	2002	455,400
Blowback system	100,000	2001	107,000
Total cost in 2002			760,061

Q.2 SCR Unit

The catalyst volume that is needed is 48 m^3, the catalyst price is approximately €10,700 $1/m^3$, and is guaranteed for three years. So the total costs for the monolith are €514,378. An reactor vessel has to be build, with an volume of approximatelly 60 m^3, because of the corrosive properties of the flue gas Coronel is used. This reactor will cost €92,757 (1998). The amount of NH_3 that has to be added to the flue gas stream is 937 ton/year (NH_3 (25%)). This will cost €131,197 per year.

Q.3 Spray Absorber

Equipment	$S(m^3)$	$C(£)$	$n(-)$	$MF(-)$	$Ce(€)$
Spray absorber	324	1250	0.6	3.4	432,700
Lime storage tank	60	1200	0.55	2.0	72,400
Mixer vessel	60	1200	0.55	2.0	72,400
Lime		Consumption (ton/year)			2,109
		Price(€)			61
		Costs (€/year)			130,000
Total		Equipment cost (€)			577,500
		Variable cost (€/year)			130,000

Q.4 Fabric Filter

The number of bags installed in the fabric filter are 336. Each bag is estimated to cost €100. This makes a total of €33,600. The housing of these bags included shake system is estimated at €100,000.

Q.5 Wet scrubbers

The purchase price is determined using the method provided by Coulson and Richardson ****. The price is calculated with the following expression:

$$Ce = C \cdot S^n \tag{Q.1}$$

Ce is in English £ in 1992, they are converted into current €. The €is 1992 English £ 0.62. The annual inflation, for which needs to be corrected, is assumed to be 7%. C and n are equipment type constants. S is the size of the vessel. This amount can be multiplied by a Material Factor (MF), for more expensive materials, such as Monel or stainless steel.

Equipment	$S(m^3)$	$C(£)$	$n(-)$	$MF(-)$	$Ce(€)$
Wet Scrubber I	163.4	1250	0.6	1.5	126,600
Wet Scrubber II	238.8	1250	0.6	1.5	159,000
Caustic soda storage tank	70	1200	0.55	1.5	61,600
Mixer tank	70	1200	0.55	1.5	61,600
Equipment	number of units	Capacity (m^3/hr)	Price $(€/unit)$	Total costs (€)	
Pump	2	1250	189,200	378,400	
Pump	2	30	31,500	63,100	
Caustic soda (50%) consumption $(ton/year)$	price $(€/ton)$	costs $(€/year)$			
1,231	427	525,000			
Total	equipment cost (e)	variable cost $(e/year)$			
	408,800	525,000			

Appendix R

Fixed Capital Costs calculation

Table R.1: Purchased Equipment Costs

Equipment ID	Specification	Material	Costs (€ x1000)
'Out of scope equipment'			
- Bunker			
- Boiler			
- Heat exchanger			
- Pumps			
Total	Estimation costs		45,000
HT Dust (F101)			
- Vessel	50 m^3	Monel	197
- Candle	D=0.6 m, h=1.5m	SiC on Al_2O_3	455
SCR (R101)			
- Vessel	60 m^3	Monel	122
Spray Absorber (R102)			
- Vessel	324 m^3	Monel	578
Bag Filter (F102)			
- Bags	D=0.025 m, h=5 m	Teflon	34
- Housing		Stainless steel	100
Wet scrubbers (R103 & R104)			
- 2 Vessels			850
Purchased equipment Costs			**47,957**

Table R.2: Fixed Capital Costs calculation

Item		Lang factor	Costs €(x1000)
PCE (see table R.1)			**47,957**
Major equipment			
f1	Equipment erection	0.45	
f2	Piping	0.45	
f3	Instrumentation	0.15	
f4	Electrical	0.1	
f5	Buildings	0.1	
f6	Utilities	omitted	
f7	Storages	0.1	
f8	Site Development	omitted	
f9	Ancillary buildings	omitted	
	Lang factor 1	**1.35**	
	Total Physical Plant Cost (PPC) (1+LF1)*PCE		112,699
f10	Design and Engineering	0.2	
f11	Contractor's fee	0.05	
f12	Contingency	0.1	
	Lang factor 2	**0.35**	
	Fixed Capital Costs (1+LF2)*PPC		152,144

Appendix S

Production costs calculation

Capital

Total Investment				%	IN € (x1000)
- Fixed Capital Costs (FCC)					304,290
- Working Capital	9% of Total Invest	Factor FCC:	10.0%		30,462
Total Investment					**334,752**

Products

Products and Wastes			OUT t/a	Sales €/t	IN €(x1000)/a
- Product	Afval		500,000	110.00	55,000
- Product	Electricty	kWh	445,312,500	0.038	16,772
Sub-total					71,772
- Waste	Fly Ash		5,735	-90.76	-520
- Waste	Flue Gas Cleaning Residue		6,903	-181.51	-1,253
- Waste	Cake		121	-363.02	-44
- Waste	Bottom-ash		110,029	-9.08	-999
Total / Gross Income					**68,956**

Raw Materials

Raw Materials		IN t/a	Purchase €/t	OUT €(x1000)/a
- Feedstock	NH3	937	140.00	131
- Feedstock	NaOH 50%	1,231	427.20	526
- Feedstock	Lime Milk	2,109	61.00	129
Total		4,276		**786**

Catalyst & Candles

Yearly catalyst & candle cost			OUT €(x1000)/a
- Catalyst Batch,	€ (x1000)	521	
- Lifetime,	years	3	
- Annual costs			174
- Candle Batch,	€ (x1000)	454	
- Lifetime,	years	4	
- Annual costs			113
Total			**287**

Summary of Annual Production (Manufacturing) Costs (€(x1000)/a)				
Cost Type	€(x1000)/a	%		Remarks
Direct				
Variable				(A)
1. Raw materials	786	34%	2%	
2. Miscellaneous materials	1,521	66%	3%	10% of maintenance
3. Utilities				Included in income on electricity
4. Shipping & packaging				Negligible
Sub-total	*2,307*	*100%*		
Fixed				(B)
Catalyst	287	1%	1%	
5. Maintenance	15,214	33%	30%	5% of fixed capital
6. Operating labour	1,500	3%	3%	15 man: operators + maintenance + other
7. Laboratory	300	1%	1%	20%
8. Supervision	300	1%	1%	20%
9. Plant overhead	750	2%	1%	50%
10. Capital charges	15,214	33%	30%	5%
11. Insurance	3,043	7%	6%	1%
12. Local taxes	6,086	13%	12%	2%
13. Royalties	3,043	7%	6%	1%
Sub-total	*45,738*	*100%*		
Total	*48,045*			(A)+(B)
Other				(C)
14. Sales expenses				Negligble
15. General overhead	*1,000*	67%		Estimation
16. Research & Dev.	*500*	33%		Estimation
Sub-total	1,500	100%	3%	
Total Production Costs				
Annual [€(x1000)/a]	**51,045**		*94%*	(A)+(B)+(C)
Per ton P [€/t]	102.09			On basis of 500.000 tons per year

Appendix T

DCFROR

NET PRESENT- & FUTURE VALUES									
	NET FUTURE VALUES (1) No Discount					**NET PRESENT VALUES** Discounted, Accumulated			
END YEAR NO.	CAPIT. COSTS		CASH FLOW		**NFV**	DISC. FACT. @ DCFROR	CAPIT. COSTS ACCUM.	CASH FLOW ACCUM.	**NPV**
	ANN.	ACCUM.	ANN.	ACCUM.					
	Dfl mill	Dfl mill	Dfl mill	Dfl mill	Dfl mill	**0.158%**	Dfl mill	Dfl mill	Dfl mill
1	167.4	167.4			-167.4	1.000	167.4		-167.4
2	167.4	**<u>334.8</u>**			-334.8	0.998	**<u>334.5</u>**		-334.5
3			17.9	17.9	-316.8	0.997		17.9	-316.6
4			17.9	35.8	-298.9	0.995		35.7	-298.8
5			17.9	53.7	-281.0	0.994		53.5	-281.0
6			17.9	71.6	-263.1	0.992		71.3	-263.2
7			17.9	89.6	-245.2	0.991		89.0	-245.5
8			17.9	107.5	-227.3	0.989		106.7	-227.8
9			17.9	125.4	-209.4	0.987		124.4	-210.1
10			17.9	143.3	-191.5	0.986		142.1	-192.4
11			17.9	161.2	-173.5	0.984		159.7	-174.8
12			17.9	179.1	-155.6	0.983		177.3	-157.2
13			17.9	197.0	-137.7	0.981		194.9	-139.6
14			17.9	214.9	-119.8	0.980		212.4	-122.1
15			17.9	232.8	-101.9	0.978		229.9	-104.6
16			17.9	250.8	-84.0	0.977		247.4	-87.1
17			17.9	268.7	-66.1	0.975		264.9	-69.6
18			17.9	286.6	-48.2	0.974		282.3	-52.2
19			17.9	304.5	-30.3	0.972		299.7	-34.8
20			17.9	322.4	-12.3	0.970		317.1	-17.4
21			17.9	340.3	5.6	0.969		334.5	0.0
22		*(3) :*	*16.7*	195.9	-138.9	0.967		193.5	-141.0
ACCUM.		**334.8**		**340.3**	**5.6**	21.639	**334.5**	**334.5**	**0.0**

RATIO : [Cash Flow / Capital] @ Disc. **1.0**

NET PRESENT VALUE : [Cash Flow - Capital] @ Disc. **-141.0**

N.B. :
1. Cash-Flows "Before Tax".
2. Earning Power = Interest, for which [Cash Flow - Capital]@Disc. = 0
   Disc. Factor = 1/(1 + r)^n with r = interest fraction
3. Rest Value = 5.0% of Capital Investment

Appendix U

Stream Summary

STREAM Nr. :		**101**	IN	201		**102**		202		203	
	Name :	Incinerator to HT-filter		Air for regeneration HT-filter		HT-filter to heatexchanger 1		Heatexchanger for SCR in		Heatexchanger for SCR out	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
H2O	18	7.18E+00	3.99E-01			7.18E+00	3.99E-01				
CO2	44	8.27E+00	1.88E-01			8.27E+00	1.88E-01				
O2	32	5.95E+00	1.86E-01			5.95E+00	1.86E-01				
N2	48	3.43E+01	7.15E-01			3.43E+01	7.15E-01				
Dust	nvt	1.08E-01				5.42E-04					
SO2	64.1	2.17E-02	3.39E-04			2.17E-02	3.39E-04				
NOx	41.6	1.90E-02	4.56E-04			1.90E-02	4.56E-04				
NH3	27	6.78E-04	2.51E-05			6.78E-04	2.51E-05				
CO	28	5.43E-04	1.94E-05			5.43E-04	1.94E-05				
CxHy	16	1.08E-04	6.77E-06			1.08E-04	6.77E-06				
Hg	200.6	2.17E-05	1.08E-07			2.17E-05	1.08E-07				
H.M.	nvt	1.85E-03				1.85E-03					
Cd	112.4	0.00E+00	0.00E+00			0.00E+00	0.00E+00				
HF	20	8.14E-04	4.07E-05			8.14E-04	4.07E-05				
HCl	36.5	6.51E-02	1.78E-03			6.51E-02	1.78E-03				
PCDD/F	nvt	5.43E-11				5.43E-11					
Total		5.59E+01	1.49E+00			5.58E+01	1.49E+00				
Enthalpy	kW										
Phase		gas		gas		gas		liquid		vapour	
Press.	Bara	0.935				0.985					
Temp	oC	750.0				740.0					

STREAM Nr. :		**103**		204		**104**		205		206	
	Name :	SCR entrance		Ammonia addition for SCR		SCR effluent		Heatexchanger after SCR in		Heatexchanger after SCR out	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
H2O	18	7.18E+00	3.99E-01			7.18E+00	3.99E-01				
CO2	44	8.27E+00	1.88E-01			8.27E+00	1.88E-01				
O2	32	5.95E+00	1.86E-01			5.95E+00	1.86E-01				
N2	48	3.43E+01	7.15E-01			3.43E+01	7.15E-01				
Dust	nvt	5.42E-04	0.00E+00			5.42E-04					
SO2	64.1	2.17E-02	3.39E-04			2.17E-02	3.39E-04				
NOx	41.6	1.90E-02	4.56E-04			3.80E-05	9.13E-07				
NH3	27	6.78E-04	2.51E-05	3.38E-05	1.25E-06	6.78E-04	2.51E-05				
CO	28	5.43E-04	1.94E-05			5.43E-04	1.94E-05				
CxHy	16	1.08E-04	6.77E-06			1.08E-04	6.77E-06				
Hg	200.6	2.17E-05	1.08E-07			2.17E-05	1.08E-07				
H.M.	nvt	1.85E-03	0.00E+00			1.85E-03					
Cd	112.4	0.00E+00	0.00E+00			0.00E+00	0.00E+00				
HF	20	8.14E-04	4.07E-05			8.14E-04	4.07E-05				
HCl	36.5	6.51E-02	1.78E-03			6.51E-02	1.78E-03				
PCDD/F	nvt	5.43E-11	0.00E+00			5.43E-11					
Total		5.58E+01	1.49E+00	3.38E-05	1.25E-06	5.58E+01	1.4900				
Enthalpy	kW										
Phase		gas		liquid		gas		liquid		liquid	
Press.	Bara	0.985				0.987					
Temp	oC	350.0				320.0					

STREAM Nr. :		**105**		207		**106**		208		**107**	
	Name :	Spray absorber in		Ca(OH)2 addition		To bagfilter		Sprayabsorber residue		To wet scrubber 1	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
H2O	18	7.18E+00	3.99E-01	5.12E+00	2.84E-01	1.71E+01	9.50E-01	$CaCl_2$		1.71E+01	9.50E-01
CO2	44	8.27E+00	1.88E-01	8.27E+00		8.27E+00	1.88E-01	6.26E-02	5.62E-04	8.27E+00	1.88E-01
O2	32	5.95E+00	1.86E-01	$Ca(OH)_2$		5.95E+00	1.86E-01	CaF_2		5.95E+00	1.86E-01
N2	48	3.43E+01	7.15E-01	6.69E-02	9.02E-04	3.43E+01	7.15E-01	5.63E-04	7.12E-06	3.43E+01	7.15E-01
Dust	nvt	5.42E-04				5.42E-04				5.42E-04	
SO2	64.1	2.17E-02	3.39E-04			2.17E-02	3.39E-04			2.17E-02	3.39E-04
NOx	41.6	3.80E-05	9.13E-07			3.80E-05	9.13E-07			3.80E-05	9.13E-07
NH3	27	6.78E-04	2.51E-05			6.78E-04	2.51E-05			6.78E-04	2.51E-05
CO	28	5.43E-04	1.94E-05			5.43E-04	1.94E-05			5.43E-04	1.94E-05
CxHy	16	1.08E-04	6.77E-06			1.08E-04	6.77E-06			1.08E-04	6.77E-06
Hg	200.6	2.17E-05	1.08E-07			2.17E-05	1.08E-07			2.17E-05	1.08E-07
H.M.	nvt	1.85E-03				1.85E-03				1.85E-03	
Cd	112.4	0.00E+00	0.00E+00			0.00E+00	0.00E+00			0.00E+00	0.00E+00
HF	20	8.14E-04	4.07E-05			3.42E-04	1.71E-05			3.42E-04	1.71E-05
HCl	36.5	6.51E-02	1.78E-03			2.44E-02	6.69E-04			2.44E-02	6.69E-04
PCDD/F	nvt	5.43E-11				5.43E-11				5.43E-11	
Total		5.58E+01	1.49E+00			6.57E+01	2.04E+00			6.57E+01	2.04E+00
Enthalpy	kW										
Phase		gas		liquid		gas		solid		gas	
Press.	Bara	0.987				0.988				0.998	
Temp	oC	210.0				150.0		100.0		140.0	

STREAM Nr. :		**107**		210		209		211		212	
	Name :	Wet scrubber I in		wetscrubber I to overflow		Overflow to spr.absorber		Emergengy water scrubber I		recycle wetscrubber I	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
H2O	18	1.71E+01	9.50E-01	2.27E+02	1.26E+01	4.81E+00	2.67E-01			2.22E+02	1.23E+01
CO2	44	8.27E+00	1.88E-01								
O2	32	5.95E+00	1.86E-01								
N2	48	3.43E+01	7.15E-01								
Dust	nvt	5.42E-04									
SO2	64.1	2.17E-02	3.39E-04								
NOx	41.6	3.80E-05	9.13E-07								
NH3	27	6.78E-04	2.51E-05	3.20E-02	1.19E-03	6.78E-04	2.51E-05			3.13E-02	1.16E-03
CO	28	5.43E-04	1.94E-05								

Appendix V

Thermodynamic properties

Compound	State	D_fH_0 (at 298k)	D_fG_0 (at 298K)	S_0 (at 298K)	Cp (at 298K)	$D_{sol}H_0$ (at298K)	Density	Boiling Point	Melting Point		Solubility
		(kJ/mol)	(kJ/mol)	(kJ/mol/K)	(kJ/mol/K)	(kJ/mol)	(kg/m^3)	oC	oC		(g/100gH_2O)
NH_3	gas	-4.59E+01	-1.64E+01	1.93E-01	3.51E-02		800.0	-33.0	-78.0		84.9-7.4
CaO	Solid(cry)	-6.35E+02	-6.03E+02	6.38E-02	4.20E-02		3400.0	2850.0	2570.0		forms Ca(OH)$_2$
$Ca(OH)_2$	Solid(cry)	-9.85E+02	-8.98E+02	8.34E-02	8.75E-02		2240.0	not appl.	580.0		0.185-0.077
	Aq	------	-8.68E+02								
NaOH	Solid(cry)	-4.26E+02	-3.80E+02	6.45E-02	5.95E-02			145.0	12.0		109-174
-50%	aq	-------	-4.19E+02				1500.0				
HCl	Gas	-9.23E+01	-9.53E+01	1.87E-01	2.91E-02	-7.48E+01	860.0	-85.0	-114.0		totally
HF	Liq	-3.00E+02	-------				950.0	20.0	-83.0		totally
	Gas	-2.73E+02	-2.75E+02	1.74E-01	2.91E-02	-6.15E+01					
HBr	Gas						1800.0	-67.0	-87.0		totally
SO_2	Liq	-3.21E+02	------				1400.0	-10.0	-76.0		22.83-4.5
at T=413K	Gas	-2.97E+02	-3.00E+02	2.62E-01	4.03E-02						
NH_4OH	liq	-3.61E+02	-2.54E+02	1.66E-01	1.55E-01		900.0	38.0	-58.0		59.9-159
$CaCl_2$	Solid(cry)	-7.95E+02	-7.49E+02	1.08E-01	7.29E-02		2100.0	1600.0	772.0		
	Aq	------	-8.10E+03								
CaF_2	Solid(cry)	-1.23E+03	-1.18E+03	6.85E-02	6.70E-02		n.a	n.a	n.a		0.0016-0.0017
$CaBr_2$							n.a	n.a	n.a		125-312
$CaSO_3$	Solid(cry)	-1.43E+03	-1.32E+03	1.07E-01	9.97E-02		n.a.	n.a	n.a.		
NaCl	Solid(cry)	-4.11E+02	-3.84E+02	7.21E-02	5.05E-02		2200.0	1413.0	801.0		35.7-39.8
	aq		-3.98E+02								
NaF	Solid(cry)	-5.77E+02	-5.46E+02	5.11E-02	4.69E-02		2800.0	1700.0	990.0		
Na_2SO_3	Solid(cry)	-1.10E+03	-1.01E+03	1.46E-01	1.20E-01		2600.0	n.a	600.0		
Hg	liq/gas	0/61.4	-/31.8	0.0759/0.1751	0.028/0.0208		13600.0	357.0	-39.0		
$HgCl_2$	gas						5400	303	277		
Dioxine	gas						n.a.	-4	305		
CO_2	gas	-3.94E+02	-3.94E+02	2.14E-01	3.71E-02		n.a.	-4	305		0.3346-0
CO	gas	-1.11E+02	-1.37E+02	1.98E-01	2.90E-02		0.8	-79	n.a.		0.0044-0
NO	gas						n.a.	-191	-205		7.34-0
NO_2	gas	3.32E+01	5.13E+01	2.40E-01	3.72E-02		1.3	-152	-164		decomposes
O_2	gas	0.00E+00	-------	2.05E-01	2.94E-02		1.5	21	-11		4.89-1.7
N_2	gas	0.00E+00	-------	1.92E-01	2.91E-02		n.a.	-183	-218		2.35-1.55
H_2O	Liq	-2.86E+02	-2.37E+02	7.00E-02	7.53E-02						
	Gas	-2.42E+02	-2.29E+02	1.89E-01	3.36E-02						