Subject
The processing of an aqueous hydrogen fluoride/hydrogen chloride - stream into economic valuable products

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Preface

This is the report of a preliminary plant design done by a team of four students of the faculty of chemical engineering at the Delft university of technology. This preliminary plant design is an obligatory subject for each fourth year student. In the scope of this subject a complete design of a total or partial chemical plant has to be made, including the main aspects of chemical engineering which have been taught in the preceding study and in a special advanced course on the structure of chemical plants. These main aspects are on the field of process structure, process control, design, financing and environment.

The cases around which the project done is normally delivered by the chemical or biotechnological industry and then distributed amongst the several teams by the faculty. This team however sought the challenge and preferred to obtain an assignment on its own and establish a direct contact with the supplying company. After a selection the assignment of the DuPont de Nemours plant at Dordrecht has been chosen. During the project a pleasant and useful contact with the DuPont employees, in particular Jaap Wassenaar, has been build up. This contact certainly has raised the final quality of the design and the pleasure while developing it.

The mission statement of the project was to find and develop a process to separate a sub-azeotropic mixture of HF, HCl and water in its components. During the past three months the DuPont FVO Dream Team has been busy accomplishing this mission. The final result as described in this report would not have been possible if not every member of the team had given his best and had not addressed all his social and technical capabilities. This long period of struggle and strive resulted in two completely developed processes which both have a high potential concerning the separation of the components.

The last weeks and nights have been devoted to writing this report and optimisation the processes to the last detail. Thus is in front in you the complete result of three months of hard work in which not only on the technical field a lot has been learned. Before the reader goes to the next page, we would like to wish him a pleasant time while reading this report and to give him one last thought:

It's finished.

The DuPont FVO Dream Team,

Manon Cremers
Isold Heemstra
Joris Kleinveld
Dirk-Jan Peet

* Voldaan aan criteria
* Optin. naar geld.
Acknowledgements

In preparing this preliminary plant design we received valuable assistance from a number of persons. It is a pleasure to express now our deep appreciation to these people for their time and efforts.

At first we would like to thank C.P. Luteijn for the advice he has given and for the sympathy shown when some of our files were lost due to crashes of a floppy disc. In the faculty several people give us also useful advice and we really appreciated that. Th. de Loos and H. van der Kooij have given us very helpful information about thermodynamic models and referred us to several other people who could give more information about water/HF/HCl-systems. We also like to thank L. van der Wielen and M. Bisschops for the help and information given about electrodialysis and the rotating disc separation column.

We cannot forget all the people of DuPont who have been a tremendous help for the completion of this preliminary plant design. Eric Hobbel gave us a good insight in the process control. Ger van Unnik’s feeling for industrial processes was very helpful for the selection of processes from the literature. Leo Hermans showed us another way of calculating the investment costs. The construction materials wouldn’t have been the same if we weren’t informed by Frank Schramm.

And last but not least we especially would like to thank Jaap Wassenaar for giving us the opportunity of doing our preliminary plant design at DuPont. He has given us a great insight in the way a process is designed in reality and also in the place of a chemical engineer in the industry. We think that he gave us very much advice and information, so that our project has got more depth than it would have had if we did the project in another way. We really appreciate that he really wanted the best for us.

The ‘win-win situation’ for DuPont and us has really occurred.

We would also like to thank Remko, Heleen, Minke and Dorien for their never ceasing understanding in the very heavy and difficult time that this FVO was and the roommates Pepijn and Joost for allowing us to use their superior hardware in the weekends. Thanks guys!

Manon Cremers
Isold Heemstra
Joris Kleinveld
Dirk-Jan Peet

We had a dream.....Team
Now it’s really finished.......finally
Summary

This preliminary plant design has been made in the scope of a part of the post-propedeutical phase of the study of Chemical Engineering at the TU in Delft. In this preliminary plant design two continuous processes have been designed to recover hydrogen fluoride from an aqueous waste water stream. The assignment was done for DuPont de Nemours at Dordrecht. The reason for this assignment for DuPont is to search for several options to treat an aqueous waste stream of hydrogen fluoride to gain anhydrous hydrogen fluoride, which can be reused in several plants at the DuPont site in Dordrecht.

The two continuous processes have been selected from six possible processes found after a profound literature study. The need for this processes exists because the hydrogen fluoride forms a maximum temperature ternary azeotrope with water and hydrogen chloride. Since the feed is sub-azeotropic the hydrogen fluoride cannot be recovered by conventional distillation based on differences in boiling point. The six possible processes were the hexane stripping, the pressure swing, the electrodialysis, the hydrogen chloride make-up, the cyclohexanol extraction and the sulphuric acid distillation process. The two processes last mentioned have been selected to be further developed. The selection was made using criteria concerning technical feasibility, energy requirements, hazards, available time and potential to meet the DuPont product specifications. The two selected processes, the cyclohexanol extraction and the sulphuric acid extractive distillation process, were both developed to be able to make a well funded choice between the two processes and thereby providing a reliable advice to DuPont about the best solution for the recovery of HF.

Both the cyclohexanol and the sulphuric acid process have been simulated with the simulation program ASPEN Plus. The feed of both the processes is 1000 kg/hr. The amount of HF in the feed is 20 wt%, of HCl 5 wt% and of water 75 wt%. Both processes are based upon extraction. Cyclohexanol extracts HF, sulphuric acid extracts water.

The sulphuric acid process yielded a hydrogen fluoride product stream of 199.269 kg/hr HF and 0.052 kg/hr HCl. The HF has a purity of approximately 100 wt% and contains 259 ppm HCl, 18 ppm water and 217 ppb sulphuric acid. This stream leaves the process at 15 °C and 300 kPa, which meets the DuPont specifications. The HCl product stream contains only 18 ppm HF and less than 1 PPB of water. The stream has a temperature of 15 °C and a pressure of 1400 kPa. This enables it to be added to the existing HCl capacity of the site. The waste water stream contains 0.730 kg/hr of HF. The concentration of HF in this stream is 0.1 wt%. It also contains 1.3 ppm of HCl and less than 1 PPB of sulphuric acid. The stream leaves the process at 15 °C and 150 kPa.

The cyclohexanol process produced a product stream of 199.280 kg/hr of HF and 0.419 kg/hr HCl. The purity of HF is 99.8 wt% and the stream contains less than 1 PPB of water and 3 PPB of cyclohexanol and leaves the process at 15 °C and 300 kPa. This meets the specifications given by DuPont. The HCl product stream contains less than 1 PPB water and cyclohexanol and 7 ppm of HF. It exits the process at 15 °C and 1400 kPa, just like in the sulphuric acid process. The waste water contains 0.720 kg/hr of HF, which equals 0.1 wt%. It also contains 1 ppm of cyclohexanol and less than 1 PPB of HCl. It exits the process at 15 °C and 190 kPa.

The streams of both processes lie within the specifications given by DuPont according to the loss of HF via the waste acid stream and concerning the composition of the HF and HCl product streams. The waste of both processes also remain within government restrictions.

The sulphuric acid requires three sections interconnected by typicals and simple process equipment to achieve this result. These sections comprise an extraction section, a sulphuric acid recovery section and the hydrogen fluoride and hydrogen chloride separation section. The cyclohexanol process requires five sections: The extraction section, the hydrogen fluoride and hydrogen chloride recovery
1. What do you mean?

2. Did you include the penalties to be paid for the untreated streams. What is your reference? Is the feed for free?

3. Negative profit and yet ROI 100%?
section, the hydrogen fluoride and hydrogen chloride separation section, the cyclohexanol recovery 
section and the water removal section. These sections are again interconnected by typicals and simple 
process equipment. All the equipment is sized according modern and accepted design rules.

In both the processes several distillation columns are used. It can be concluded that for these columns 
packed bed columns are easier to construct and the column height is smaller. Exception is the 
extraction column in the cyclohexanol process, for which the rotating disc column is used at the 
expense of the sieve plate and packed column.

The average investment costs for the sulphuric acid process are 27278.56 kdfl. The total production 
costs per year are 10040.70 and the total revenues are 5130.89 kdfl. That means that the profit will be 
-4909.82 kdfl.

The average investment costs of the cyclohexanol process are 28698.30 kdfl. The total production 
costs are 9845.28 kdfl and the revenues will also be 5130.89 kdfl. This result in a profit of -4714.40 

kdfl. The investment costs of the cyclohexanol process are higher than those of the sulphuric acid 
process. This is logical because the cyclohexanol is a more complex process and requires more 
equipment.

For both processes a Return On Investment of 10 % has been taken. This is for a project in the 
environmental scope a good value. This results for both processes in an internal rate of return of 
12.3% and a pay out time of 2.6 years. An internal rate of return of 12.3 % is not very high, but it is not so low that the entire project cannot be carried out. A project which has a pay out time of 2.63 is a very viable project.

As are most waste treatment processes the project is loss-making. However this project together with 
the thermal converter guarantees the continuity of the DuPont site in Dordrecht. This because if in the 
future still HFC’s and CFC’s are emitted to the environment the entire site will be threatened with a 
shut down. By building the thermal converter unit and one of the developed processes the emissions 
to the air are significantly reduced and the disposed waste streams are within draining limits. This 
saves a levying for the waste streams and, more importantly, guarantees the continuity of the plant.

Finally a comparison is made of the two developed processes and a choice for one of them is 
presented. Criteria for this choice are complexity, operability, process conditions, feasibility of the 
technology, product and waste specifications, corrosiveness and construction materials, process 
control, finances, Aspen simulations and safety, health and environment aspects. Based on these 
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At last a few recommendations concerning this further development are given.
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1 Introduction

In the scope of the post-propedeutic phase of the study of Chemical Engineering at Delft University of Technology a preliminary plant design has to be made. Several assignments of different companies have been acquired and the assignment of DuPont de Nemours in Dordrecht has been chosen. The aim of the assignment is to do the job of an engineering's agency and give a well funded advice to DuPont to choose what process route is the best for the recovery of hydrogen fluoride and hydrogen chloride from an aqueous waste water stream.

The feed with a temperature of about 30 °C is a waste water stream of 1000 kg/hr and consists of 75 wt% water, 20 wt% HF and 5 wt% HCl. The product stream of HF must not contain more than 100 PPM water and 2% HCl. Further details of the FVO DuPont assignment description can be found in appendix A.

I. The temperature and pressure of the product streams will be 15-20 °C and 1-3 bar for the HF and water stream and 15-20 °C and 14 bar for the HCl stream respectively.

1.1 Background of the assignment

The site of DuPont de Nemours at Dordrecht, The Netherlands, has several business units for the production of e.g. Lycra®, Teflon®, Delrin® and Viton®. During the production processes a lot of by-products are formed. In the past these by-products were emitted to the environment. An overview of the process at the site is displayed in figure 1.1.

In the F-22 process HF and CHCl₃ react to form F-22 (CHClF₂). In the TFE process, F-22 is converted to tetra-fluor-ethylene (C₂F₄) and in the HFP-process to hexafluoropropylene (C₃F₆). TFE alone can be used in homo-polymerisation processes and TFE with HFP in co-polymerisation processes.

As a result of government restrictions and the policy of the company itself, a thermal converter has been designed to reduce emissions of HFC’s, CFC’s and other gases. This reduction can be achieved with a hydro-dehalogenation process or thermal combustion process. DuPont has chosen for the last option, because the feedstock consists of fluctuating concentrations and flows of HFC-23, CFC’s, HCFC’s, water and inerts. Since the hydro-dehalogenation process requires a specified feed, thermal combustion is the only proven technology option to convert the chloro-fluoro-hydrocarbons to products like HF and HCl.

At this moment the Thermal Converter is built on the DuPont site. The DuPont Thermal Converter is a special designed reactor for this kind of gas treating. At high temperature (1250 °C), light- and under pressure, a residence time of two seconds and excess air and natural gas, the feedstock is converted into hydrogen fluoride (HF), hydrogen chloride (HCl), carbon dioxide (CO₂) and water (H₂O). After combustion the outlet gases are quenched with water to a temperature of 90 °C. A more detailed description of the thermal converter and a schematic overview can be found in appendix A.2.

Presently the waste water of this unit, consisting of an aqueous solution of 20 wt% HF and 5 wt% HCl, is fetched by a specialised company to be processed elsewhere. Because in the future another solution for the aqueous HF-stream may has to be found, DuPont is searching for several options to recover the HF from the waste water. Since recovery by normal conventional distillation is not possible due to the sub-azeotropic composition of the stream other options have to be found. The preliminary plant design performed here is meant to investigate, select and develop this options.
1.2 Product properties and applications

In this paragraph the chemical properties, the impact of the substances on humans and applications of HF and HCl are discussed.

### 1.2.1 Hydrogen fluoride

Anhydrous hydrogen fluoride is a colourless liquid having a boiling point of 19.5 °C at atmospheric pressure. It is a corrosive, hazardous material, fuming strongly, which causes severe burns upon contact. Applications of hydrogen fluoride vary from glass etching and foundry scale removal to production of uranium reactor fuel for commercial electric power generation (lit. HE2). At the DuPont site in Dordrecht HF is used to make F-22, which is the raw material for the production of e.g. TFE and HFP.

HF and water form a strong azeotrope. At atmospheric pressure and 25 °C the azeotropic composition is 38 wt% HF in a binary system of HF and water. The azeotrope is a maximum temperature azeotrope and the boiling point of the azeotrope is 119 °C at atmospheric pressure. The binary T-xy diagram of the HF/water system has been included in appendix A.4. Due to the fact that this azeotrope occurs, the distillation of these two components is very complicated. The situation gets even more complicated, when a third component is introduced. A ternary diagram of HF, HCl and water can be found in appendix A.5.

### 1.2.2 Hydrogen chloride

HCl is also produced as a by-product. Anhydrous HCl is a colourless gas that condenses to a colourless liquid at -85 °C at atmospheric pressure. It is irritant, severely effecting the eye and the respiratory tract. HCl in the lungs can cause pulmonary edema, a life threatening condition. HCl can be used in many processes such as metal cleaning operations, chemical manufacturing, petroleum well activation, and in the production of food and synthetic rubber.

1.3 Existing process routes for recovery of hydrogen fluoride

From a patent-literature search several processes for the recovery of hydrogen fluoride have been found. In chapter 2.2 these processes will be mentioned and described by means of the block diagrams in appendix B. It cannot be said with certainty that the processes found in the literature have been applied in the industry.

1.4 Market capacity

Hydrogen fluoride is the most important manufactured fluorine compound in the world. It is the largest in terms of volume, and serves as the raw material for most other fluorine-containing chemicals. The global HF production capacity was 875,000 metric tons in 1992. An additional 204,000 metric tons were used captivity for production of aluminium fluoride. The market in the Netherlands for HF was 7,000 metric tons. HF is available either in anhydrous form or as an aqueous solution (usually 70%).

Assuming that the thermal converter unit which produces the feed stream for the process operates 350 days/year the total HF feed to the process is 1670 tons/year. The other days are used for maintenance and cleaning. With this feed the production capacity of the process has to be at least 1670 tons/year HF. This is about 8% of the total need of HF at the DuPont site in Dordrecht. The total loss of HF in
the designed processes must not exceed 1 kg/hr due to government regulations. Since the total HF flow is 200 kg/hr the production stream has to be greater than or equal to 199 kg/hr HF. The remaining HF in the produced waste water stream of 750 kg/hr has to be disposed of.

In 1993 the production of the HCl capacity was about 2.92 million metric tons (lit HE2). At DuPont the HCl-production can be added to the existing capacity of 4500 kg/hr and will probably be used captivity.

1.5 Environmental and sustainability aspects

The idea behind the design of this process is to give a sustainable solution for the problem of waste water that is produced by the thermal converter. Producing a usable form of HF will enable a more efficient use of HF when recycled to the Freon-22 process. This in stead of the current situation in which the HF solution is fetched by a specialised company to be handled elsewhere. This means that the HF can't be used as a raw material. Thus by building a HF recovery plant a saving in the raw material costs for the Freon 22-process can be made.

Together with the thermal converter the dehydration of HF forms a solution for the problem of all the gaseous waste products of the DuPont-site in Dordrecht. The dehydration is the last step in this process. The entire processing of the waste gases has a very positive effect on the environment, because the exhaust gases, containing CFC's, HCFC's and HFC's, are prevented from being emitted to the environment as is the case in the current situation. This also satisfies restrictions supposed by government regulations.

1.6 The report structure

In the following chapters the search for, the selection of and the development of the processes for the recovery of HF will be described.

In the next chapter the literature search and several process routes will be mentioned and a choice will be made for the process(es) for which the complete design will be done. Also the external specifications and boundary conditions will be discussed.

In chapter three the process structure will be justified and the process flows will be discussed by means of the process flow diagrams. In chapter four the calculations of the dimensions of all the process equipment will be given. In chapter five the mass and energy balances are discussed. In chapter six the specification of all the process equipment, calculated in chapter four, is given in equipment lists and equipment forms.

Chapter seven consist of the discussing of the process control for all the types of process equipment and also the justification for several analysers. Chapter eight discusses the maintaining of the process safety, health and environment aspects. Also an overview of the effects that the hazardous components can cause is given. In chapter nine a limited HAZOP analysis is given and in chapter 10 the calculation of the investment cost, the operation cost and several economic criteria will be discussed.

In the last chapter the conclusions will be given and several recommendations will be given for future FVO-teams.
2 Starting points and basic principles

In this chapter an overview of the literature will be given and the possible processes for the recovery of HF will be discussed. After a this discussion a few of these processes will be selected to be further developed. In the chapter the external specifications and boundary conditions will be treated as well.

2.1 Literature research

During two weeks a profound literature study has been done. In several libraries handbooks and encyclopaedia (lit. HE) have been studied and an on line and CD-ROM search has been performed. Together with a thorough search for suitable patents (lit. P.) in the European Patent Office in Rijswijk this resulted in six possible process routes for the recovery of HF from a wastewater stream containing 20wt% HF, 5wt% HCl and 75wt% water.

The literature search started in the library of the faculty of Chemical Engineering at the Delft University of Technology. Here the basic information about azeotropic and extractive distillation was found and profoundly studied. Also important information of the used components and their general properties were generated. In the Chemical Abstract Series and in other handbooks information about existing processes for the recovery of HF out of aqueous mixtures was found. After having been through all the available chemical abstracts in the library (50 years) the literature search was continued by searching on-line. In the library of the university it was possible to search on CD-ROM.

The whole research until this point resulted in several patent references, so the next step was the European Patent Office in Rijswijk. In this office we searched on all CD's and in all textbooks for Dutch, European and world patents of the past 40 years. This resulted in several Dutch and foreign patent references. An overview of interesting patents is given in appendix Q. The following step was to make a selection out of all the found patents. This was done in corporation with DuPont de Nemours at Dordrecht and resulted in six possible processes for the recovery of HF. In the next paragraph a detailed description of the selected processes is given.

2.2 Processes for recovering hydrogen fluoride

In the next paragraphs the selected processes for the recovery of HF from an aqueous solution will be described. Hereby again is mentioned that a conventional distillation is not possible due to the sub-azeotropic composition of the feed. All the possible processes described are a result of the performed literature research. For clarity each process will be illustrated in a block diagram. These block diagrams were developed using lit. HE 17 and HE18. The block diagrams represent the battery limits of the process. The processes that can be used for the purpose of dehydration hydrogen fluoride are summarised in table 2.1

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2.2.1 Hexane gas stripping process

The hexane stripping process (lit. P1 and P2) is a gas stripping process. The process block diagram is given in appendix B1. The process uses gaseous hexane to strip the HF and HCl out of the waste water feed stream. After condensation the HF is recovered. Disadvantages of using a gaseous extractant are the large explosion hazard and the high energy requirements due to the continuous hexane vapourisation. A short summary of the process will be given underneath.

Hexane(g) is led into extraction unit [1] to strip the HF and HCl (2) from the aqueous feed (1). The top stream consists of HF, HCl, hexane and water (2) and is led into condensation section [2]. Traces of hexane and water (4) are here removed from the HF/HCl mixture (3) whereas the top stream (3) is led into a flash DONA-unit [3] (lit. DP16) in which HCl is separated from the HF by stripping the mixture with an inert gas. The bottom stream (4) of the condensation section is fed to an evaporation section where traces water (8) are removed from gaseous hexane (9). Stream (6) of the extraction section [1], containing water and hexane, is send to a purification section where most of the water (7) is removed and hexane (8) via the evaporation section is recycled to the stripping section.

The basic unit operation of the hexane stripping process, the first column, where the HF is stripped from the water, has been simulated using the flowsheet simulation package ASPEN Plus vs. 9.02. The simulation however was not successful.

2.2.2 Electrodialysis process

Electrodialysis is a very clean process which doesn't require any additives like extractant or substances that break the HF / water azeotrope. The process block diagram is given in appendix B2. The principle of the process is the use of anion and cation selective membranes in electrodialysis equipment [3] (lit.P12 in specific, lit. EI in general). When a potential is applied across the solution the cat ions are attracted by the anode and the anions by the cathode. Because the membranes are selective for anions and cat ions, the middle stream is concentrated and the outer streams are diluted.

A schematic overview of this principle is shown in figure U1 in appendix U. The outer streams can be recycled to an azeotropic distillation unit [1]. The middle stream (5) can be concentrated in this manner to 55 wt% HF (6). The HF can than simply be distilled to yield pure HF and the azeotropic mixture. This mixture can be recycled to the electrodialysis equipment. Stream (6) is fed into a DONA-unit [2] (lit.DP16) where the HCl (8) is removed from the mixture stripping it with an inert gas (7). The resulting azeotropic mixture is then fed into a HF distillation unit [4] where the HF (10) is separated from the azeotropic mixture (11). The azeotropic mixture can be mixed with the process stream (4).

The simulation of this process in ASPEN has to be done with a “user-defined block”. To use this block, a vast amount of information has to be put in this block to get it to function correctly.

Since other processes described later in this chapter have proven to be more interesting the electrodialysis process will not be looked into any further. Because it’s still an interesting and elegant option several literature titles and references to persons, institutes and companies specialised in electrodialysis can be found in the literature and reference lists. That is lit. EL1 till EL5 and IN3 and ref. 17 till 19.

2.2.3 Pressure swing distillation

The principle of the pressure swing distillation is the variation of the azeotropic composition by varying pressure. The process block diagram of this process is given in appendix B3. The waste water feed (1) is led into the first pressure section. In this section the pressure of the anhydrous mixture is changed and as a consequence the position of the azeotrope has altered. When
the mixture is below its azeotropic composition it is thermodynamically possible to distil water. For this reason it is possible to distil water from the mixture to its azeotropic composition. Water will leave this section at the top and the bottom stream is again the azeotropic mixture. This section again illustrates that it is impossible to recover the HF from the sub-azeotropic feed in one simple distillation step.

Since the second pressure section [3] is at a lower pressure the azeotrope of the mixture has shifted to a lower HF concentration. Therefore the feed from the first section which was at the higher pressure now comes in at a sub-azeotropic composition. Thus HF and HCl can be distilled from the remaining mixture and will leave section [3] at the top. The bottom contains the azeotropic mixture matching the prevailing pressure. This mixture is recycled to the feed of the process. HF and HCl can be separated in a distilling unit [2] at high pressure.

The feasibility of the pressure swing distillation is low since the azeotropic composition doesn’t vary much when varying the pressure. This was the result of a small research to the thermodynamics of the ternary azeotrope done in Aspen. Thus the pressure differences between the two distillation columns should be very large in order to achieve an obvious and usable difference in azeotropic composition.

2.2.4 The azeotropic distillation column
In all the processes an amount of water has to leave the process. This can be done with a distillation column, which separates a part of the water of the aqueous HF stream and generates a stream with the azeotropic composition that will leave the bottom. This stream can now be further processed in the rest of the process. The simulation of this unit yielded some problems, due to convergence errors. Simulation with just HF and water was no problem, but when only a few weight percentages of HCl were introduced, the simulation would not converge with any realistic thermodynamic model like NRTL for electrolytes. A number of thermodynamic models have been tried, but none gave a sufficient result. This was confirmed by V.V. de Leeuw who works at AspenTech in Brussels. His recommendations can be found in appendix S.

2.2.5 HCl-make up process
In appendix B4 the process block diagram of the HCl-make up process is displayed. For more information about this process see also lit. P8. The stream from the thermal converter (1) will first be fed into a water removal section [1]. Part of the water will be separated to yield an azeotropic mixture (3). Pure water is removed (2). The azeotropic mixture is fed into the top of stripping section [2]. HCl gas (14) is fed into the bottom of this section. The HCl will strip the HF from mixture and leaves the section (5) (Hanson, lit. P8). The remaining mixture (7) from the stripping section contains water, HCl and probably still some HF. This stream can be recycled and mixed with the feed stream (1) to the water removal section [1].

The HF, HCl stream (5) which probably contains some water is separated in a second water removal section [3] to produce a mixture of HF and HCl (7) and anhydrous HF with some HCl (8). Stream (7) is fed into separation section [4] where HF leaves the bottom (10) and HCl leaves the top (9). Part of the HCl (12) can be recycled to the stripping section and stream (11) can be added to the HCl-capacity of the plant.

The simulation of the HCl-make up process went relatively well at the start, but caused some difficulties along the way. This was again due to Aspen convergence problems as explained in appendix S.
Figure 2.1 Battery limit of the cyclohexanol process

Figure 2.2 Extraction and separation section of the cyclohexanol process

Figure 2.3 Total overview of the cyclohexanol process
2.2.6 Cyclohexanol extraction process

This process bases on the extraction of HF (and HCl) using cyclohexanol as extractant. The different development stages of the process block diagram can be found in figures 2.1 to 2.3. The first figure can be considered as the block diagram that represents the battery limit. The final block diagram has been included in appendix B5. For the process partially use has been made of a patent by Halcon International (lit. P3). The patent describes that it is possible to extract HF from an aqueous stream by cyclohexanol or another organic compound containing an oxygen atom. The advantage of this process compared with the hexane process as mentioned in 2.2.1 is that the cyclohexanol can be applied as a liquid. This eliminates the explosion hazard and reduces energy requirements.

The extraction section [1] will remove nearly all the HF and the HCl from the waste water feed. The HF and HCl extracted in the cyclohexanol will leave (4) the top of this section, probably together with some water due to co-extraction. This stream is fed into an HF and HCl recovery section [2] to recover waterfree HCl and HF (6) from the cyclohexanol (7). The mixture of HF and HCl (6) will be separated in section [4]. HCl will leave this section by stream (10) and HF by stream (11).

The bottom stream (5) of the extraction section [1] will consist of a mixture of water and probably some co-extracted cyclohexanol. This water is separated from this co-extracted cyclohexanol in a water removal section [3]. The water stream (13) is discarded, the cyclohexanol is recycled (12) to the extraction column to function as extractant again. Stream (7), containing the remaining cyclohexanol, the co-extracted water and probably a remainder of the HF is fed into the cyclohexanol recovery section [5]. The cyclohexanol (9) is recycled to extraction column to be re-used as extractant. The co-extracted water and the probable remainder of the HF (8) are recycled to the feed.

The simulation in ASPEN will be described in more detail in chapter 3.

2.2.7 Extractive distillation process with sulphuric or phosphoric acid

The principle of this process is shifting the azeotrope by absorbing the water with sulphuric or phosphoric. This enables the HF to be distilled of. In figures 2.4 to 2.6 the different development stages of the process block diagram can be found. The final block diagram has been included in appendix B6. The waste water stream from the quench reactor is fed into the extraction section [1]. The other feed (3) into the section is the extractant (sulphuric acid; 90 wt% pure, lit. P1O). The sulphuric acid that is lost by purging/bleeding in the entire process is compensated for by feed stream 2. The recycle from section [3] is mixed up with this feed and led into the extraction section [1].

The sulphuric acid will absorb the water with only traces of HF in it (5). HF and HCl (4) leave the top of the extraction section to be fed to the HF/HCl separation section [2] to separate the HCl (6) from HF (7).

The liquid stream (5) from the extraction section [1] is lead into a H₂SO₄ recovery section [3]. The top product (8) is pure water with probably some traces of HF. The concentrated sulphuric acid (9) will be recycled and mixed with feed (2).

In stead of sulphuric acid, phosphoric acid can be used as well. The process block diagram will remain the same. Since phosphoric acid is a milder acid than sulphuric acid it is questionable whether the product specifications can be achieved. A short simulation in Aspen confirmed this. Therefore it is hereby stated that when this process is considered for further development sulphuric acid will be used as extractant.
Figure 2.4 Battery limit of the sulphuric acid process

Figure 2.5 Extraction and separation section of the sulphuric acid process

Figure 2.6 Total overview of the sulphuric acid process
2.3 Choice of the process routes

Since the process that has to be designed is not a very big and complicated one, the option to work out more than one process can be left open. This has the advantage that after a founded choice between the processes a good advice can be given about the best process to be built on the site.

The first stage of choosing the process(es) to make the preliminary plant design of is to narrow down the number of possibilities by eliminating processes. This can be done by a discarding processes that are not feasible in an industrial application or that cost too much time. As a guidance for discarding this processes technological insight, common sense and the opinion of experts in the field (see references) can be used. This supported by short basic Aspen simulations as described in paragraph 2.2 enable a founded choice between the processes. After careful consideration several processes have been put aside. These processes include the electrodialysis, the pressure swing and the hexane stripping process. The reasons for discarding these processes are already mentioned in 2.2 as negative points in the process descriptions. In brief this reasons were the following:

The hexane stripping process is easily replaced by the less hazardous and energy consuming cyclohexanol process. Therefore the cyclohexanol process is a more attractive option and the hexane process is discarded. The pressure swing process is not feasible because the small variations of the azeotrophic compositions with pressure and thus can never be applied in practice. The electrodialysis is discarded because of the limited time available. For the sake of completeness literature and references have been reported in the literature and reference lists.

This left three other processes: the sulphuric acid process, the cyclohexanol extraction process and the HCl-make up process. In these three processes more effort has been put into. All three processes have been simulated for several weeks with the computer program Aspen. The most promising results were achieved with the cyclohexanol and the sulphuric acid extraction process, as both processes reached the specifications given by DuPont. For the HCl process the DuPont product specifications were not achieved. Therefore this process was discarded as well.

The last two processes, the extractive distillation with sulphuric acid and the extraction with cyclohexanol, both are feasible processes for the recovery of the hydrogen fluoride from the feed stream. To be able to give a well founded advice about which process should be used to perform this separation both the two processes will be developed further. After this development a good choice between them can be made. This choice will be made in chapter eleven. Criteria for this choice will be complexity, operability, process conditions, feasibility of the technology, product and waste specifications, corrosiveness and construction materials, process control, finances, Aspen simulations and safety, health and environment aspects.

2.4 External specifications and boundary conditions

In this paragraph the external specifications and boundary conditions for the products, raw materials, utilities, location, surrounding restrictions and used technology will be mentioned.

2.4.1 Specifications of feeds and product streams

The product and feed streams of the designed processes have to meet several specifications. The specifications have been commissioned by DuPont in Dordrecht.

In table 2.2 the specification of the waste water feed stream are given:
Table 2.2 Specifications of the feed

<table>
<thead>
<tr>
<th>Component</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>75</td>
</tr>
<tr>
<td>HF</td>
<td>20</td>
</tr>
<tr>
<td>HCl</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2.3 gives the specifications for the product streams of HF and HCl in both the extraction processes:

Table 2.3 Quality standards produced HF and HCl

<table>
<thead>
<tr>
<th>Component</th>
<th>HF-product stream</th>
<th>HCl-product stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>&gt; 98 wt %</td>
<td>&lt; 10 PPM</td>
</tr>
<tr>
<td>HCl</td>
<td>&lt; 2 wt %</td>
<td>balance HCl</td>
</tr>
<tr>
<td>water</td>
<td>&lt; 100 PPM</td>
<td>&lt; 1 PPM</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>&lt; 50 PPM</td>
<td>&lt; 100 PB</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>&lt; 50 PPM</td>
<td>&lt; 100 PB</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Pressure bar(a)</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Phase</td>
<td>liquid</td>
<td>gas</td>
</tr>
</tbody>
</table>

The total loss of HF in the entire process must not exceed 1 kg/hr. The loss of HCl must be less than 50 kg/hr. So the production streams must be >199 kg/hr HF, 750 kg/hr water and 50 kg/hr HCl. The waste water stream must have a pressure of 3 bar(a) and a temperature of about 30 °C or lower.

2.4.2. Utility specifications

The specifications for the utilities that are used are given in table 2.4:

Table 2.4 Utilities

<table>
<thead>
<tr>
<th>Utility</th>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cool tower water</td>
<td>winter P, T</td>
<td>500 kPa(g), 17 °C</td>
</tr>
<tr>
<td></td>
<td>summer P, T</td>
<td>500 kPa(g), 24 °C</td>
</tr>
<tr>
<td>Coolant Brine (80wt% water, 20wt% methanol)</td>
<td>P, T</td>
<td>600 kPa(g), 5 °C</td>
</tr>
<tr>
<td>Coolant Brine (65wt% water, 35wt% methanol)</td>
<td>P, T</td>
<td>600 kPa(g), -15 °C</td>
</tr>
<tr>
<td>Coolant Brine (100wt% methylene-chloride)</td>
<td>P, T</td>
<td>900 kPa(g), -30 °C</td>
</tr>
<tr>
<td>Coolant Brine (100wt% methylene-chloride)</td>
<td>P, T</td>
<td>900 kPa(g), -45 °C</td>
</tr>
<tr>
<td>HP Steam</td>
<td>P, T</td>
<td>25 psi(g), 135 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75 psi(g), 165 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180 psi(g), 195 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250 psi(g), 215 °C</td>
</tr>
</tbody>
</table>
2.4.3 Location
The location of the process to be designed is the DuPont de Nemours site in Dordrecht, Holland, which is located on the industrial area "Staart" near the "Merwede". The intention is to built the designed plant near the thermal converter, which disposes the waste water streams, in order to limit the transport distance and therefore the amount of piping and control needed. The process will be built in existing still-house.

The industrial area is located next to a living area. The distance between the process to be built and the houses is approximately 500 M. The safety precautions taken by DuPont for the existing processes are so strict that no additional safety precautions have to be taken. The future process has no influence on the risk contours since these are heavily dominated by a spherical HF storage unit. Other aspects of safety health and environment are treated in chapters eight and nine.

2.4.4 List of components
In appendix A.3 the properties of all the components used are mentioned. The properties mentioned are boiling points, densities as a function of the temperature, MAC-values and so on are included.

2.4.5 Assumptions
To accomplish this preliminary plant design a number of assumptions have to be made, because not every detail can be taken into account. The most important assumptions are stated below:
- No electrolyte forming of the used components
- No electrolyte forming of the processes not simulated in the flowsheet
- ASPEN simulations done with the standard thermodynamics model for electrolytes (Elec-NRTL) unless stated otherwise
- Apparent component approach within the thermodynamic model
- No accumulation of impurities
- The packing of the columns not concerned in simulating the columns
- Neglectance of the heat balance the heat loss to surroundings in the pipes and equipment neglected for calculations
- Simulation based upon a steady state process, so start up and shut down not involved in the simulations
- For the calculations of the economic analysis, the process will run for 350 days in a year; standard in process industry
- No heat integration, because it is not useful to do. Further reasons will be given in paragraph 3.2.6.
3 Process structure and process flowsheet

In chapter 2 six different processes were discussed. Two processes were chosen to be worked out further into a basic design, namely the sulfuric acid and the cyclohexanol process. In this chapter the process structures and process flowsheets of the sulfuric acid process and the cyclohexanol process will be discussed. For both processes, the different sections will be discussed. Thereafter, the heat integration and the flowsheets will be described. The process flowsheets and process flow diagrams (PFD’s) can be found respectively in appendices C, D, J and K.

3.1 Thermodynamic model

Before the two processes can be described in detail, the thermo model should be specified. The binary system HF/water has got an azeotrope at 38 wt% HF at 1 bar and 25 C. For a two liquid phase system the Elec-NRTL-model (Non Random Two Liquid equation) can be used. In some cases the NRTL-HF model can be used, but this model causes a lot of problems during simulation (no convergence of columns and recycles). Therefore the standard NRTL-electrolyte model is preferred.

Systems containing HF, HCl and water are very difficult to describe with the standard Elec-NRTL-model. At this moment, a lot of research is done in the United States for describing this kind of systems. Dr. ir. V. de Leeuw from AspenTech in Brussels has been contacted to ask if it’s allowed to use the standard Aspen electrolyte NRTL-model for HF/HCl/water systems. His reaction (see also appendix S) was that it’s difficult to use the standard Aspen dataset for describing a ternary system.

Because we don’t have a dataset for the ternary system at the TU Delft (and the time was too short to import one from the States) all simulations have been executed with the standard Elec-NRTL-model.

If a recovery plant will be built in the future all simulations should be checked with the DuPont Aspen dataset and another ternary dataset (e.g. the one of Yunda Liu at AspenTech in the USA) The cyclohexanol extraction column has been simulated with the UNIQUAC-model (UNIversal QUAsi Chemical model) because it is the recommended model for liquid-liquid distribution coefficients which are needed in this column. Using this coefficients and the NRTL-model is not possible.

For the sake of completeness the electrolyte equilibrium equations are given:

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]  
\[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \]  
\[ \text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- \]  
\[ \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \]  

Equation 1.4 does not apply for the cyclohexanol process.
3.2 Sulphuric acid process structure

The process structure consist of three sections:

1. The extraction section with sulfuric acid
2. The HF/HCl separation section and
3. The water removal section.

First all sections will be described. After that briefly the flowsheet will be discussed.

3.2.1 The extractive distillation section.

In the patent of Kemira OY (Helsinki, Finland, lit. P10) there is briefly described that a mixture of HF and water under the azeotropic composition (< 38.5 wt% HF at 1 bar; 25°C) can be distilled by adding an acid like sulfuric or phosphoric acid. This procedure has been used for breaking the HF/water azeotrope. Two possible extractants are sulfuric acid and phosphoric acid. There is chosen for sulfuric acid as the extractant in the process, because it’s cheaper and during simulation the results with sulfuric acid corresponded better with the specifications given by DuPont.

3.2.1.1 Operation and conditions

The feed [102] is added to the extractive distillation column together with approximately 4000 kg/hr sulfuric acid (88% pure) [409]. The feed composition consists of 1000 kg/hr with 75 wt% water, 20 wt% HF and 5 wt% HCl. The main target for this column is the (total) recovery of anhydrous HF and HCl. This is accomplished by using a reboiler and no condenser in the distillation column. Thus, HF and HCl are leaving the top of the column as a gaseous mixtures [103] at a pressure of 150 kPa and a temperature of 42.0°C. The bottom product [104] contains all the water and sulfuric acid and in solution HF at specs 170 kPa and 130.2°C. Detailed specifications of the streams are included in appendices E and F.

3.2.2 The hydrogen fluoride/hydrogen chloride separation section

The HF/HCl separation section is needed to separate the HF from the HCl. The HF and HCl must be recovered water free (spec: <100 PPM water). Therefore the extractive distillation section have to perform optimal so that this specification could be achieved. Water in the product stream must be prevented at all time. For the exact stream compositions see appendices E and F.

3.2.2.1 Operation and conditions

First the HF/HCl product stream [103] is cooled and condensed to -24.2°C. All the HF and HCl is liquid then. For this option is chosen because a compressor is not needed now. Advantages for using a
pump in stead of a compressor are the lower costs (economic advantage) of the pump and the smaller flow in m³/hr. A small disadvantage is the lower temperature (-24°C).

Thereafter, the HF/HCl stream [207] is pumped into the separation column. The typical section I (will be described in 4.1.2) is used to prevent cavitiation in pump P2 and for keeping the product stream on the right temperature. After typical I, the HF will be distilled at a pressure of 1400 kPa in the HF/HCl separation section. The top product (HCl) has a temperature of -21.3°C and a pressure of 14 bar. The bottom product will be the HF at a pressure of 1450 kPa and 110°C. The HCl product stream will be heated and the HF product stream will be cooled and flashed to battery limit specifications (HCl: 1400 kPa; 15°C, HF: 300 kPa and 15°C).

### 3.2.2.2 Selection of the column
In §3.2.1.2 there is already described that two types of distillation columns can be used namely the sieve plate and packed columns. To be able to make a comparison and a choice both the types will sized.

### 3.2.3 The water removal section
The water removal section is the third main section in the sulfuric acid process. This unit operation is needed for removal of the water. Looking at the waterbalance, it’s obvious that 750 kg/hr water must leave the process. If that’s not the case, the water will accumulate in the process. Thus, the main target for the water removal column is to remove 750 kg/hr water from the acid stream [104].

#### 3.2.3.1 Operation and conditions
The bottom stream [104] (170 kPa; 130.2°C) of the extractive distillation section is fed to typical section 2. This is done to cool stream [104] to 30.1°C and reduce the pressure to 250 kPa. The top stream pressure [601] of the water removal column is just above atmospheric pressure (150 kPa) and has a temperature of 111.4°C. The bottom stream [602] (a solution of 88wt% sulfuric acid) has a pressure of 170 kPa and a temperature of 147.3°C and is fed to the typical III section. From this buffer vessel the sulfuric acid is recycled to the acid feed of the extraction section. The water product stream [603] is cooled to 15°C and transported to the DuPont waste water tank V8 on site. From this tank the water can be disposed.

#### 3.2.3.2 Selection of the column
In §3.2.1.2 and §3.2.2.2 there is already described that two types of distillation columns can be used namely the sieve plate and packed columns. To be able to make a comparison between both types, the dimensions of both columns were calculated.

### 3.2.4 The sulphuric acid flowsheet
The sulfuric acid Aspen flowsheet and Process Flow Diagram can be respectively found in appendix C and D. The 20 wt% HF feed [101; 20°C, 200 kPa] is fed to the extraction column C1 together with 4000 kg/hr the sulfuric acid [409]. The top product (water free HF and HCl op C1 is condensed and cooled in E1 to -24.2°C and fed to typical I. From the typical I section the HF/HCl stream is pumped with P2 (1400 kPa) to the HF/HCl separation column C2. The top product of this column [501] is HCl (water- and HF-free). The HCl-product stream [503; 49,948 kg/hr] is heated to 15°C and the HF-product stream [505; 199,325 kg/hr] is cooled to 15°C.

The bottom stream of the extraction column [104] is fed to typical section II. There this stream is cooled with cooler E4 to 30.1°C. The pressure is of this acid stream is increased to 250 kPa, because
the water removal column is operating at just above atmospheric pressure. Stream [307] from typical section II is fed to the water removal column. There 750 kg/hr water is distilled from the acid/water mixture. The water product stream (0.1 wt% HF, 1.3 PPM HCl, < 1 ppb acid) is cooled to 15 °C and can be disposed. The acid stream [602] is fed to typical section III and cooled from 147.3 °C to 30.1 °C. From typical III the acid is recycled [409] to the extraction column.

3.2.5 Start up procedures
With the design of a plant the start up procedures have to be taken into account. With the start up the process is first operated with only the extractant in C1 and C3 (acid recycle is running well). When this system is running sufficiently, the real feed is added slowly. At first there will be water in the top stream so the top stream will not be sent to the HF/HCl separator, because the construction material of column C3 cannot handle the corrosive circumstances. The stream will collected and transported to a buffer tank, until the water concentration is low enough to feed it to column C2. The pressure will be built up by a total reflux of the top stream of C2 until the pressure has reached the operating level. Then the HCl can be split of and can leave the column as a product stream.

The storage tanks must be so large, that they can contain the volume of the entire process. The way that the dimensions of these vessels are calculated can be found in chapter 4.1.2. The mixture in the storage tank can be recycled to the feed of the process to ensure that no hazardous material has to be drained. The storage tanks are an essential part of the process to guarantee, that start up procedures will go smoothly.

3.2.6 The heat integration
The heat integration will be discussed in this paragraph. Energy saving plays an important role in the design of a process. Implementation of heat integration of heat reduces costs and fossil fuels. In the next paragraphs an overview of the heated or cooled streams are given for both the sulfuric acid and the cyclohexanol process.

However for this process specifying the heat integration is not useful for several reasons:
- The saving in energy and money is not very large, because the throughput of the processes is too small.
- With heat integration the complexity of the system will increase very much.
- This process is part of a waste gas treatment and it will be more useful to do the heat integration with the thermal converter instead of doing it for the HF recovery section alone.
- In this stage of the designing of a not yet existing process heat integration is not a priority: when a PID will be made, heat integration is one of the points of attention.

To recognize the importance of heat integration a summary of the different streams has been made and an advice will be given which streams can be heat integrated with each other for a more detailed design of the process.

In table 3.1 an overview of the streams through the heat exchangers are displayed. Cooling took place by water and brine of diverse temperatures, and heating is done with high pressure steam of diverse pressures and temperatures.
Table 3.1 Overview of the heated/cooled streams in the sulfuric acid process

<table>
<thead>
<tr>
<th>Stream</th>
<th>heating/cooling</th>
<th>( T_{in} ) (K)</th>
<th>( T_{out} ) (K)</th>
<th>( Q ) (kWatt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>404</td>
<td>cooling</td>
<td>303.3</td>
<td>280.2</td>
<td>-434.5</td>
</tr>
<tr>
<td>103</td>
<td>cooling</td>
<td>315.2</td>
<td>249.0</td>
<td>-30.9</td>
</tr>
<tr>
<td>C1 reboiler</td>
<td>heating</td>
<td>403.3</td>
<td>408.2</td>
<td>228.9</td>
</tr>
<tr>
<td>204</td>
<td>cooling</td>
<td>251.0</td>
<td>249.0</td>
<td>-0.9</td>
</tr>
<tr>
<td>304</td>
<td>cooling</td>
<td>303.3</td>
<td>280.2</td>
<td>-294.4</td>
</tr>
<tr>
<td>C2 condenser</td>
<td>cooling</td>
<td>251.9</td>
<td>249.2</td>
<td>-4.8</td>
</tr>
<tr>
<td>C2 reboiler</td>
<td>heating</td>
<td>383.2</td>
<td>388.2</td>
<td>26.2</td>
</tr>
<tr>
<td>502</td>
<td>cooling</td>
<td>383.2</td>
<td>288.2</td>
<td>-12.3</td>
</tr>
<tr>
<td>C3 condenser</td>
<td>cooling</td>
<td>384.6</td>
<td>381.2</td>
<td>1400.1</td>
</tr>
<tr>
<td>C3 reboiler</td>
<td>heating</td>
<td>420.5</td>
<td>425.2</td>
<td>2091.4</td>
</tr>
<tr>
<td>501</td>
<td>heating</td>
<td>251.9</td>
<td>288.2</td>
<td>0.5</td>
</tr>
<tr>
<td>601</td>
<td>cooling</td>
<td>384.6</td>
<td>288.2</td>
<td>-84.5</td>
</tr>
</tbody>
</table>

\[ Q_{net} = 2884.8 \]

During the design of this process, a different brine or high pressure steam has been used for each stream. No combination of diverse cooling or heating flows took place. When the process should be designed in more detail, more attention should be paid to whether an already used stream of brine or HP steam could be further used at a different place in the process. The temperatures or required pressures of the already used streams could be easily altered by reducing or increasing its pressure to the wished specifications. So it is very important to be able to couple the streams with different heat contents in such a way that energy will be saved. Just in case no direct heat from the process is available utilities are needed to cool or heat the process.

According to the temperatures the following stream can be heat integrated with each other: 501 with 502

### 3.3 The cyclohexanol process structure

The cyclohexanol process consists of five main sections:

1. The extraction section
2. The hydrogen fluoride and hydrogen chloride recovery section
3. The water removal section
4. The cyclohexanol recovery section
5. The hydrogen fluoride/hydrogen chloride separation section

The process will be discussed per section. For each section the main principle, the operation and conditions will be explained. Also the presence and the necessarily of each unit will be accounted for. While discussing the process references will be made to the ASPEN flowsheet and the Process Flow Diagram (PFD) in appendices J and K respectively. The mass-flows and stream-compositions can be found in appendix M. All the pressures and temperatures stated in this appendix are taken from ASPEN. All the equipment and stream numbers refer to the PFD unless stated otherwise. At the end of the chapter a review will be given for the total process.

#### 3.3.1 The extraction section

In this section hydrogen fluoride and hydrogen chloride in the feed should be extracted into the extracting medium. In this section the separation between water and the extractant should be perfect. Below the extractant selection, the possible equipment and the conditions will be discussed.
3.3.1.1 Selection of the extractant

In the designed process cyclohexanol has been chosen as extractant. As mentioned in lit. P3 other oxygen containing hydrocarbons can also be used. Three properties (lit. DC1 and DC2, ASPEN) were used to compare the different extractants:

1. Distribution coefficient
2. Water miscibility
3. Boiling point

A high distribution coefficient is preferable because less extractant is needed. A higher water miscibility leads to more co-extraction of water in the extractant stream and vice versa. This co-extraction is not preferable since the co-extracted water and extractant have to be removed later on in the process. This can be done either by a relative cheap decanter or by a more expensive distillation column. The boiling point, has its influence in this distillation column. Since always some water miscibility is present the distillation column is the best option and guarantees a complete separation.

When the distillation column is used it is preferable to have an extractant with a boiling point lower than that of water. A lower boiling point avoids an energy intensive and thus expensive process in which water has to removed by distillation over the top. On the other hand a relative higher boiling point is preferable if the mass flow of water in the stream to be separated is much less than that of the extractant. In this situation the heat that has to be put in the process is less than in the situation described before. Whether a right choice is made concerning the boiling point of the extractant apparently correlates with its water miscibility.

Although some extractants possess a higher distribution coefficient cyclohexanol is preferred. This because of the fact that most of the better extractants also have a better water miscibility. As will appear later in the process, the boiling point of cyclohexanol does not form any problem. Another reason for choosing for cyclohexanol is the fact that it is a cheap and industrial easy available chemical. Combined with the fact that for the cyclohexanol process references can be made to lit. P3, cyclohexanol seems a good choice as the extractant.

Since the whole design of the section and process is based on the extractive and physical properties (appendix A) of the extractant, pilot-plant tests should be performed to measure the performance of the different extractant.

3.3.1.2 Column types

The feed and the cyclohexanol have to be contacted with each other in order to extract the HF. As extraction column two different column types can be used:

1. Sieve plate column
2. Rotating disc contactor
3. Packed column
4. Spray tower

The types mentioned here will be treated and sized in chapter 4.2.1.

3.3.1.3 Operation and conditions

The feed [100] to the extraction column C1 consists of 75wt% water, 20wt% hydrogen fluoride and 5wt% hydrogen chloride and has a flow of 1000 kg/hr. Via typical 1 (see 3.4) in which the feed has been mixed with recycle stream [60] the feed enters the top of the extraction column. In this column the HF and HCl are extracted with clean cyclohexanol which flows counter-currently through the column. According to lit. P3 the mass-flow of cyclohexanol should be about 6 times the mass-flow of HF. In this design the flow is set to about 2000 kg/hr to insure a complete extraction of the HF. This
saves an extra extraction column. The extraction efficiencies for both HF and HCl at this flowrate are then almost 100%.

As according to lit. DC1 and DC2 the temperature has in this situation no influence on the distribution coefficients, there is no need to operate the column at elevated temperature. This also implies that the feed streams don’t have to be preheated as well. Therefore the column is operated at 20°C. The pressure in this column is 500 kPa. The reason for this pressure is that this pressure guarantees a spontaneous flow throughout the process without any supporting pumps. The conditions of the feed and the cyclohexanol stream then both are required to be 500 kPa and 20°C.

The top stream [301] consists of cyclohexanol, the extracted HF and HCl and some co-extracted water. The bottom stream [302] consists of water and some cyclohexanol. For the exact figures see also the stream reports in appendix M. The co-extraction of water in cyclohexanol and vice versa undoubtedly gives rise for the need of two extra or at least one water/cyclohexanol separation column. The ASPEN simulation gives about the same results as are achieved in lit. P3 which improves the reliability.

### 3.3.2 The hydrogen fluoride and hydrogen chloride recovery section

This section is needed because the hydrogen fluoride and hydrogen chloride need to be recovered from the cyclohexanol. The HF and HCl should be recovered water free. This because of the product specifications which demand HF with a water content lower than 100 PPM. According to lit. P3 this should be possible if the column is operated at the appropriate conditions. The ASPEN simulation comes up with the same result. Underneath the selection, conditions and the construction material of the column will be treated. For the exact stream compositions we refer to appendix M.

#### 3.3.2.1 Column types

The distillation of HF and HCl out of a mixture comprising mainly cyclohexanol and some water can be done in two types of columns:

1. Sieve plate column
2. Packed bed column

To be able to make a choice between the columns and to verify the expectation that the packed bed column performs better and requires a lower column height both the columns will be sized. An advantage of the packed bed column at small diameters is the relative easy construction.

#### 3.3.2.2 Operation and conditions

The column [C2] is fed with the stream [301] cyclohexanol containing the extracted HF and HCl and some co-extracted water coming from the extraction column [C1]. According to lit. P3 the column should be able to produce water free HF and HCl when the column operates at the appropriate conditions. Following the ASPEN simulations these conditions should be 51.6°C and 350 kPa in the top of the column and 156.6°C and 380 kPa in the bottom. The found temperatures are dependent on the chosen pressure. According to the ASPEN simulations the pressure had no significant influence on the performance of the column when kept between 5 and 1 bar. Because of this the pressure has been adjusted in such a way that a spontaneous flow in the process can be maintained, namely a top pressure of 350 kPa. This with in mind that a pressure drop of about 1 bar is enough to guarantee this spontaneous flow. The top product stream [401] consists of water free HF and HCl. The bottom stream [402] contains the cyclohexanol and water and part of the HF. The mass-flow HF in this stream is more than the waste water restrictions allow, so another separation step will be necessary to recycle this HF. Also a separation step for the produced HF and HCl will be needed.
3.3.3 The water removal section
This section is needed because somewhere in the process water has to be removed. If not, water will accumulate and disturb the process. Since this is the only section in the process where water removal takes place all the water that enters the process via the feed from the thermal converter should be removed. The section is placed directly after the extraction column and is fed with the depleted water stream. In the following paragraphs the selection of the column type and the operation of the section will be discussed.

3.3.3.1 Column types
For this separation two column types can be used:
- Sieve plate column
- Packed bed column
For the reasons as mentioned in paragraph 3.3.2.1 both the columns will be sized.

3.3.3.2 Operation and conditions
The feed to the section is the bottom stream [302] of the extraction column and consists of water, a few cyclohexanol and a trace HF. For the exact compositions see appendix M. The stream is at 20 °C and 500 kPa. The bottom stream [502] is pure water containing the trace HF which is at 134.7 °C and 310 kPa. Via cooler [E11] this stream is brought to the specified product temperature after which it is led into the existing waste acid drum [V8]. The top exit stream [501] of the column is at 280 kPa and 128.6 °C and consists of water and all the cyclohexanol. To minimize the cyclohexanol consumption this stream is recycled to typical 2 (see 3.4) and is thus brought back into the extraction column [C1]. The pressure in the column again has no significant influence in the range 400 - 100 kPa so the pressure is chosen in such a way that a spontaneous flow can be maintained. The pressure is thus chosen to be 280 kPa in the top, with a total pressure drop of 30 kPa.

3.3.4 The cyclohexanol recovery section
In this section the excess of hydrogen fluoride present in the bottom stream of the HF/HCl recovery section needs to be recovered and then recycled to the extraction column. This because the amount of HF is higher than the amount which can be disposed of. The main task for this section however is the recovery of the cyclohexanol in which the HF is taken up. In this way a closed recycle loop can be established for the cyclohexanol, which minimizes the cyclohexanol consumption and reduces operating costs.

Separating the feed stream to this column and then recycle both the product streams to the same extraction column gives rise to questions about the usefulness of this column. Simulations have proven however that this column is needed to be able to operate the extraction column in its current configuration in an effective way. 
A combination of this column with column [C3] and thus a combination of stream [302] and [402] is impossible since else a part of the hydrogen fluoride still present in the cyclohexanol in stream [402] would be taken up in the exit water stream. This would cause the HF content of this waste stream to be above specifications. In the following paragraphs the column type and the column conditions will be discussed.

3.3.4.1 Selection of the column
Again two columns are appropriate to perform this separation. Namely:
- Sieve plate column
- Packed bed column
As mentioned in 3.3.2.1 both the columns will be sized.
3.3.4.2 Operation and conditions
The feed comes from the bottom of the HF/HCl recovery column and consists of cyclohexanol, a bit of water and a considerable amount of hydrogen fluoride. The pressure and temperature of the stream are 380 kPa and 156.6 °C respectively. Since the pressure in this column has no considerable influence between 380 and 100 kPa the pressure is set to 250 kPa to guarantee a spontaneous flow throughout the process. If the bottom temperature due to this pressure is too high considering the available steam or column material strength then this temperature can easily be lowered by reducing the pressure.

At the chosen pressure the top stream has a pressure and temperature of 250 kPa and 95.6 °C respectively. It mainly comprises HF, water and cyclohexanol. The stream is recycled to typical 1 and thus via the extraction column brought back into the process. The bottom stream is at 200.1 °C and 280 kPa and consists of pure cyclohexanol. Via typical 2 this stream is recycled to the extraction column as well.

3.3.5 Hydrogen fluoride / hydrogen chloride separation section
This section is needed to separate the hydrogen fluoride and hydrogen chloride recovered from the extractant cyclohexanol. This separation should be performed in such a way that the HF and the HCl product stream achieve the product specifications specified in chapter 2.3. The HF/HCl distillation is a proven technology process and should easily achieve the required results. Since a low water content, lower than 100 PPM and 1 PPM for HF and HCl respectively, is required in both the products the performance of column C2 is essential for the final product quality.

3.3.5.1 Selection of the column
As mentioned before two column types will be dimensioned, namely the sieve plate and the packed bed column.

3.3.5.2 Operation and conditions
The feed to this section is the top-product stream of column [C2]. This stream is condensed completely by cooling it to 7 °C in cooler [E7] and then fed to typical 3 (see 3.4). In this typical the fluid is brought to a pressure of 1430 kPa. The reason for first condensing and then pressurizing the gaseous HF/HCl stream and not directly compressing the gas is that this saves a very expensive compressor. The high pressure has the advantage that a higher temperature in the top of column C5, the HF/HCl separation column, can be maintained. This reduces the need for very cold brine.

After the typical the feed to the column is at 1430 kPa and 8.7 °C. This higher temperature is caused by the pump duty. The top-product of the column consists of pure HCl which is at 1400 kPa and -21.3 °C. Since product specifications demand a temperature of 15 °C the stream is brought to this temperature with heater E11. The HCl leaves the process by product stream. The bottom product stream of the column consists of pure HF with a water content lower than 1 PPB. The stream is at 1450 kPa and 109.8 °C. The stream is brought to the product specifications of 15 °C and 300 kPa by cooler E15 and valve V7. The HF leaves the process by product stream [805].

3.3.6 The overall process
Above all the different sections and their position and function in the process were described. In brief the integration of these units to form the total process was pointed out. In this paragraph the remaining facts about this integration concerning the simulation and optimization will be mentioned.
3.3.6.1 The ASPEN simulation
After the function and position of the different units were established the process was simulated. First all the sections and columns have been simulated individual. After optimization of each single unit the process was linked together. This was done with open recycles and excluding the typicals. The exclusion of the typicals was done because of the fact that each typical would bring in an extra recycle and make the simulation more complex. Therefore these typicals have been simulated apart.

After the process simulation converged the recycles were closed one by one to finally obtain a converging flowsheet. This flowsheet is included in appendix J. The simulation resulted in the mass- and heat-balance taken up in Appendice L and M. All the heat-duties and other optimized unit specifications needed for the sizing done in chapter 4 are taken from this simulation and the simulation of the typicals. Therefore the exact input used for the simulation and the results are taken up in that chapter.

3.3.6.2 The Process Flow Diagram
After completing the simulation of the process the process flow diagram (PFD) was developed. In this diagram the complete process, including typicals, is represented. This representation includes the definitive stream numbers, temperatures, pressures and process control loops. The control loops will be accounted for in chapter 7. The PFD itself is included in appendix K.

3.4 Start up procedures
The start up of the cyclohexanol will go similar to the start up of the sulfuric acid process. With the start up the process is first operated with only the extractant in C1, C2 and C4 (cyclohexanol recycle is running well). When this system is running sufficiently, the real feed is added slowly. At first there will be water in the top stream of C2 so the top stream will not be sent to the HF/HCl separator, because the construction material of column C5 cannot handle the corrosive circumstances. The stream will collected and transported to a buffer tank, until the water concentration is low enough to feed it to column C5. The pressure will be built up by a total reflux of the top stream of C2 until the pressure has reached the operating level. Then the HCl can be split of and can leave the column as a product stream. By adding the feed C3 will be fed slowly and after the column is running well with the right specifications the cyclohexanol can also be recycled to column C1. The water will be collected in the waste water storage tank from which it can be drained.

3.5 The heat integration
In table 3.2 an overview of the streams through the heat exchangers of the cyclohexanol process are displayed. Also here cooling took place by water and brine of diverse temperatures, and heating by HP steam of diverse pressures. Also for this process more attention need to be paid to the integration of the diverse streams. When this is possible, less utilities available at DuPont are needed and as a consequence the costs will be reduced.

Looking at the temperatures the suggestion is made to heat integrate the following streams with each other:

- Condenser C3 with reboiler C5
- 801 with 803

As already mentioned in paragraph 3.2.6, to integrate these streams with each other is a rough estimate. The heat integration can be worked out in greater detail by using the guidelines from chapter 8 from lit. HE18.
Table 3.2 Overview of the heated/cooled streams in the cyclohexanol process

<table>
<thead>
<tr>
<th>Stream</th>
<th>heating/cooling</th>
<th>$T_{in}$ (K)</th>
<th>$T_{out}$ (K)</th>
<th>$Q$ (kWatt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>cooling</td>
<td>293.2</td>
<td>280.2</td>
<td>-70.5</td>
</tr>
<tr>
<td>204</td>
<td>cooling</td>
<td>312.0</td>
<td>280.2</td>
<td>-119.5</td>
</tr>
<tr>
<td>C2 condenser</td>
<td>cooling</td>
<td>324.8</td>
<td>321.2</td>
<td>-30.5</td>
</tr>
<tr>
<td>C2 reboiler</td>
<td>heating</td>
<td>429.8</td>
<td>435.2</td>
<td>310.4</td>
</tr>
<tr>
<td>C3 condenser</td>
<td>cooling</td>
<td>401.8</td>
<td>393.2</td>
<td>-334.3</td>
</tr>
<tr>
<td>C3 reboiler</td>
<td>heating</td>
<td>407.9</td>
<td>415.2</td>
<td>463.9</td>
</tr>
<tr>
<td>401</td>
<td>cooling</td>
<td>324.8</td>
<td>302.2</td>
<td>-26.4</td>
</tr>
<tr>
<td>703</td>
<td>cooling</td>
<td>281.9</td>
<td>280.2</td>
<td>-0.8</td>
</tr>
<tr>
<td>C4 condenser</td>
<td>cooling</td>
<td>304.2</td>
<td>297.2</td>
<td>-596.0</td>
</tr>
<tr>
<td>C4 reboiler</td>
<td>heating</td>
<td>473.3</td>
<td>476.2</td>
<td>588.7</td>
</tr>
<tr>
<td>502</td>
<td>cooling</td>
<td>407.9</td>
<td>288.2</td>
<td>-104.9</td>
</tr>
<tr>
<td>C5 condenser</td>
<td>cooling</td>
<td>251.9</td>
<td>249.2</td>
<td>-4.7</td>
</tr>
<tr>
<td>C5 reboiler</td>
<td>heating</td>
<td>383.0</td>
<td>388.7</td>
<td>21.4</td>
</tr>
<tr>
<td>801</td>
<td>heating</td>
<td>251.9</td>
<td>288.2</td>
<td>0.5</td>
</tr>
<tr>
<td>803</td>
<td>cooling</td>
<td>383.0</td>
<td>288.2</td>
<td>-12.3</td>
</tr>
</tbody>
</table>

$Q_{net}=85.0$
4 Process flowsheeting and equipment calculations

In the next paragraphs the equipment calculations of all the unit operations are made. For both the sulfuric acid and the cyclohexanol process this is done for the columns, the heat exchangers and the pumps.

4.1 The sulphuric acid process flowsheet

In this paragraph the equipment calculations are done for the sulfuric acid process.

4.1.1 Separation columns

The dimensions of all the columns of the H₂SO₄ and the cyclohexanol process are calculated. The extractive distillation column in the H₂SO₄ process is a distillation column with two feeds and no direct condenser. The other two columns are regular distillation columns with one feed, a condenser and a reboiler.

The calculations have been done for both sieve plate and packed columns. This has been done to get a good insight in the difference between different types of columns. After deliberation with DuPont we decided to use packed columns. The reason why packed columns are used as a standard at DuPont are stated below:

- When D < 0.6 m a packed column is preferred
- More robust
- Smaller
- Can better handle a fluctuation in the feed
- Better turndown ratio
- Less foaming
- Less corrosion problems
- Better performance

4.1.1.1 Packed columns

After deliberation we decided to use packed columns for the distillation units in both the processes. DuPont provided information of different types of packing from the supplier of packings, Norton Chemical Process Products Corporation. Part of the information was a computer program, The Packed Tower Design Program, to calculate the tower diameter and area, when the liquid and vapour loadings, together with the type of packing were given as input. From lit. DP12 a procedure was given to calculate the dimensions of the column in a relative simple way. This method is used to calculate the dimensions of all the columns.

4.1.1.1.1 Dimensions

The diameter and the area of the columns were calculated by the Packed Tower design Program (Lit. DP13). The HETP was calculated with a brochure from Norton. Each column consists of at least two packed beds with a distributor plate between the beds. The height of a packed bed must not exceed 3 m, because otherwise channeling might occur. The height of the total packing is calculated by multiplying the number of stages, obtained from the Aspen simulations with the HETP.
4.1.1.1.2 Packing of the columns

The packing for the different columns were recommended by DuPont. The types of packing are sufficient for these distillations. In table 4.2 the packings per column can be found together with their construction materials.

Table 4.1 Packing specifications

<table>
<thead>
<tr>
<th>Column</th>
<th>Section</th>
<th>Type of packing</th>
<th>Construction material</th>
<th>Size [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 extraction column</td>
<td>rectifying stripping</td>
<td>super-intalox</td>
<td>Polypropylene</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>super-intalox</td>
<td>Tefzel</td>
<td>16</td>
</tr>
<tr>
<td>C2 HF/HCl separation</td>
<td>all sections</td>
<td>IMTP No. 15</td>
<td>Carbon steel</td>
<td>13</td>
</tr>
<tr>
<td>C3 water/sulphuric acid</td>
<td>rectifying stripping</td>
<td>super-intalox</td>
<td>Tefzel</td>
<td>25</td>
</tr>
<tr>
<td>separation</td>
<td></td>
<td>super-intalox</td>
<td>Ceramic</td>
<td>25</td>
</tr>
</tbody>
</table>

The density, the active area and the packing factor, taken from lit. HE10, table 11.3, can also be found in appendix G1 for all the types of packing. With the porosity, which is given by Norton, the weight of the packed beds can be calculated.

4.1.1.1.3 Calculation of the HETP, the Norton variant

From the Intalox High-performance Separation Systems guide some other properties can be calculated. This has been done for all the packed columns of the sulphuric acid process. The flow parameter of a column can be calculated with next equation:

\[ X = \frac{L_w}{V_w} \sqrt{\frac{\rho_v}{\rho_i}} \]  

(4.1)

The \( L_w \) and the \( V_w \) have been taken from the Aspen simulation.

From a figure in which the capacity factor has been plotted as a function of the flow parameter, the capacity factor can be determined for different types of packing. With this capacity factor \( C_0 \) the efficient capacity \( C_w \) can be calculated with

\[ C_w = C_0 \left[ \frac{\sigma}{20} \right]^{0.16} \left[ \frac{\mu}{0.2} \right]^{-0.11} \]  

(4.2)

\( \sigma \) and \( \mu \) have to be estimated; \( \sigma = 19 \) and \( \mu = 0.1 \).

The capacity of a column is calculated with the following equation:

\[ C_s = V_w \sqrt{\frac{\rho_v}{\rho_i - \rho_g}} \]  

(4.3)

With the capacity and a coefficient varying for different types of packing the pressure drop in mm per meter of packed height can be calculated. Multiplied with the total packing height this gives the total pressure drop for the total column. With another equation the System Base HETP can be calculated:

\[ \text{System Base HETP} = A \left[ \frac{\sigma}{20} \right]^{-0.16} (1.78)^k \]  

(4.4)
This equation is valid for $\mu \leq 0.4c_p$ (lit. DP 12). The coefficient $A$ varies with the different types of packings. The HETP calculated this way, has been used to calculate the packing height. The ratio of the capacity and the efficient capacity is called the capacity rating.

In appendix G1 the equations to calculate the dimensions have been put into the spreadsheets. For several equations from lit. DP12 the maximal vapour rate, the density of the vapour and the maximum allowable vapour velocity have to be known. The maximum vapour rate can be taken from the Aspen reports, the vapour density can be calculated with the ideal gas law, because the pressure is not too high:

$$\frac{n}{V} = \frac{P}{RT} \tag{4.5}$$

The factor $n/V$ has to be multiplied by the average molar weight and so the density in kg/m$^3$ can be calculated. The height of the column can be calculated by adding the heights of the different parts of the columns:

$$H_{\text{total}} = H_{\text{condenser}} + H_{\text{reboiler}} + H_{\text{skirt}} + H_{\text{packing, section}} \tag{4.6}$$

The height of the condenser and reboiler are about 15% of the packed section and the height of the skirt has been chosen on the basis of previous designs and design specifications of lit. HE11.

### Table 4.2 Dimensions of the packed columns of the sulphuric acid process

<table>
<thead>
<tr>
<th>Column</th>
<th>Type</th>
<th>Number of trays</th>
<th>Height [m]</th>
<th>Diameter [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>extractive distillation</td>
<td>10</td>
<td>7.41</td>
<td>0.20</td>
</tr>
<tr>
<td>C2</td>
<td>normal distillation</td>
<td>10</td>
<td>6.41</td>
<td>0.18</td>
</tr>
<tr>
<td>C3</td>
<td>normal distillation</td>
<td>10</td>
<td>7.41</td>
<td>0.55</td>
</tr>
</tbody>
</table>

#### 4.1.1.1.4 Wall thickness

The wall thickness of the distillation columns can be calculated with a relation for the design of thin-walled vessels under internal pressure. The wall thickness can be calculated with equation 13.39a from lit. HE11:

$$e = \frac{P_i * D_i}{2 \cdot f} \tag{4.7}$$

$J$ has to be estimated and represents the joint factor of the welds and $f$ is the design stress. $D_i$ is the diameter of the column and $P_i$ is the pressure in the column. For the HF-HCl separator carbon steel can be used. For the other distillation columns different materials have to be used. A Teflon-lined metal will be used. The metal will be stainless steel 316 and for that material the minimum wall thickness can be calculated.

#### 4.1.1.1.5 Minimum number of stages

With the Fenske equation the minimum number of stages can be calculated. The equation is:

$$N_{\text{min}} = \frac{\log \left[ \frac{x_{LK}}{x_{LK}} \right] \log \left[ \frac{x_{HK}}{x_{LK}} \right]}{\log \alpha_{LK}} \tag{4.8}$$
The relative volatility \( \alpha_{L,K} \) can be calculated by the next formula:

\[
\alpha_{L,K} = \frac{y_{L,K} x_{H,K}}{y_{H,K} x_{L,K}}
\]  

(4.9)

With all the formulas above the relevant properties of all the distillation columns have been calculated.

### 4.1.1.2 Sieve plate columns

The calculations for the sieve plate columns were based on the design rules stated in Coulson & Richardson's Chemical engineering vol. 6. The wall thickness and the minimum number of trays are calculated as is described in paragraph 4.1.1.4 and 4.1.1.5.

#### 4.1.1.2.1 Diameter and height

In appendix G2 a summary of the input and output parameters from the Aspen simulation for the all columns is given. For the following calculations these data are used. The column diameter, \( D_e \), can be calculated with:

\[
D_e = \sqrt{\frac{4V_w}{\pi \rho_v u_v}}
\]  

(4.10)

For this equation (lit. HE11) the maximal vapour rate, the density of the vapour and the maximum allowable vapour velocity have to be known. The maximum vapour rate can be taken from the Aspen reports, the vapour density can be calculated with the ideal gas law:

\[
n/\rho_v = \frac{P}{RT}
\]  

(4.11)

The factor \( n/\rho_v \) has to be multiplied by the average molar weight and so the density in kg/m\(^3\) can be calculated. The maximum allowable vapour velocity can be calculated after the plate spacing has been chosen. The \( u_v \) is:

\[
u_v = (-0.17 l_i^2 + 0.27 l_i - 0.047)[(\rho_i - \rho_v)/\rho_v]
\]  

(4.12)

The designing velocity that has been used for the dimensions of the columns is 0.8 of the velocity calculated with equation 4.3. The height of the column can be calculated by adding different parts of the columns:

\[
H_{\text{total}} = H_{\text{condenser}} + H_{\text{reboiler}} + H_{\text{skirt}} + H_{\text{tray section}}
\]  

(4.13)

The height of the condenser, reboiler are 15% of the tray section and the height of the skirt has been chosen on the basis of previous designs and design specifications of lit. HE11. The height of the tray section is the number of plates multiplied by the plate spacing where HETP is estimated. The results for all the columns of the sulfuric acid process are given in the table 4.3:

<table>
<thead>
<tr>
<th>Column</th>
<th>Type</th>
<th>Number of trays</th>
<th>Height</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>extractive distillation</td>
<td>10</td>
<td>13.2</td>
<td>1.35</td>
</tr>
<tr>
<td>C2</td>
<td>normal distillation</td>
<td>10</td>
<td>9.4</td>
<td>0.32</td>
</tr>
<tr>
<td>C3</td>
<td>normal distillation</td>
<td>10</td>
<td>7.7</td>
<td>1.02</td>
</tr>
</tbody>
</table>
The plates of all the distillation columns will be sieve plates, because this is the standard in the industry and it is sufficient for all the distillations. The operating area of the columns must be checked to ensure that no flooding, weeping, excessive entertainment, coning or downcomer back-up will occur.

4.1.1.2.2 Flooding
To ensure that no flooding will occur, the actual vapour velocity must not exceed the maximum vapour velocity. The maximum vapour velocity can be calculated by equation 4.5. $K_1$ is a constant which can be obtained by figure 11.27 of lit. HE 11. $K_1$ is dependent of the flowfactor $X$, which can be calculated with equation 4.1. When the surface tension is different from 0.02, $K_1$ has to be corrected. When the plate active area is different from 0.10, $K_1$ has to be corrected for that as well.

$$u_f = K_1 \sqrt{\frac{\rho_l - \rho_v}{\rho_v}} \quad (4.14)$$

4.1.1.2.3 Entertainment
When the actual vapor velocity and the maximum vapor velocity are known, the percentage of flooding can be calculated. With this percentage and the flow factor from equation 4.6 the fractional entertainment $\psi$ can be determined with figure 11.29 from lit. HE11. This fractional entertainment has to be less than 0.1 to ensure that no entertainment will occur.

4.1.1.2.4 Weeping
To make sure that no liquid will leak through the holes, the actual vapour velocity through the holes of a sieve plate must be larger than the minimum vapour velocity, which can be calculated with equation 4.7:

$$u_h = \frac{[K_2 - 0.90(25.4 - d_h)]}{\sqrt{\rho_v}} \quad (4.15)$$

To determine the factor $K_2$ the weir height and the weir crest have to be known. With these two parameters the factor $K_2$ can be determined with figure 11.30 from lit. HE11. The weir height is 50 mm, which is standard in the industry and is recommended by lit. HE11. The weir crest can be calculated with equation 4.8:

$$h_{we} = 750 \left( \frac{L_w}{\rho \cdot l_w} \right)^{2/3} \quad (4.16)$$

$l_w$ is the weir length and for which a factor of 0.77 of the diameter can be taken as a good initial use according to lit. HE11. That means that the area of the downcomer will be 12% of the total cross area of the distillation column. The height of the weir has been chosen to be 50 mm. With the weir crest and the weir height the factor $K_2$ can be determined by figure 11.30. The vapour velocity calculated by equation 4.14 must be corrected for the area of the holes in the plates to yield the vapour velocity through the holes. Now the vapour velocity through the holes can be compared with the minimum vapour velocity. The hole diameter of the sieve plates has been chosen to be 5 mm, this is recommended by lit. HE11.
Figure 4.1 Schematic overview of a Diabon® heat exchanger
4.1.2 The typicals
The typicals, see fig. 7.1, are a construction of a buffer vessel, a pump, and a cooler. This construction is used for several reasons. The stream is cooled to prevent cavitation in the pump. It is also used as a buffer for the feed to a distillation column. By using this buffer vessel in this manner, disturbances in the feed to a distillation column will be damped out, which is inherently safe, because the fluctuations in the feed of the distillation column will be flattened out, insuring an optimal performance of the distillation column. The magnitude of the vessels are so large, that they can also be used for start-up procedures.

The magnitude of the vessels for the typicals can be calculated by:

\[ V = \phi_v \cdot H_t \]  
(4.17)

\( H_t \) is the hold up-time and is set to 25 min for the vessels in typical 1 and 2. The volume of the storage vessel for the storage vessel for the extraction agent is:

\[ V = V_{\text{typicals}} + V_{\text{equipment}} + V_{\text{piping}} \]  
(4.18)

The magnitude of this vessel is so large, because all the process streams have to be stored if an accident occurs. The volume of the piping has been taken as 50% of the volume of the typicals and the equipment. The vessels in typical 3 must contain the total volume of the process including piping, for it must be a buffer vessel for the extractant. The volumes of the vessels can be found in appendix G.3 for the sulphuric acid process.

4.1.3 The valves
The valves have been placed in the process to decrease the pressure, where necessary.

4.1.4 The heat exchangers
In the following paragraph the heat-transfer equipment will be discussed for the H\(_2\)SO\(_4\) process. See for a Diabon heat exchanger figure 4.1

4.1.4.1 Introduction
The transfer of heat to and from process fluids is an essential part of most chemical processes. The most commonly used type of heat-transfer equipment is the ubiquitous shell and tube heat exchanger. Shell and tube exchangers are used for all applications (lit. HE11). Exchangers in which a process fluid is heated or cooled by a plant service stream are referred to as heaters and coolers.

4.1.4.2 Basic design procedure and theory
The general equation for heat transfer across a surface is:

\[ Q = U \cdot A \cdot \Delta T_m \]  
(4.19)

The prime objective in the design of an exchanger is to determine the surface area required for the specified duty (rate of heat transfer) using the temperature differences available. The overall coefficient is the reciprocal of the overall resistance to heat transfer, which is the sum of several individual resistance's. For heat exchange across a typical heat-exchanger tube the relationship between overall coefficient and the individual coefficients, which are the reciprocals of the individual resistance's, is given by:
The magnitude of the individual coefficients will depend on the nature of the heat-transfer process, on the physical properties of the fluids, on the fluid flow-rates and on the physical arrangement of the heat-transfer surface. As the physical layout of the exchanger cannot be determined until the area is known the design of an exchanger is of necessity a trial and error procedure. The steps in a typical design procedure are given below:

Define the duty: heat-transfer, fluid flow-rates, temperatures.
1. Collect the fluid physical properties required: density, viscosity, thermal conductivity.
2. Decide on the type of exchanger to be used.
3. Select a trial value for the overall coefficient, U (C&R).
4. Calculate the mean temperature difference, \( \Delta T_m \).
5. Calculate the area required from equation (4.19).
6. Decide the exchanger layout.
7. Calculate the individual coefficients.
8. Calculate the overall coefficient and compare with the trial value. If the calculated value differs significantly from the estimated value, substitute the calculated for the estimated value and return to step 6.
9. Calculate the exchanger pressure drop; if unsatisfactory return to steps 7 or 4 or 3, in that order of preference.
10. Optimise the design: repeat steps 4 to 10, as necessary, to determine the cheapest exchanger that will satisfy the duty. Usually this will be the one with the smallest area.

One heat-exchanger is designed completely according this procedure. Only the global surface areas are determined for the rest of the heat-exchangers by making a rough estimate of the overall coefficient, U. See appendix H7. The utilities used, in the exchangers, reboilers and condensers, for heat-transfer are mentioned in chapter I.

4.1.4.3 Detailed design of heat-exchanger E1 of the H₂SO₄-process
1. The heat duty, Q, is derived from Aspen. The process-stream of HF and HCl is cooled from 42 °C to -24.2 °C with brine of -30 °C (100wt% methylenechloride CH₂Cl₂). The brine is heated to -25 °C.
2. Density, viscosity and thermal conductivity were collected from Perry, C&R and Physical Transport Phenomenon (lit. HE6).
3. The type of heat-exchanger to be used is a "internal floating head with clamp ring". This type is not suitable for graphite heat exchangers. This type of heat-exchangers are more versatile than fixed head and U-tube exchangers. They are suitable for high-temperature differentials and, as the tubes can be rotated from end to end and the bundle removed, easier to clean and can be used for fouling liquids. Disadvantages are that this type is more expensive and that the clearance between the outermost tubes in the bundle and the shell must be made greater than in the fixed and U-tubes designs to accommodate the floating-head flange, allowing fluid to bypass the tubes. The clamp ring (split flange design) is used to reduce the clearance needed. There will always be a danger of leakage occurring from the internal flanges in these floating head designs. In the external floating head designs, the floating-head joint is located outside the shell, and the shell sealed with a sliding gland joint employing a stuffing box. Because of the danger of leaks through the gland, the shell-side pressure in this type is usually limited to about 20 bar, and flammable or toxic materials should not be used on the shell side.
4. A trial value for the overall coefficient, U, for the HF/HCl and brine fluids is estimated by table 12.1 C&R (lit. HE11).
5. The logarithmic mean temperature was calculated and corrected with a correction factor, F, to give \( \Delta T_m \). The correction factor is given by:
\[
F_t = \frac{\sqrt{(R^2 + 1) \ln \left( \frac{1 - S}{1 - RS} \right)}}{(R - 1) \ln \left( \frac{2 - S[R + 1 - \sqrt{(R^2 + 1)}]}{2 - S[R + 1 + \sqrt{(R^2 + 1)}]} \right)}
\]

This deviation is given by Kern and can be used for any exchanger with an even number of tube passes. The temperature difference is calculated for a heat-exchanger with one shell pass and two tube passes.

6. The area required is calculated from equation (4.19).

7. For the tube dimensions are chosen a tube inside diameter, \(d_i\), of 16 mm, an outside diameter, \(d_o\), of 20 mm and tube length 7.32 m. Small diameters (16 to 25 mm) are preferred for most duties, as they will give more compact, and therefore cheaper, exchangers. For a given surface area, the use of long tubes will reduce the shell diameter; which will generally result in a lower cost exchanger, particularly for high shell pressures. The tube pattern is triangular. Triangular and rotated square patterns give higher heat-transfer rates, but at the expense of a higher pressure drop than the square pattern. The recommended tube pitch (distance between tube centers) is 1.25 times the tube outside diameter. With this layout the outside tube surface, number of tubes, bundle diameter and the shell diameter are calculated. The material used for the tubes will be impregnated (Teflon, PVDF) graphite because the process stream and the utilities used are corrosive. The shell of the heat-exchanger can be made of stainless steel.

8. The tube side coefficient is calculated according to Kern’s method and the shell side coefficient according to Bell’s method (lit. HE11). Fouling coefficients of the fluids used are estimated according to table 12.2 (lit. HE11) and amount 5000 (W/m² K).

9. The overall coefficient is calculated by equation (4.20) and compared with the initial estimation for \(U\). In the beginning these values differed too much, so the calculated \(U\) was substituted in the estimated value for \(U\) and returned was to step 6, the final calculated value of \(U\) was 31 W/m² K with an estimation of 50 W/m² K.

10. The pressure drop over the tube was calculated for two tube passes. The pressure drop can be increased by increasing the number of tube passes. The pressure drop over the shell-side can be calculated according to Bell’s method. This pressure drop was reduced by increasing the baffle pitch to 60% of the shell diameter.

11. Optimisation of the design took place by choosing among others the right \(U\), number of tube passes, tube layout etc. The cheapest exchanger that will satisfy the duty will be the one with the smallest area.

### 4.1.5 The pumps

In this section the pumps will be discussed

#### 4.1.5.1 Introduction

For the pumping of liquids or gases from one vessel to another or through long pipes, some form of mechanical pump is usually employed. The energy required by the pump will depend on the height through which the fluid is raised, the pressure required on delivery, the length and diameter of the pipe, the rate of flow, together with the physical properties of the fluid, particularly its viscosity and density.

Because of the wide variety of requirements, many different types are in use including centrifugal, piston, gear, screw and peristaltic pumps, though in the chemical and petroleum industries the centrifugal type is often the most important.
4.1.5.2 Pumping equipment for liquids
The two main forms are the positive displacement type and centrifugal pumps. In the former, the volume of liquid delivered is directly related to the displacement of the piston and therefore increases directly with speed and is not appreciably influenced by the pressure. In this group are the reciprocating piston pump and the rotary gear pump, both of which are commonly used for delivery against high pressures and where nearly constant delivery rates are required. The centrifugal type depends on giving the liquid a high kinetic energy which is then converted as efficiently as possible into pressure energy.

The following factors influence the choice of pump for a particular operation:
- The quantity of liquid to be handled
- The head against which the liquid is to be pumped
- The nature of the liquid to be pumped
- The nature of the power supply

4.1.5.3 Centrifugal pumps
The centrifugal pump is by far the most widely used type in the chemical and petroleum industries. It will pump liquids with very wide ranging properties and suspensions with a high solids content including, and may be constructed from a very wide range of corrosion resistant materials. The whole pump casing may be constructed from plastics such as polypropylene or it may be fitted with a corrosion-resistant lining. Because it operates at high speed, it may be directly coupled to an electric motor and it will give a high flow rate for its size. The advantages and disadvantages of the centrifugal pump are:

Main advantages:
- Simple in construction, so it can be made in a wide range of materials.
- No valves present.
- Operates at high speed, in general, the higher the speed the smaller the pump and motor for a given duty.
- It gives a steady delivery.
- Maintenance costs are lower than for any other type of pump.
- No damage is done to the pump if the delivery line becomes blocked, provided it is not run in this condition for a prolonged period.
- It is much smaller than other pumps of equal capacity.
- Liquids containing high proportions of suspended solids are readily handled.

Main disadvantages:
- The single-stage pump will not develop a high pressure. It is generally better to use very high speeds in order to reduce the number of stages required.
- It operates at a high efficiency over only a limited range of conditions: this applies especially to turbine pumps.
- It is not usually self-priming.
- Very viscous liquids cannot be handled efficiently.

4.1.5.4 The design of the centrifugal pump P1 of the H₂SO₄ process
The properties of the inlet and outlet stream of P1 are mentioned in appendix H3 and in the specification form for pumps (appendix H8). The power required for pumping an incompressible fluid is given by:
The pump's efficiency can be estimated according to fig. 10.62 from lit HE10. The efficiency of centrifugal pumps depends on their size. The difference between the power calculated in theory and in practice is this efficiency factor.

The pump is designed to bring the inlet stream of 2 bar to a pressure of 3 bar. Pressure loss over the pipes is neglected because the layout of the plant needed not to be determined for this FVO assignment. To make a proper estimate of the in- and outlet diameter of the pump it is necessary to estimate the pipe's diameter first. This diameter can be calculated according to 2:

\[
d = 293 \cdot (\Phi_v \cdot \rho)^{0.53} \cdot \rho^{-0.37}
\]  

Equation (4.2) leads to a diameter of 11.6 mm: according to this a nominal diameter for the lift- and discharge line has been set to 15 mm.

The centrifugal pump which can handle such \( \Phi_v \) and \( \Delta P \) is a single-stage centrifugal pump, with 1450 rpm. Working pressure is 1 bar (safety margin) and no mechanical seals are applied. Other construction details and materials are mentioned in the specification form of a centrifugal pump.

### 4.1.6 The ASPEN simulation

Each piece of equipment used in the sulfuric acid process has been simulated in the ASPEN Plus simulation package version 9.02. For this simulation the correct input parameters need to be supplied. In this chapter a short survey will be given of the number and the kind of the used parameters of each piece of equipment. For the exact input parameters we refer to appendix C2.

RADFRAC models were used to simulate the columns. The reason to use the RADFRAC columns is that many parameters can be given as an input and the model is the most reliable and gives the best results. Each column used in the sulfuric acid process has been simulated. For the simulation itself it does not matter whether the column is a packed bed or a sieve plate column. This because of the fact that the simulation program works with the number of equilibrium stages which is the basis for final calculations concerning the sized of the columns.

For a correct simulation of the columns the correct input parameters need to be supplied. Among others these parameters concern the number of stages, the reflux ratio or a correlated flow, the distillate to feed ratio or a correlated flow, the pressure and the temperature. A good and initial estimation for these parameters can either be obtained by making rough calculations based on basic design rules and physical properties, either by technological insight and experience. After the initial estimation the parameters can be optimized and fine-tuned by continuously adjusting these parameters and comparing the results with the desired output. The main results of the simulation are the mass- and heat-balances presented in appendix E. Also the heat duties from the reboilers and condensers, if present, follow from these simulations.

For each heat exchanger other than column-reboiler or column-condenser used in the process the input parameters are quite obvious. Two parameters have to be given out of the final temperature, final pressure or final vapor fraction to specify the exit stream of the exchanger. Again the used parameters are reported in appendix C2. The simulation results in the heat-duty of the coolers and heaters. Together with the mass-flows this duty forms the bases for the sizing of the exchanger.
Since for the simulation of the valves the same simulation-model is used as for the heat-exchangers, the same parameters have to be entered here. For the simulation of the pumps only the end-pressure needs no be specified. Again this is a quite obvious parameter. The input parameters used for the four pumps are mentioned in appendix C2.

The optimization for the results of the ASPEN simulations have been done by viewing the content of the different components in the product streams and readjusting the inputs of the different separators. This was done until the specifications given in the assignment (appendix A2) were achieved, while keeping an eye on the available utilities.

4.1.7 Construction materials
The choice for a construction material is a function of a few parameters:
- the pressure of a unit operation
- the temperature of a unit operation
- the corrosiveness of the medium in the unit operation

In the sulphuric acid process no extreme conditions concerning pressure and temperature occur. Therefore no special properties on the field of material strength are required. The aggressive environment caused by the presence of HF, HCl and H2SO4 in combination with water though requires corrosion resistant materials. Especially the presence of HF in the concentration range 20% till 80%, which occurs quite often in this process, has a negative influence on common construction materials like carbon and stainless steel. Thus HF resistant materials should be used. Since these materials are often expensive or not available the industrial practice is to use a plastic lining like Teflon or PVDF (poly-vinylidene-fluoride) on a carrier material like steel. If hardly no water is present the mixture is much less corrosive. In this case plain carbon steel or stainless steel can be used and no lining is required. For a brief review of material properties and prices see appendix A6, taken from lit. HE11. For all the stainless steel mentioned in this paragraph stainless steel 316 is used for its higher corrosion resistance.

Two columns (C1 and C3) of the sulfuric acid process operate at conditions in which the combination of hydrogen fluoride, acids and water occurs. These columns should therefore be constructed with Teflon lined stainless steel 316. The remaining column, C2, is operated at low temperatures. In this column the separation of HF and HCl is performed and practically no water is present. Because of the absence of water the column can be built of cold resistant carbon steel. The construction materials of the columns mentioned above are used for both the sieve plate and the packed bed columns.

The packing material of the packed columns is adjusted its the circumstances as well. In column C1 polypropene super-intalox and Tefzel super-intalox packings are used. Both these materials possess the required corrosion-resistance. The polypropene can be used in the rectifying section because of the lower temperature in this section. Due to the higher temperature in the stripping section the heat-resistant tefzel must be used there.

In column C2 carbon steel IMTP packings are used. This because the less corrosive circumstances in this column do not require special materials. In column C3 again corrosive circumstances are present. The temperatures are slightly higher than in column C1, so tefzel and ceramic super-intalox packings are used in the rectifying and stripping section respectively.

The heat-exchangers in the sulfuric acid process also have to deal with corrosive circumstances. Since the corrosive mixture is mostly led through the tube-side of the heat-exchanger only the tube-side is affected. Because a high heat-transfer coefficient is desired a Teflon or other plastic lining can’t be used. This is due to the low transfer coefficients these materials possess. A good alternative can be found in graphite which is a chemical inert and conducting construction material. To raise the
corrosion resistance the graphite is impregnated with Teflon. This is the construction material for the tube-side. The shell-side however is not submitted to corrosive materials and can be constructed of stainless steel. This stainless steel also protects the vulnerable graphite tube-side.

The pumps of the sulfuric acid all are subjected to corrosive circumstances and are therefore constructed of PVDF (poly-vinylidene-fluoride) lined steel, a common pump construction material for corrosive solutions.

The vessels in the typicals are constructed of the same material as the column following after this typical. Thus vessels 3 and 5 are constructed of Teflon lined stainless steel and vessel 1 of cold resistant carbon steel.

To insure process safety, control and continuity all the heat-exchangers and the rotating equipment will be manufactured of the construction materials described above, although some of them might be manufactured of a cheaper material due to less corrosive circumstances. This insures that no damage to this equipment is done when a more corrosive fluid than the design specs flows through. This for example during start-up, shutdown, accidents or any other cause. To reduce costs column C2 and vessel V1 are constructed of the cheaper cold resistant carbon steel. Extraordinary circumstances are less likely here due to the buffer-function of this equipment. A summary of the construction materials is given in table 4.4.

Table 4.4 Construction materials used in the sulfuric acid process

<table>
<thead>
<tr>
<th>Equipment number</th>
<th>Construction material</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Teflon lined stainless steel</td>
</tr>
<tr>
<td>C1 packings (rect / strip)</td>
<td>Polypropene / tefzel (super-intalox)</td>
</tr>
<tr>
<td>C2</td>
<td>Cold resistant carbon steel</td>
</tr>
<tr>
<td>C2 packings (rect / strip)</td>
<td>Carbon steel (IMTP)</td>
</tr>
<tr>
<td>C3</td>
<td>Teflon lined stainless steel</td>
</tr>
<tr>
<td>C3 packings (rect / strip)</td>
<td>Tefzel / ceramic (super-intalox)</td>
</tr>
<tr>
<td>Exchangers E1 till E12 (tube / shell)</td>
<td>Teflon impregnated graphite / stainless steel</td>
</tr>
<tr>
<td>Pumps</td>
<td>PVDF lined steel</td>
</tr>
<tr>
<td>Vessel 1</td>
<td>Cold resistant carbon steel</td>
</tr>
<tr>
<td>Vessels 3 and 5</td>
<td>Teflon lined stainless steel</td>
</tr>
</tbody>
</table>

4.2 The cyclohexanol process flowsheet

In appendix N1, N2 and N3 the equipment calculations of all the columns for the cyclohexanol process can be found.

4.2.1 The extraction column

An important parameter for the design of an extraction column is the contact time of the feed and the extractant in the column (can be handled with diameter and height). An extraction process has got advantages above e.g. distillation because the maintenance is low and the process is automatically and simple. Next to that temperature and pressure are mild.

\[\text{hold-up of an extraction column is virtually zero!}\]
In the industry two types of extraction columns are used: columns with a centrifugal force and the columns based on gravity. Possible columns for HF recovery with an organic extractant are
1. sieve plate columns
2. rotating disc columns
3. packed columns.
4. a spray tower

Spray towers are not used frequently any more, because the efficiency is low and a maximal of 5 equilibrium steps could be achieved. Next to that a lot of energy is lost (negative economic cost aspect). A packed column is better than a spray tower, because the packing corrects the phase contact and reduces back mixing. Problems of packed extraction columns (liquid-liquid) are disturbances in the packing structure (direct consequence for the separation) and up-scaling can cause major problems. For liquid-liquid extraction columns the best option is to use a sieve plate column or a rotating disk column. In this report both columns are worked out further and the best performing column will chosen to implanted in the process.

4.2.1.1 The sieve plate column
In sieve plate columns the phase contact occurs in steps. If the light phase is dispersed then flows this phase through the plates. Drops occur and are rising through the continuous phase. On the underside of the upper laying plate the light phase coalescence’s and flows again through the holes of the plates.

For the design of the sieve plate column the next procedure is used (see also lit. HE16):

1. Choose diameter of the hole in the plate 0.003 m < dh < 0.008 m
2. Determine the velocity through the hole with the Weber number (We = 4.33 Eo 0.36) Important is that: 0.15 < uh < 0.35.
3. Calculate Sauter diameter dp of the drop.
4. Calculate the active surface Ah of the holes.
5. Determine the downcomer surface Ad.
6. Calculate the column diameter DT (DT = V(Ah/T))
7. Calculate the velocity Us and holdup h of the dispersed phase
8. Choose the distance Ht between two plates (Ht ~ 0.40 m)
9. Determine the plate efficiency (Murphee plate efficiency) Em
10. Determine overall column efficiency

For the design of the liquid-liquid extraction sieve plate column, there is the possibility to choose the extractant (cyclohexanol) as the continuous or dispersed phase. The option with the best H/D will be chosen. For all detailed formulas see lit HE16.

The specific calculations of the design of the sieve plate column are included in appendix N1.1. The most important results (number of trays, height, diameter) of the column calculations are given in table 4.5.

**Table 4.5 Results of the design of the sieve plate and rotating disc column**

<table>
<thead>
<tr>
<th>Column</th>
<th>Cont phase</th>
<th>Type</th>
<th>Number of trays</th>
<th>Height</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve plate</td>
<td>cyclohexanol</td>
<td>liquid-liquid</td>
<td>30</td>
<td>15.98</td>
<td>0.37</td>
</tr>
<tr>
<td>Sieve plate</td>
<td>water (feed)</td>
<td>liquid-liquid</td>
<td>30</td>
<td>23.29</td>
<td>0.35</td>
</tr>
</tbody>
</table>
4.2.1.1 The rotating disc column

The Rotating Disk Contactor (RDC) is given in figure 4.2. The column consists of a series of compartments above each other, separated by stator rings. In every compartment there is a disk which is driven by a vertical axis. On both sides of the column a grating is installed to reduce turbulences, caused by the rotating of the discs. In table 4.6 the ratio of the diameter and height in a RDC is given.

Table 4.6 Ratio of dimensions in a RDC

<table>
<thead>
<tr>
<th>Specification</th>
<th>0.06-0.3</th>
<th>0.3-1.0</th>
<th>&gt; 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [m]</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>S/D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R/D</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>H/D</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The main design calculations are based on the column diameter (capacity) and the column height (separation). The diameter and height are related to the droplet size. This size can be influenced by the number of revolutions $N$ of the rotordiscs.

For the design of the RDC the next procedure is used (see also lit. HE16):
1. Choose droplet size $d_p$ ($d_p = 0.002m$)
2. Calculate powersupply
3. Determine the holdup $h$, calculate the slipvelocity and column diameter
4. Calculate number of revolutions with Reynolds-relation
5. Determine overall height of mass transfer stage $HT_{TU}$
6. Determine $HDU_{oc}$ out of the axial dispersion
7. Calculate the height of a theoretical stage $H_{ETS}$ form $HT_{TU}$ and $HDU_{oc}$
8. Calculate the height of the column.

As mentioned above, for liquid-liquid systems, there is the possibility to choose the extractant (cyclohexanol) as the continuous or the dispersed phase. The option with the best $H/D$ will be chosen. For all detailed calculations and formulas see lit HE16.

The specific calculations (spreadsheet) of the design of the RDC column are included in appendix N1.2. The most important results (number of trays, height, diameter) of the column calculations are given in table 4.7.

Table 4.7 Results of the design of the rotating disc column

<table>
<thead>
<tr>
<th>Column</th>
<th>Cont phase</th>
<th>Type</th>
<th>Number of trays</th>
<th>Height</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotating Disc Contactor</td>
<td>cyclohexanol</td>
<td>liquid-liquid</td>
<td>30</td>
<td>4.10</td>
<td>0.28</td>
</tr>
<tr>
<td>Rotating Disc Contactor</td>
<td>water (feed)</td>
<td>liquid-liquid</td>
<td>30</td>
<td>3.78</td>
<td>0.28</td>
</tr>
</tbody>
</table>

It is obvious from table 4.5 and 4.7 that the calculated column height lower is with a RDC column (economic aspect). Besides that, the column performance of a RDC is better than the performance of a sieve plate column (separation aspect). Therefore, a Rotating Disc Contactor column will be used as an extraction column in the cyclohexanol process. The continuous phase will be the feed (water phase) and the dispersed phase the cyclohexanol.

4.2.2 The packed columns

The dimensions of the packed columns were calculated with the relative simple Norton procedure and the results can be found in table 4.8. The spreadsheet in which the dimensions are calculated can be found in appendix N2. For one column, the HF/HCl-separator, the HETP was calculated with the
Figure 4.3 Examples of a gas-injection and a simple packing support
more elaborate designing procedure stated in lit HE10. In the next paragraph that procedure will be
described. The details for the calculations can be found in appendix N2.1.

4.2.2.1 Calculation of the HETP, the Coulson & Richardson variant
The HETP can also be calculated according to the more conventional methods, which are well
described in lit. HE10. This has been done for the HF/HCl separator.
The equation to calculate the HETP is:

\[
HETP = H_{OG} \cdot \ln(m \cdot \frac{G_m}{L_m}) / (m \cdot \frac{G_m}{L_m} - 1)
\]

(4.22)

\(m\) can be determined from the xy-diagram of HF and HCl. In this equation \(H_{OG}\) is the height of an
overall gas-phase transfer unit. To calculate the \(H_{OG}\) the \(H_G\), the height of a gas-phase transfer unit,
and the \(H_L\), the height of a liquid transfer unit, have to be known. The \(H_G\) and the \(H_L\) are according to
Cornell’s method a function of the Schmidt number of the gas and the liquid phase, the diameter of
the column, the height of a packed bed and three factors: \(K_3\), \(\psi_h\) and \(\phi_h\). These factors can be obtained
from figures 11.41, 11.42 and 11.43 from lit. HE10.

Cornell’s method can be used for Raschig rings and Berl saddles. The method and equations in
Coulson & Richardson are stated for Berl Saddles. The packing used for the column, that has been
calculated is the IMTP No. 15 packing. The mass transfer of the IMTP-packing is probably better,
than that of Berl saddles, but at least the magnitude of the \(H_G\) and the \(H_L\) can be determined.

The height of a packed bed has been calculated from an initial estimate for the HETP. By filling in
this packed bed height a different HETP was calculated. With an iterative procedure the packed bed
height and the HETP were brought into concurrence with each other. By multiplying the number of
gas-phase transfer units with the height of an overall gas-transfer unit, the estimate of the packed bed
height can be checked.

4.2.2.1.1 Flooding in packed columns
With the flow factor from equation 4.1 and the pressure drop per meter packing the factor \(K_4\) and the
factor \(K_4,\text{flooding}\) can be determined. By dividing these factors the percentage of flooding can be
calculated. The pressure drop per meter has been taken from the brochure of Norton, because in that
brochure the pressure drop per meter can be calculated as a function of the type of packing. Since the
Norton packing will be used, this is the most reliable method. After \(K_4\) has been determined the gas
mass flow-rate per unit column cross-sectional area, \(V_{w^*}\), can be calculated:

\[
V_{w^*} = \frac{K_4 \rho_M (\rho_f - \rho_M)}{13.1 F_r (\mu_f / \rho_f)^{0.1}}
\]

(4.23)

With this \(V_{w^*}\) the minimum area and with that the minimum diameter, that is required can be
calculated.

4.2.2.1.2 Packing support and liquid distributors
For the packing a wide spaced grid can be used to support the packing. A layer of larger packings can
be stacked on the grid to prevent the smaller packings to fall through the grid. An example of a gas-
injection and a simple packing support are given in fig 4.3.

Another option is to use a gas-injection packing support, which has a better gas distribution, but the
support is more expensive. There are two types of liquid distributors that can be used to redistribute
the liquid:
Figure 4.4 Picture of a weir through liquid distributor
The perforated pipe liquid distributor is more expensive than the weir through. The liquid distribution of a weir through liquid distributor is better. The dimensions of the packed columns for the cyclohexanol process inserted in Table 4.8. A picture of the weir through liquid distributor can be found in Figure 4.4.

**Table 4.8 Dimensions of the columns of the cyclohexanol process**

<table>
<thead>
<tr>
<th>Column</th>
<th>Type</th>
<th>Number of trays</th>
<th>Height</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>normal distillation</td>
<td>10</td>
<td>6.41</td>
<td>0.27</td>
</tr>
<tr>
<td>C3</td>
<td>normal distillation</td>
<td>12</td>
<td>7.49</td>
<td>0.21</td>
</tr>
<tr>
<td>C4</td>
<td>normal distillation</td>
<td>20</td>
<td>9.31</td>
<td>0.5</td>
</tr>
<tr>
<td>C5</td>
<td>normal distillation</td>
<td>10</td>
<td>5.88</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**4.2.3 The sieve plate columns**

The method to calculate the dimensions of the sieve plate columns is already described in paragraph 4.1.1.2. In Appendix N3 the results for the regular distillation columns can be found.

**Table 4.9 Dimensions of the sieve plate columns of the cyclohexanol process**

<table>
<thead>
<tr>
<th>Column</th>
<th>Type</th>
<th>Number of trays</th>
<th>Height</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>normal distillation</td>
<td>10</td>
<td>8.87</td>
<td>0.49</td>
</tr>
<tr>
<td>C3</td>
<td>normal distillation</td>
<td>12</td>
<td>10.86</td>
<td>0.34</td>
</tr>
<tr>
<td>C4</td>
<td>normal distillation</td>
<td>20</td>
<td>15.77</td>
<td>0.91</td>
</tr>
<tr>
<td>C5</td>
<td>normal distillation</td>
<td>10</td>
<td>8.87</td>
<td>0.28</td>
</tr>
</tbody>
</table>

**4.2.4 The typicals**

The volumes of the vessels in the typicals have been calculated in the same way as in the sulphuric acid process, which is described in 4.1.2. The dimensions of the vessels can be found in Appendix N.4.

**4.2.5 The heat exchangers**

In the following paragraph the heat-transfer equipment will be discussed for the Cyclohexanol process. For more detailed information about heat-transfer equipment, see 4.1.4. In Appendix O9 the specification form of heat exchanger E1 for the cyclohexanol process is given. Appendix O2 contains the total equipment list of heat exchangers. The utilities used, in the exchangers, reboilers and condensors, for heat-transfer are mentioned in Chapter 1.

**4.2.6 The pumps**

For more information about pumps in general and about the centrifugal pump in specific, see 4.1.5.

**4.2.6.1 The design of the centrifugal pump P1**

The properties of the in- and outlet stream of P1 are mentioned in Appendix O10 and in the specification form, Appendix O3. The power required for pumping an incompressible fluid is given by (4.22):
\[ P = \frac{\Delta P \cdot \Phi}{\eta_p} \]

The pump's efficiency can be estimated according to fig. 10.62 from lit. HE11. The efficiency of centrifugal pumps depends on their size. The difference between the power calculated in theory and in practice is this efficiency factor.

The pump is designed to bring the inlet stream of 2 bar to a pressure of 2.5 bar. Pressure loss over the pipes is neglected because the layout of the plant needed not to be determined for this FVO assignment.

To make a proper estimate of the in- and outlet diameter of the pump it is necessary to estimate the pipe's diameter first. This diameter can be calculated according to (4.23).

Equation (4.23) leads to a diameter of 11.6 mm: according to this a nominal diameter for the lift- and discharge line has been set to 15 mm. The centrifugal pump which can handle such \( \Phi \) and \( \Delta P \) is a single-stage centrifugal pump, with 1450 rpm. Working pressure is 1 bar (safety margin) and no mechanical seals are applied. Other construction details and materials are mentioned in the specification form of a centrifugal pump (appendix O3).

### 4.2.7 The ASPEN simulation

For the cyclohexanol process each piece of equipment has been simulated in the ASPEN simulation package. For this simulation correct input parameters are required. For simulated distillation columns, exchangers, valves and pumps the same parameters apply as described in 4.1.6 for the sulfuric acid process. The exact values of these parameters are included in appendix J2.

The only column with a parameter set different from the parameter sets used so far is the cyclohexanol extraction column. This extraction column has to be supplied with parameters concerning the expected top and bottom key component and a first estimation of the distribution coefficient. The first two parameters are quite obvious, the last estimation can be obtained from literature DC1 and DC2. This estimation consequently leads to the distribution coefficient as mentioned in appendix N1.1 and N1.2.

Since the whole process depends on this coefficient the ASPEN result was checked on its own consequence. In each situation the program returned to a consistent value. The further simulations are therefore reliable. The optimisation for the results of the ASPEN simulations have been done by viewing the content of the different components in the product streams (HF and HCl) and readjusting the parameters of the different separators. This was done until the specifications given in appendix A.1 were achieved.

### 4.2.8 Construction materials

For the cyclohexanol process the same requirements apply as for the sulfuric acid process when the combination of HF, HCl and water is concerned. The difference with the situation as described in paragraph 4.1.7 is that cyclohexanol is present as well. This however has no influence on the corrosion requirements of the construction materials. Since in columns C3 and C4 almost no HF is present and a less severe corrosion requirement exists, for the columns monel steel can be used in stead of Teflon lined stainless steel. This also avoids problems in column C4 in which the bottom temperature is too high for a Teflon lining. The construction materials for the cyclohexanol process are presented in table 4.10. The construction materials mentioned for the columns are suitable for all the possible column types. Packing materials are reported apart. For further detailed information we refer to paragraph 4.1.7.
Table 4.10  Construction materials of the cyclohexanol process

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Construction material</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Teflon lined stainless steel</td>
</tr>
<tr>
<td>C2</td>
<td>Teflon lined stainless steel</td>
</tr>
<tr>
<td>C2 packing (rectifying / stripping)</td>
<td>Tefzel / ceramic (super-intalox)</td>
</tr>
<tr>
<td>C3</td>
<td>Monel</td>
</tr>
<tr>
<td>C3 packing (rectifying / stripping)</td>
<td>Tefzel / ceramic (super-intalox)</td>
</tr>
<tr>
<td>C4</td>
<td>Monel</td>
</tr>
<tr>
<td>C4 packing (rectifying / stripping)</td>
<td>Tefzel / ceramic (super-intalox)</td>
</tr>
<tr>
<td>C5</td>
<td>Cold resistant carbon steel</td>
</tr>
<tr>
<td>C5 packing (rectifying / stripping)</td>
<td>Carbon steel (IMTP)</td>
</tr>
<tr>
<td>Heat exchangers E1 till E15 (tube / shell)</td>
<td>Teflon impregnated graphite / stainless steel</td>
</tr>
<tr>
<td>Pumps P1 till P4</td>
<td>PVDF lined stainless steel</td>
</tr>
<tr>
<td>Vessel 1 and 2</td>
<td>Teflon lined stainless steel</td>
</tr>
<tr>
<td>Vessel 5</td>
<td>Cold resistant stainless steel</td>
</tr>
</tbody>
</table>
5 Mass and energy balance

In this chapter the mass and energy balances of all the flows in the processes are described. The overall mass and heat balance is obtained from Aspen and calculated.

5.1 The mass balances

With the simulation program Aspen Plus the composition and enthalpy of every stream is calculated. The total flow of incoming components must be equal to the total flow of outgoing components. So in the overall mass balance these will not be found. In appendix E the mass and energy balances of the sulphuric acid process can be found. The stream numbers of the incoming and outgoing streams can be found in the PFD in appendix C. A summary of the mass balance is given in table 5.1:

Table 5.1 Summary of the mass balances of the H$_2$SO$_4$ process

<table>
<thead>
<tr>
<th>Component</th>
<th>HF [kg/hr]</th>
<th>HCl [kg/hr]</th>
<th>water [kg/hr]</th>
<th>H$_2$SO$_4$ [kg/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream No.</td>
<td>IN</td>
<td>OUT</td>
<td>IN</td>
<td>OUT</td>
</tr>
<tr>
<td>101: Feed</td>
<td>200</td>
<td>50</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>503: Product stream HCl</td>
<td>0.001</td>
<td>49.947</td>
<td></td>
<td></td>
</tr>
<tr>
<td>505: Product stream HF</td>
<td>199.269</td>
<td>0.052</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>701: Waste water stream</td>
<td>0.730</td>
<td>0.001</td>
<td>749.996</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>200</td>
<td>200</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

The same overview can be given for the cyclohexanol extraction process. The table of the mass and energy balances can be found in appendix L. To view where the streams are situated the stream numbers can be found in the PFD in appendix J. A summary of the cyclohexanol process mass balance is given in table 5.2:

Table 5.2 Summary of the mass balances of the cyclohexanol process

<table>
<thead>
<tr>
<th>Component</th>
<th>HF [kg/hr]</th>
<th>HCl [kg/hr]</th>
<th>water [kg/hr]</th>
<th>cyclohexanol [kg/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream No.</td>
<td>IN</td>
<td>OUT</td>
<td>IN</td>
<td>OUT</td>
</tr>
<tr>
<td>100: Feed</td>
<td>200</td>
<td>50</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>802: Product stream HCl</td>
<td></td>
<td></td>
<td></td>
<td>49.581</td>
</tr>
<tr>
<td>805: Product stream HF</td>
<td>199.280</td>
<td>0.419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>504: Waste water stream</td>
<td>0.720</td>
<td></td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>200</td>
<td>200</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>
5.2 The energy balances

The energy balances for the sulfuric acid and the cyclohexanol process can be found in appendix E and appendix L respectively. The data for the stream enthalpies and heat duties have been taken from the ASPEN-reports. A summary of the heat-balances is given in tables 5.3 and 5.4. The heat duties can be calculated by multiplying the specific heat with the temperature difference. The heat duties will be used for the sizing of the heat equipment.

Table 5.3 Energy balance for the sulfuric acid process

<table>
<thead>
<tr>
<th>Stream enthalpies</th>
<th>Overall heat-balance (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
</tr>
<tr>
<td>Feed stream [101]</td>
<td>-4213.4</td>
</tr>
<tr>
<td>Exit stream HCl [503]</td>
<td>-35.5</td>
</tr>
<tr>
<td>Exit stream HF [505]</td>
<td>-770.2</td>
</tr>
<tr>
<td>Exit stream H2O [701]</td>
<td>-3319.5</td>
</tr>
<tr>
<td><strong>Equipment</strong></td>
<td></td>
</tr>
<tr>
<td>Heat duty P1</td>
<td>0.0</td>
</tr>
<tr>
<td>Heat duty P2</td>
<td>1.2</td>
</tr>
<tr>
<td>Heat duty P3</td>
<td>1.1</td>
</tr>
<tr>
<td>Heat duty P4</td>
<td>1.2</td>
</tr>
<tr>
<td>Exchanger E1</td>
<td></td>
</tr>
<tr>
<td>Exchanger E2</td>
<td></td>
</tr>
<tr>
<td>Exchanger E3</td>
<td></td>
</tr>
<tr>
<td>Exchanger E4</td>
<td></td>
</tr>
<tr>
<td>Exchanger E5</td>
<td></td>
</tr>
<tr>
<td>Exchanger E6</td>
<td></td>
</tr>
<tr>
<td>Exchanger E7</td>
<td></td>
</tr>
<tr>
<td>Exchanger E8</td>
<td></td>
</tr>
<tr>
<td>Exchanger E9</td>
<td></td>
</tr>
<tr>
<td>Exchanger E10</td>
<td></td>
</tr>
<tr>
<td>Exchanger E11</td>
<td></td>
</tr>
<tr>
<td>Exchanger E12</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>-1862.9</td>
</tr>
</tbody>
</table>


Table 5.4 Energy balance for the cyclohexanol process

<table>
<thead>
<tr>
<th>Stream enthalpies</th>
<th>Overall heat-balance (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
</tr>
<tr>
<td>Exit stream HCl [802]</td>
<td>-370.5</td>
</tr>
<tr>
<td>Exit stream HF [805]</td>
<td>-3318.9</td>
</tr>
<tr>
<td>Exit stream H2O [504]</td>
<td>-2824.7</td>
</tr>
</tbody>
</table>

Equipment

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Heat duty P1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat duty P2</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Heat duty P3</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Heat duty P4</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Exchanger E1</td>
<td>70.5</td>
<td></td>
</tr>
<tr>
<td>Exchanger E2</td>
<td>119.5</td>
<td></td>
</tr>
<tr>
<td>Exchanger E3</td>
<td>30.5</td>
<td></td>
</tr>
<tr>
<td>Exchanger E4</td>
<td>310.4</td>
<td></td>
</tr>
<tr>
<td>Exchanger E5</td>
<td>334.3</td>
<td></td>
</tr>
<tr>
<td>Exchanger E6</td>
<td>463.9</td>
<td></td>
</tr>
<tr>
<td>Exchanger E7</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>Exchanger E8</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Exchanger E9</td>
<td>596</td>
<td></td>
</tr>
<tr>
<td>Exchanger E10</td>
<td>588.7</td>
<td></td>
</tr>
<tr>
<td>Exchanger E11</td>
<td>104.9</td>
<td></td>
</tr>
<tr>
<td>Exchanger E12</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Exchanger E13</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Exchanger E14</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>Exchanger E15</td>
<td>12.2</td>
<td></td>
</tr>
</tbody>
</table>
6 Specification of the equipment

6.1 The sulphuric acid process

In chapter 4 the manner in which the equipment has been designed has been stated. Each piece of equipment is specified in the equipment list in appendix H for the sulphuric acid process. For each type of process equipment a appendix has been made (appendices H.1 until H.3). The types of process equipment are:
- Columns and vessels
- Heat exchangers
- Pumps

The more detailed specification forms for the extractive distillation column, the HF/HCl separator, the water removal column, the heat exchanger E1 and the pump P1 can be found in appendices H4 until H8. The place in the flowsheet of the more detailed equipment can be found in appendix C.

6.2 The cyclohexanol process

The equipment lists for the cyclohexanol extraction process can be found in appendices O.1 until O.3. For this process the more detailed specification forms for the extraction column, the HF/HCl separation column, the water removal column, the heat exchanger E1 and the pump P1 can be found in appendices O.4 until O.7. The place in the flowsheet of the more detailed equipment can be found in appendix J.
In this chapter the main features of the process control loops will be described. Process control is necessary since the process will show disturbances in production rate and purity due to external influences and feed-fluctuations.

7.1 Introduction

For both the processes the objective of process control is to keep the production rate and the purity within given limits while preventing equipment from getting damaged. As mentioned before, this comes down to the complete separation of a feed with a flow varying around 1000 kg/h and with a composition of approximately 20wt% HF, 5wt% HCl and 75wt% water into its components. Since the feed can vary in flow and composition the production rate and purity have to be controlled.

While developing the control schemes to achieve this goal, a few restrictions and guidelines have to be taken into account. The main restriction is the degree of freedom present. In general this means that two independent control objectives can't be achieved by manipulating the same control variable. Thus in the final process control scheme each single control objective is controlled by manipulating one variable. Another guideline is to make as much as possible inherent safe control loops, in which occurring disturbances are damped out in a fast way and especially don't interact and strengthen each other. This is not directly recognizable in the current process control schemes, but has had it's influence in for example the position of equipment in the process and the construction of so called 'typicals' (7.2.4 / 7.3.6). See figure 7.1. The last condition to be satisfied was the avoidance of situations in which equipment could possibly be damaged.

7.2 Unit operations of the sulfuric acid process

In the next paragraphs the control loops of the different units used in the H₂SO₄ extractive distillation process will be described. Where necessary a link will be made to the overall control of this process and how this specific unit contributes to the overall control objective.

7.2.1 The extractive distillation column

In this column (C1) the feed is contacted with a proportional amount of H₂SO₄. In case of a lower feed-flow this amount has to be adjusted to the new situation. Thus a ratio controller has been applied. A second reason for this controller is the bottom temperature of the column. A relative higher flow of H₂SO₄ leads to a higher H₂SO₄ concentration in the bottom. As a result the boiling temperature rises. When this temperature becomes too high, the column construction material will be damaged. The ratio controller prevents this.

To prevent the situation in which the column runs dry due to a zero feed-flow and thus also a zero flow of H₂SO₄, a minimum feed-flow should be guaranteed. This can be achieved by putting in an extra water stream (not in process flow diagram) which takes over when the feed suddenly falls out.

The column is crucial for the product purity. Any water that leaves the column over the top of the column will lead to higher water content of the HF product stream. To act as soon as possible in the process, it's important to control the water content in the top stream. This is done by placing a fast analyzer (see 7.4) in the top stream and apply composition control. Since there is no condenser the condenser temperature and the reflux ratio can't be used as control variable. The variable to be used
Figure 7.1 The typical construction
is the setpoint of the $\text{H}_2\text{SO}_4$/feed ratio. A relative higher $\text{H}_2\text{SO}_4$ flow corresponds to a lower water content, so by small adjustments of the ratio the water content can be controlled.

- The top-pressure in the column is controlled by a valve in the top-stream.
- The temperature in the bottom of the column is kept constant by varying the steam flow through the reboiler. Since the required temperature is influenced by the $\text{H}_2\text{SO}_4$/feed ratio an intelligent or more advanced controller could be used.
- The liquid level in the column is, apart from the minimal flow control, controlled by the flow of the bottom-product.

### 7.2.2 The hydrogen fluoride/hydrogen chloride separation column

A fairly constant flow with constant temperature to this column (C2) is provided by typical 1 (see section 7.2.4). Since existing columns using proven technology achieve much better results than the specifications dictate, there is no need for an expensive analyser. Keeping the top and bottom temperature constant will ensure two product streams within specifications. Other control loops are:

1. The top temperature is controlled by the brine flow through the condenser.
2. The top-pressure is controlled by a valve in the top-stream.
3. The bottom temperature of the column is controlled by the steam-flow through the reboiler.
4. The liquid-level in the column is controlled by the bottom product flow.

### 7.2.3 The water removal column

Because of the waste water restrictions imposed by the local government, it's very important to be sure that no HF leaves the top of this column (C3). To control this, an analyzer should be installed. The analyzer can be used to control the composition of the waste water stream. This can be done by manipulating the reflux-ratio. Apart from this loop, the following control loops have been designed:

- The top-temperature is controlled by the coolant-flow through the condenser.
- The top-pressure is controlled by a valve in the top-outlet.
- The bottom-temperature is controlled by the steam-flow through the reboiler.
- The liquid level is controlled by the bottom-product flow.

### 7.2.4 The typicals

A typical consists of the following units: a vessel, a pump, a cooler and a valve. Typicals function as storage vessels with a small after-cooling or a larger cooling facility. Apart from damping by installed controllers the typicals damp out disturbances in flow, composition and temperature because of present vessels. In the $\text{H}_2\text{SO}_4$ process three typicals are present:

- typical 1: V1, P2, E3, V2
- typical 2: V3, P3, E4, V4
- typical 3: V5, P4, E5, V6

The process control is the same for each typical. The pressure in the storage vessel is controlled by a valve in the gas-vent. The pump which removes fluid from the vessel has a low-level and a high-level interlock to prevent damage to the pump. The temperature of the recycle stream is controlled by the coolant flow through the heat exchanger. Since the recycle and the product stream have a nearly constant ratio, this temperature control suffices to control the temperature in the vessel and thus the temperature of the exit stream. The pressure of the recycle stream is controlled by a valve. Finally the level in the vessel controller is controlled by the exit flow. This controller must not be tuned too tight, since a fairly constant flow to the next column is convenient.
7.2.5 Remaining control equipment
The feed is determined by the exit flow of the thermal converter which is out of the battery limit. Thus it is fixed and can't be controlled.

- The temperature of the streams leaving the remaining heat exchangers (e.g. E1, E7, E9 and E11) is controlled by the flow of the coolant or heating medium through this heat exchanger.
- The exit pressure of the valves is controlled by the valve position
- The level in the waste acid tank (V8) is controlled by the flow of the exit stream

7.3 Unit operations of the cyclohexanol process

Underneath the control loops of the different units used in the cyclohexanol extraction process will be described. Where necessary a link will be made to the overall control of this process and how this specific unit contributes to the overall control objective.

7.3.1 The extraction column
For the extraction of HF and HCl a fixed proportional amount of cyclohexanol is needed. For this reason a ratio controller depending on the feed-flow is applied to the cyclohexanol flow. Since the cyclohexanol is a recycle stream the adjustment of this flow is limited. Because of this it's important to have a good setpoint for the ratio controller, an estimation for this setpoint could be obtained by doing pilot-plant extraction experiments. Because the column (C1) only functions as a contactor, no further process control is needed.

7.3.2 The hydrogen fluoride and hydrogen chloride recovery column
This column (C2) is crucial for the water content in the final HF product stream. To observe this water as early as possible in the process and take a fast corresponding control action it's important to control the water content in the top-stream. This is done by placing a fast analyzer in the top-stream and via composition control vary the reflux ratio. Apart from this composition control, the following control loops have been applied:
1. The temperature of the top-stream is controlled with the coolant flow through the condenser
2. The top-pressure is controlled with a valve in the top-stream
3. The bottom temperature is controlled with the steam flow through the reboiler
4. The liquid level in the bottom of the column is controlled by the bottom product flow

7.3.3 The water removal column
In this column (C3) pure water leaves the bottom. The hydrogen fluoride concentration in this stream must be below specified limits. To check this and perhaps take any control actions, analyser is placed in the bottom stream. The composition is controlled with the bottom temperature. The bottom temperature itself is controlled by the steam flow through the reboiler. Other control loops are:
1. The liquid level in the bottom is controlled by the bottom product flow
2. The top temperature is controlled by the coolant flow through the condenser
3. The top pressure is controlled by a valve in the top stream

7.3.4 The cyclohexanol recovery column
This column (C4) is provided with the following standard control loops:
- The top pressure is controlled with a valve in the top stream
- The top temperature is controlled by the coolant flow through the condenser
- The bottom temperature is controlled by the steam flow through the reboiler
- The liquid level in the column is controlled by the flow of the bottom exit stream
To be able to control the reflux ratio in cases when needed, an extra flow controller is installed in the top product stream.

7.3.5 The hydrogen fluoride/hydrogen chloride separation column
The control loops for this column (C5) are the same as for the identical column in the sulfuric acid process (C2, 7.2.2).

7.3.6 The typicals
In this process again three typicals are present:
- typical 1: V1, P2, E3, V2
- typical 2: V3, P3, E4, V4
- typical 3: V5, P4, E5, V6

These typicals are controlled in the same way as the typicals described in 7.2.4 for the sulfuric acid process.

7.3.7 Remaining control equipment
The feed to the extraction process is determined by the exit stream of the thermal converter and can’t be controlled. The exit temperature of the heat exchangers (E7, E13, E11, E15) is controlled by the coolant or steam flow through the heat exchanger. The exit stream pressure after a valve (V7) is controlled by the valve position. The level in the waste acid tank (V8) is controlled by the exit flow.

7.4 Analysers
Since analysers are expensive it’s important to install as less analysers as possible. As explained above, two analysers are inevitable. They are crucial for measuring and controlling the process performance. In both the H$_2$SO$_4$ and the cyclohexanol process the same two analysers are used. The first analyser is an analyser which analyses the water content at PPM level in a gaseous stream of HF and HCl. The pressure and temperature in the H$_2$SO$_4$ process are 150 kPa and 42 °C. For the cyclohexanol process they are 350 kPa and 51.6 °C respectively. The kind of analyzer suitable for this analysis is a near infrared analyser (NIR). The second analyser is an analyser which analyzes the HF content at PPM level in water. In the H$_2$SO$_4$ process the pressure and temperature are 150 kPa and 111.4 °C. In the cyclohexanol process 310 kPa and 134.7 °C respectively. The kind of analyser suitable for this analysis is a toroidal conductivity analyser.
In this chapter all the aspects of process safety of the designed processes will be discussed. An summary of the hazardous components is given and also a preliminary HAZOP-analysis of the two processes will be presented in chapter 9.

8 Process Safety

8.1 Chemical processes

During the design of a process, the installations and the equipment necessary, but also during the control of the process, much attention has to be given to the prevention of the unsafeness of the total process. Possible causes of potential hazard have to be traced and measures have to be taken to prevent process insecurities. One has to deal with possible risks and hazards for the personal, the surroundings and the environment, the so called Safety, Health and Environment (SHE) aspects. Important basic factors determining the magnitude of chemical hazards and risks are:

1. Scale of operations, amounts of materials/size of equipment and numbers of installations
2. Physical and chemical properties of the materials
3. Types of operations
4. Process conditions
5. Complexity of the operations
6. The age of the plant
7. The siting and layout of the plant
8. Vulnerability of the surroundings
9. Preventive and protective measures taken
10. Risks of human error
11. The effectiveness of management in mitigating risk

8.1.1 Safety

Safety studies should be undertaken throughout the life of a project. The properties of the materials also need to be considered during the conceptual design. Changes in operating pressures need to be examined, and checked whether they will move into the explosion range. The inventory of any hazardous materials should be minimized, and the operation of special safety systems should be considered. The total process safety analysis of a process design consists of five parts:

1. Identification undesired events
2. Quantification of the results of the undesired events
3. Quantification of the chance on the occurrence of the identified undesired events
4. Quantification of the risk of the industrial activity
5. Risk evaluation

Hazard identification is the pinpointing of material, system, process, and plant characteristics that can produce undesirable consequences through the occurrence of an accident. A few parts of the process need some extra attention, considering the possible occurrence of undesired events:

- the components are very toxic and hazardous
- high temperatures in the columns
- large recycle streams

Hazard evaluation is the analysis of the significance of hazardous situations associated with a process or activity. A good method for analysing the risks and safety aspects of the designed process is by making a HAZOP-analysis (Hazard and Operability Study).
HAZOP is essentially a qualitative procedure in which a proposed design is examined by generating questions about it in a systematic manner. The aim of such an analysis is to overtake the critical units in the designed process. For both the sulphuric acid and the cyclohexanol process the HAZOP's can be found in chapter 9.

Appendix T contains the risk outlines of the site of DuPont in Dordrecht. These risk outlines are not influenced by the addition of the sulfuric acid or cyclohexanol process to the thermal converter unit. Thus no extra precautions have to be taken. The risk contours are dominated by the spherical HF storage facility. In appendix T the behaviour of escaped clouds of HF or HCl can be found in a worst case scenario. That worst case is little wind and a hot day. Green areas represent lethal areas, the red areas are the irreversible areas and the yellow areas are the reversible areas. The concentrations can be found as a function of both the time and the place.

8.1.2 Health
Health risks of a component or process are identified by the toxic properties and the exposure. The total exposure is determined by the exposure level and exposure time. The basis of toxicity is the interference of a chemical agent with the normal biochemistry of humans. The toxicity is determined by the ability of the agent to penetrate into the organism and its reactivity. To be able to manage the toxic risks, there are a few essential concepts:

- **Hazard analysis**
  This comprises of hazard identification, and determination of the exposure-effect relation, which shows the relation between the exposure and the occurring effects

- **Exposure analysis**:
  Exploring the location and routes of the emission

- **Risk estimation and evaluation**:
  The toxic risk can be evaluated using official norms. A good example of an official norm of the toxicity of components is given by the MAC value. A MAC value is a governmental norm for the maximal acceptable concentration of gases in the air in the working environment. For the used components in the two processes the MAC values are given in appendix A, table A1 and A2.

- **Risk control**:
  According to the “ARBO-wet”, a Dutch labour law, the following restrictions should be taken to control health risk:
  - source restrictions/substitution of components
  - ventilation
  - exposure limitation
  - personal protection

The identification of the hazards of the components used in both the processes can be found in paragraph 8.2.

8.1.3 Environmental aspects
The processes are closed systems and there is no emission during the operation. To be able to look at the implications of the processes on the environment, the processes out-streams should be monitored. Apart from the product streams, there are several gas vents installed in the typicals. In the sulfuric acid process as well as in the cyclohexanol process three typicals are present. Normally these gas vents are closed by a valve, only when the pressure in the vessels of the typicals rise too high these valves will be opened and gas vent will be released to the air. When emission of these gas vents takes place, an excess of gaseous components, present in the vessels in the typicals, is released to the environment.
The water product stream contains very little HF and HCl and can therefore be dumped, because the levels are below the dumping criteria. Also the amount of HCl produced is so high, that all the HCl can be dumped. The dumping criteria will not be reached. The HCl will be so pure, that re-use is preferred, when possible.

8.2 Hazardous components

Before making a HAZOP analysis an overview of the hazardous components used in the process will be given in order to track down the hazards for the surroundings and the environment.

8.2.1 Hydrogen fluoride

Although it is widely recognized as a hazardous substance, large volumes of HF are safely manufactured, shipped and used, and have been for many years. The hydrogen fluoride industry has undertaken a significant effort to investigate the behavior of HF releases so as better to define the risks associated with an accidental spill, and to design effective mitigation system.

- **Exposure:**
  Mild exposure to HF via inhalation can irritate the nose, throat, and respiratory system. The onset of symptoms may be delayed for several hours. Severe exposure via inhalation can cause nose and throat burns, lung inflammation, and pulmonary edema, and can also result in other systemic effects including hypocalcemia, which if not promptly treated can be fatal.

- **Consequences:**
  Both liquid HF and the vapour can cause severe skin burns which may not be immediately painful or visible. HF can penetrate skin and attack underlying tissues, and large burns may cause hypocalcemia and other systemic effects which may be fatal. Even very dilute solutions may cause burns. Both liquid and vapour can cause irritation to the eyes, corneal burns, and conjunctivitis.

- **Carcinogenicity:**
  HF is not a carcinogen, however, HF is highly reactive and heat or toxic fumes may be evolved. Reaction with certain metals may generate flammable and potentially explosive hydrogen gas.

8.2.2 Hydrogen Chloride

Hydrogen chloride in air is an irritant, severely affecting the eye and the respiratory tract.

- **Exposure:**
  The inflammation of the upper respiratory tract can cause edema and spasm of the larynx. The vapour in the air, normally absorbed by the upper mucus membranes, is lethal at concentrations of over 0.1% in air, when exposed for a few minutes. HCl is detectable by odour at 1-5 PPM level and becomes objectionable at 5-10 PPM. The maximum concentration that can be tolerated for an hour is about 0.01% which, even at these levels, causes severe throat irritation. The maximum allowable concentration under normal working conditions has been set at 5 PPM. Exposure of concentrated hydrochloric acid to the skin can cause chemical burns or dermatitis. Whereas irritation is noticed readily, the acid can be water flushed from the exposed area. Copious use of running water is the only recommended safety procedure for any external exposures. Ingestion is seldom a problem because hydrochloric acid is a normal constituent of the stomach juices. If significant quantities are accidentally swallowed, it can be neutralised by antacids.

- **Consequences:**
  Hydrogen chloride in the lungs can cause pulmonary edema, a life threatening condition. In order for HCl in air to reach the lungs, it must be transported either as an aerosol or as a deposit on soot.
particles of less than 3 m in diameter.

- **Toxicity:**
  Hydrogen chloride in air can also be a phytotoxicant. Tomatoes, sugar beets, and fruit trees of the Prunus family are sensitive to HCl in air.

### 8.2.3 Sulphuric acid

Sulphuric acid is injurious to the skin, mucosa and eyes. Dangerous amounts of hydrogen may develop in reactions between weakened acid and metals. Sulfuric acid at high concentrations reacts vigorously with water, organic compounds and reducing agents.

- **Precautions:**
  Do not get in eyes, on skin or on clothing. Wear chemical goggles, face shield, rubber gloves and full protective clothing whenever there is a danger of exposure. Wash thoroughly after handling.

- **Toxicity:**
  Sulphuric acid aerosol (mist) is a significantly pulmonary irritant. Sulphuric acid mist inhalation are highly dependent on the particle size of the aerosol. Other factors affecting the physiological response of inhaling sulfuric acid mist are humidity, temperature, and previous exposure.

### 8.2.4 Cyclohexanol

Cyclohexanol is a colourless, viscous liquid with a camphoraceous odour. It is used chiefly as a chemical intermediate, a stabiliser, and a homogeniser for various soap detergent emulsions, and as a solvent for lacquers and varnishes.

- **Exposure:**
  Cyclohexanol is slightly toxic by the oral route of exposure and is slightly irritating to the skin. It can cause severe eye irritation and transient corneal injury. The vapour is irritating to the eyes of humans above 100 PPM.

- **Precautions:**
  Precautions that should be observed as a matter of course in using cyclohexanol include adequate and proper ventilation, avoidance of prolonged breathing of vapour or contact of the liquid with the skin, avoidance of ingestion, and protection of the eyes against splashing liquids.
9 Preliminary HAZOP-analysis

In the following chapter limited HAZOP-analyses are made of the equipment used in the flow schemes for both the sulfuric acid and the cyclohexanol process. These analyses can function as a basis to make a Process and Instrumentation Diagram (P&ID). A complete and well worked out P&ID is the basis for a real HAZOP-analysis. Such an analysis cannot be made by chemical engineers only; a multidisciplinary is required to make one.

9.1 The sulphuric acid process

For this process, several tables of HAZOP-analysis for the diverse equipment have been made in order to trace possible hazards and risks aspects for the surroundings and environment. For the \( \text{H}_2\text{SO}_4 \)-process this is done for the pumps, one buffer and storage tank (vessel), the sulfuric acid extraction column, two heat exchangers, and the HF/HCL distillation column.

Meanings of used abbreviations:
- LFA: Low Flow Alarm
- HFA: High Flow Alarm
- LPA: Low Pressure Alarm
- HPA: High Pressure Alarm
- LLA: Low Level Alarm
- HLA: High Level Alarm
- LTA: Low Temperature Alarm
- HTA: High Temperature Alarm
- LCA: Low Concentration Alarm
- HCA: High Concentration Alarm

Pump P1 is the feed pump of the waste water stream into the sulfuric acid extraction column, C1. The pump has to increase the pressure from 2 bar to 3 bar. \( T_\text{in}=20.0^\circ\text{C} \) and \( T_\text{out}=20.1^\circ\text{C} \). The mass flow is 1000 kg/hr and contains 0.75 wt% H\(_2\)O, 0.2 wt% HF and 0.05 wt% HCl.

Table 9.1 HAZOP-analysis of Pump P1

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No or not</td>
<td>No product flow</td>
<td>Defect pump</td>
<td>No waste water feed stream to extraction column C1</td>
<td>Repair/replace pump P1</td>
</tr>
<tr>
<td>More</td>
<td>More product flow</td>
<td>-Flow valve open after P1</td>
<td>-Column overflows</td>
<td>-Install HFA in C1</td>
</tr>
<tr>
<td></td>
<td>More pressure</td>
<td>-Pressure valve defect</td>
<td>-Feed pressure too high</td>
<td>-Replace valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-Install HPA in C1</td>
</tr>
<tr>
<td>Less</td>
<td>Less product flow</td>
<td>-Flow valve closed</td>
<td>-Column dries up</td>
<td>-Install LFA in C1</td>
</tr>
<tr>
<td></td>
<td>Pressure</td>
<td>-Pressure valve defect</td>
<td>-Feed pressure too low, no feed can enter the extraction column</td>
<td>-Replace valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-Install LPA in C1</td>
</tr>
</tbody>
</table>

Pumps P2, P3, P4 are the pumps installed in the three typicals after the vessels, respectively, V1, V3 and V5. Pump P2 increases the HF/HCl stream from 1.5 bar to 14.3 bar. P3 increases the \( \text{H}_2\text{O}/\text{HF}/\text{H}_2\text{SO}_4 \) stream from 1.4 to 2.5 bar and pump P4 increases the \( \text{H}_2\text{O}/\text{HF}/\text{H}_2\text{SO}_4 \) stream from 1.4 to 3 bar.
Table 9.2 HAZOP-analysis of Pump P2, P3 and P4 (installed in the typicals)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No or not</td>
<td>No flow</td>
<td>No flow to columns</td>
<td>Repair/replace pump</td>
<td></td>
</tr>
<tr>
<td>More</td>
<td>- More flow</td>
<td>- Flow valve open</td>
<td>- Column overflows</td>
<td>- Install HFA</td>
</tr>
<tr>
<td></td>
<td>- More pressure</td>
<td>- Pressure valve defect</td>
<td>- Feed pressure to column too high</td>
<td>- Replace valve</td>
</tr>
<tr>
<td>Less</td>
<td>- Less product flow</td>
<td>- Flow valve closed</td>
<td>- Column dries up</td>
<td>- Install LFA in C1</td>
</tr>
<tr>
<td></td>
<td>- Less pressure</td>
<td>- Pressure valve defect</td>
<td>- Feed pressure too low</td>
<td>- Replace valve</td>
</tr>
</tbody>
</table>

In typical T3 the H₂SO₄ with H₂O and HF is stored in vessel V5 at a temperature of 30.0 °C and 1.4 bar.

Table 9.3 HAZOP-analysis of the intermediate storage and buffer tank section of H₂SO₄ (V5)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>No flow</td>
<td>- No sulfuric acid available at intermediate storage</td>
<td>- Loss of feed to column section and reduced output</td>
<td>- Ensure good communication with intermediate storage operator</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Pump P4 fails</td>
<td>- Pump P4 overheats</td>
<td>- Install LLA in extraction column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Valve closed</td>
<td></td>
<td>- Institute kickback on P4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Line fracture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>More</td>
<td>More flow</td>
<td>LCV fails open or LCV bypass open in error</td>
<td>Extraction column overfills</td>
<td>- Install HLA in tank</td>
</tr>
<tr>
<td>More</td>
<td>More pressure</td>
<td>LCV closes when pump P4 running</td>
<td>Transfer line subjected to full pump delivery or surge pressure</td>
<td>- Install kickback on P4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Install HPA in C1</td>
</tr>
<tr>
<td>More</td>
<td>More temperate</td>
<td>- Thermal expansion in an isolated valved section due to fire or strong sunlight</td>
<td>- Line fracture</td>
<td>- Install thermal expansion relief valve on valved section</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High intermediate storage temperature</td>
<td>- Higher pressure in transfer line and extraction column</td>
<td>- Check whether there is adequate warning of high temperature at intermediate storage. If not, install</td>
</tr>
<tr>
<td>Less</td>
<td>Less flow</td>
<td>Leaking flange or valve stub not blanked and leaking</td>
<td>- Material loss</td>
<td>- Institute regular patrolling and inspection of transfer line</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Less HF recovery in C1</td>
<td>- Install kickback on P4 pump</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Install LPA in C1</td>
</tr>
<tr>
<td>Less</td>
<td>Less temperate</td>
<td>Winter conditions</td>
<td>Water sump and freezing of drain line</td>
<td>- Lag water sump down to drain valve, and steam trace drain valve and drain line downstream</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Install LTA in C1</td>
</tr>
</tbody>
</table>

The sulfuric acid extraction column separates the H₂O from the waste water mixture (H₂O, HF and HCl) by adding H₂SO₄. Outlet conditions: P_top=1.5 bar, T_top=42.0 °C, P_bottom=1.7 bar, T_bottom=130.2 °C.
Table 9.4 HAZOP-analysis of the H₂SO₄ - extraction column (C1)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbance</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
</table>
| No          | No sulfuric acid feed stream | -No sulfuric acid available at intermediate storage  
-Defect in feed-pipe  
-Valve closed  
-Leaking | -No extractant to the column, so no recovery of HF from the waste water stream | -Ensure good communications with storage operator  
-Check storage tank of sulfuric acid  
-Check pipe  
-Check valve  
-Install LFA |
| No          | No waste water feed stream | -No waste water available from thermal converter  
-Defect in feed-pipe  
-Defect pump P1  
-Valve closed  
-Leaking | -No waste water in extraction column | -Check pipe connection with thermal converter  
-Check pipe  
-Repair/replace pump (kickback on pump P1)  
-Check valve  
-Install LFA |
| No          | No reboiling of the bottom stream | -Defect in reboiler | -No distillation | -Install LTA in column  
-Install HLA in column  
-Install LLA in column  
-Repair reboiler  
-Column shutdown |
| No          | No bottom stream of H₂O and H₂SO₄ | -Leaking pipe or closed valve  
-Valve closed  
-Reboiler temperature too high | -No stream to buffer and storage tank  
-Column overflows | -Check/repair pipe or valve  
-Install HLA in column  
-Install HTA  
-Reduce reboiler temperature |
| No          | No top stream of HF and HCl | -Leaking pipe or closed valve  
-Valve closed  
-Reboiler temperature too low | -No stream to buffer and storage tank  
-Column overflows | -Check/repair pipe or valve  
-Install HLA in column  
-Install LTA  
-Increase reboiler temperature |

The heat exchanger E1 is placed in the top stream of the sulfuric acid extraction column to cool off the HF/HCl mixture from 42.0 °C to -24.2 °C at a pressure of 1.5 bar.

Table 9.5 HAZOP-analysis of the HF/HCl - cooler (E1) with brine

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
</table>
| No/Not      | No brine flow | Valve brine feed | -No cooling of the stream | -Check valve  
-Install Tout alarm |
| More        | More brine flow | Valve brine feed | -Lower temperature of stream | -Close valve more  
-Install Tout alarm |
| Less        | Less brine flow | Valve brine feed | -Higher temperature of stream | -Open valve more  
-Install Tout alarm |

Reboiler E2 heats the bottom stream of the sulfuric acid extraction column with high pressure steam of 75 psig(1) and 165 °C. The bottom stream is heated from 130.2 °C to 135.0 °C.

Table 9.6 HAZOP-analysis of heater E2 with HP steam

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
</table>
| No/Not      | No HP steam flow | Valve HP steam feed | -No heating of stream | -Check valve  
-Install Tout alarm |
| More        | More HP steam flow | Valve HP steam feed | -Stream temperature too high | -Close valve more  
-Install Tout alarm |
| Less        | Less HP steam flow | Valve HP steam feed | -Lower temperature of stream | -Open valve more  
-Install Tout alarm |
The HF/HCl distillation column separates the HF from the HCl. The outlet conditions of the streams are: P<sub>top</sub>=14 bar, T<sub>top</sub>=−21.3 °C, P<sub>bottom</sub>=14.5 bar, T<sub>bottom</sub>=110.0 °C.

Table 9.7 HAZOP-analysis of the HF/HCl - distillation column (C2)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No / not</td>
<td>No feed flow</td>
<td>-No HF/HCl available at intermediate storage</td>
<td>-No distillation, C2 dries up</td>
<td>-Install LFA in distillation column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Valve closed</td>
<td></td>
<td>-Install LCF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Pump P2 defect</td>
<td></td>
<td>-Check valve</td>
</tr>
<tr>
<td>No/not</td>
<td>-No top flow</td>
<td>-Reboiler C2 defect</td>
<td>-No separation in C2</td>
<td>-Repair/replace reboiler</td>
</tr>
<tr>
<td></td>
<td>-No bottom flow</td>
<td>-Reboiler too high</td>
<td>-Column dries up or accumulates</td>
<td>-Install LCA</td>
</tr>
<tr>
<td>More</td>
<td>More feed flow</td>
<td>-Flow valve P2 defect</td>
<td>-C2 overflows</td>
<td>-Install HFA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Reboiler C1 too high</td>
<td>-Products impure</td>
<td>-Turn down reboiler</td>
</tr>
<tr>
<td>More</td>
<td>-More top stream</td>
<td>-Suck pressure P2 too high</td>
<td>-Pressure too low</td>
<td>-Lower such pressure</td>
</tr>
<tr>
<td></td>
<td>-More bottom stream</td>
<td>-Reboiler C2 too low, valve open</td>
<td>-Column dries up</td>
<td>-Turn up reboiler</td>
</tr>
<tr>
<td>Less</td>
<td>Less feed flow</td>
<td>-Pump P2 defect</td>
<td>-Less flow to C2, column dries up</td>
<td>-Install LLA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Leaking valve</td>
<td></td>
<td>-Repair/replace pump P1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-Column dries up</td>
<td>-Check/replace valve</td>
</tr>
<tr>
<td>Less</td>
<td>-Less top steam</td>
<td>-Pump P2 defect</td>
<td>-Less products</td>
<td>-Repair/replace reboiler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Reboiler too low</td>
<td></td>
<td>-Check pump</td>
</tr>
<tr>
<td></td>
<td>-Less bottom stream</td>
<td>-Reboiler too high</td>
<td>-Less products</td>
<td>-Install LCA</td>
</tr>
</tbody>
</table>

9.2 The cyclohexanol process

Also for this process, several tables of HAZOP-analysis have been made in order to trace possible hazards and risks aspects for the surroundings and environment. For the cyclohexanol process this is done for the pumps, one storage and buffer tank (vessel), the cyclohexanol extraction column and two heat exchangers, one cooler and one reboiler. The HF/HCl distillation column operates the same as in the sulfuric acid process, see paragraph 9.1, so in this paragraph this column will not be discussed any further.

Pump P1 is the feed pump of the waste water stream into typical T1 and thus into the cyclohexanol extraction column, C1. The pump has to increase the pressure from 2 bar to 2.5 bar. T<sub>in</sub>=20.0 °C and T<sub>out</sub>=20.0 °C. The mass flow is 1000 kg/hr and contains 75 wt% H₂O, 20 wt% HF and 5 wt% HCl.

Table 9.8 HAZOP-analysis of Pump P1

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No or not</td>
<td>No product flow</td>
<td>Defect pump</td>
<td>No waste water feed stream to vessel V1</td>
<td>Repair/replace pump P1</td>
</tr>
<tr>
<td>More</td>
<td>-More product flow</td>
<td>-Flow valve open</td>
<td>-Column overflows</td>
<td>-Install HFA in V1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Pressure valve defect</td>
<td>-Feed pressure too high</td>
<td>-Replace valve</td>
</tr>
<tr>
<td>Less</td>
<td>-Less product flow</td>
<td>-Flow valve closed</td>
<td>-Column dries up</td>
<td>-Install LPA in V1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Pressure valve defect</td>
<td>-Feed pressure too low, no feed can enter vessel V1</td>
<td>-Replace valve</td>
</tr>
</tbody>
</table>

55
Pumps P2, P3 and P4 are the pumps installed in the three typicals after the vessels, respectively, V1, V3 and V5. Pump P2 increases the HF/HCl stream from 2.2 bar to 5 bar. P3 increases the H$_2$O/HF/H$_2$SO$_4$ stream from 2.5 to 5 bar and pump P4 increases the H$_2$O/HF/H$_2$SO$_4$ stream from 3.5 to 14.3 bar.

Table 9.9: HAZOP-analysis of Pump P2, P3 and P4 (installed in the typicals)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No or not</td>
<td>No flow</td>
<td>No flow to columns</td>
<td>Repair/replace pump</td>
<td></td>
</tr>
<tr>
<td>More</td>
<td>-More flow</td>
<td>-Defect pump</td>
<td>-Column overflows</td>
<td>-Install HFA</td>
</tr>
<tr>
<td></td>
<td>-More pressure</td>
<td>-Pressure valve defect</td>
<td>-Feed pressure to column too high</td>
<td>-Replace valve</td>
</tr>
<tr>
<td>Less</td>
<td>-Less flow</td>
<td>-Flow valve open</td>
<td>-Column dries up</td>
<td>-Install LFA in column</td>
</tr>
<tr>
<td></td>
<td>-Less pressure</td>
<td>-Pressure valve defect</td>
<td>-Feed pressure too low</td>
<td>-Replace valve</td>
</tr>
<tr>
<td></td>
<td>-Less product flow</td>
<td>-Flow valve closed</td>
<td>-Feed can not enter s column</td>
<td>-Install LPA in column</td>
</tr>
</tbody>
</table>

Vessel V3 in typical T2 is used as a storage and buffer tank of cyclohexanol and water. The vessel is placed before the cyclohexanol extraction column and held at a temperature of 20 °C and 2.5 bar.

Table 9.10: HAZOP-analysis of the intermediate storage and buffer tank section of C$_6$H$_{12}$O (V3)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>No flow out</td>
<td>-No cyclohexanol available at intermediate storage</td>
<td>-Loss of feed to column section and reduced output</td>
<td>-Ensure good communications with intermediate storage operator</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Pump P3 fails</td>
<td>-Pump P3 overheats</td>
<td>-Install LLA in extraction column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Valve closed</td>
<td>-Check valve</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Line fracture</td>
<td>-Install kickback on P3</td>
<td></td>
</tr>
<tr>
<td>More</td>
<td>More flow out</td>
<td>LCV fails open or LCV bypass open in error</td>
<td>Extraction column overfills</td>
<td>-Install HLA in tank</td>
</tr>
<tr>
<td>More</td>
<td>More pressure</td>
<td>LCV closes when pump P3 is running</td>
<td>Transfer line subjected to full pump delivery or surge pressure</td>
<td>-Install kickback on pump</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Line fracture</td>
<td>-Check line</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Higher pressure in transfer line and extraction column</td>
<td>-Install HPA in C1</td>
<td></td>
</tr>
<tr>
<td>More</td>
<td>More temperature</td>
<td>Thermal expansion in an isolated valved section due to fire or strong sunlight</td>
<td>-Check whether there is adequate warning of high temperature at intermediate storage if not, install</td>
<td>-Install HTA in C1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-High intermediate storage temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Less</td>
<td>Less flow out</td>
<td>Leaking flange or valve stub not blanked and leaking</td>
<td>Material loss</td>
<td>-Institute regular patrolling and inspection of transfer line</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Less recovery of HF in C1</td>
<td>-Install kickback on P4 pump</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Water sump and freezing of drain line</td>
<td>-Install LTA in C1</td>
<td></td>
</tr>
</tbody>
</table>

The cyclohexanol extraction column separates the water from the waste water stream by adding cyclohexanol. The outlet conditions of the streams are: P=5 bar, T=20 °C.
Table 9.11 HAZOP-analysis of the Cyclohexanol - extraction column (C1)

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbance</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>No cyclohexanol feed stream</td>
<td>-No cyclohexanol available at intermediate storage</td>
<td>No extraction, so no HF recovery from the waste water stream</td>
<td>-Ensure good communications with storage operator</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Defect in feed-pipe</td>
<td></td>
<td>-Check storage tank of cyclohexanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Valve closed</td>
<td></td>
<td>-Check valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Leaking pipe</td>
<td></td>
<td>-Check pipe</td>
</tr>
<tr>
<td></td>
<td>No waste water feed stream</td>
<td>-No waste water available from thermal converter</td>
<td>No waste water in extraction column, so no HF recovery</td>
<td>-Check pipe connection with thermal converter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Defect pump P2</td>
<td></td>
<td>-Repair/replace pump</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Valve closed</td>
<td></td>
<td>-Check valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Leaking</td>
<td></td>
<td>-Install LFA</td>
</tr>
<tr>
<td></td>
<td>No reboiling of the bottom stream</td>
<td>-Defect in reboiler</td>
<td>No distillation of feed streams</td>
<td>-Install LTA in column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Leaking pipe</td>
<td></td>
<td>-Install HLA in column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Closed valve</td>
<td></td>
<td>-Install LFA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Reboiler temperature too high</td>
<td></td>
<td>-Repair reboiler</td>
</tr>
<tr>
<td></td>
<td>No bottom stream of H₂O and Cyclohexanol</td>
<td>-Leaking pipe</td>
<td>No feed to C3, Column C1 overflows</td>
<td>-Column shutdown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Closed valve</td>
<td></td>
<td>-Check/repair pipe or valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Reboiler temperature too high</td>
<td></td>
<td>-Check valve</td>
</tr>
<tr>
<td></td>
<td>No top stream of HF and HCl and Cyclohexanol</td>
<td>-Leaking pipe or closed valve</td>
<td>No feed stream to C2, Column overflows</td>
<td>-Install HLA in column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Reboiler temperature too low</td>
<td></td>
<td>-Increase reboiler temperature</td>
</tr>
</tbody>
</table>

Heat exchanger E11 is installed in the bottom stream of column 3. The stream consists of water and is cooled from 134.7 °C to 15 °C with brine.

Table 9.12 HAZOP-analysis of heat exchanger E11

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No/Not</td>
<td>No brine flow</td>
<td>Valve brine feed</td>
<td>-No cooling of the stream</td>
<td>-Check valve, Install Toot alarm</td>
</tr>
<tr>
<td>More</td>
<td>More brine flow</td>
<td>Valve brine feed</td>
<td>-Lower temperature of stream</td>
<td>-Close valve more, Install Toot alarm</td>
</tr>
<tr>
<td>Less</td>
<td>Less brine flow</td>
<td>Valve brine feed</td>
<td>-Higher temperature of stream</td>
<td>-Open valve more, Install Toot alarm</td>
</tr>
</tbody>
</table>

Reboiler E4 heats the bottom stream of water, cyclohexanol and HF with high pressure steam of 180 psi(g) and 195 °C. The bottom stream is heated from 156.6 °C to a temperature of 162.0 °C.

Table 9.13 HAZOP-analysis of heater E4 with HP steam

<table>
<thead>
<tr>
<th>Guide words</th>
<th>Disturbances</th>
<th>Possible causes</th>
<th>Consequences</th>
<th>Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No/Not</td>
<td>No HP steam flow</td>
<td>Valve HP steam feed</td>
<td>-No heating of stream</td>
<td>-Check valve, Install Toot alarm</td>
</tr>
<tr>
<td>More</td>
<td>More HP steam flow</td>
<td>Valve HP steam feed</td>
<td>-Stream temperature too high</td>
<td>-Close valve more, Install Toot alarm</td>
</tr>
<tr>
<td>Less</td>
<td>Less HP steam flow</td>
<td>Valve HP steam feed</td>
<td>-Lower temperature of stream</td>
<td>-Open valve more, Install Toot alarm</td>
</tr>
</tbody>
</table>
10 Cost Engineering and economics

In this chapter the economic feasibility of both the sulphuric acid and the cyclohexanol will be discussed. By evaluating the costs, the revenues and the most important economic criteria a good comparison in the economic field can be made between the two processes. An economic study for a process design in this state can be determined, whether a the process will go into the next step of designing.

10.1 The sulphuric acid process

First the sulphuric acid process will be discussed. The procedure of calculating the total investment, the costs and the revenues will be presented. Also a number of economic criteria will be reviewed.

10.1.1 The total investment

There are a number of methods to estimate or calculate the investment costs, which have to be made to build and design an industrial process. Three methods to calculate the investment costs will be presented in this paragraph. For the total investment costs, with which further calculations will be done, the average investment costs can be taken.

10.1.1.1 The calculation with the DuPont method

The method to calculate the final project costs for a project at DuPont de Nemours can be divided in five stages.

- High-spot estimate
- Informal Venture Guidance Appraisal (VGA)
- Formal VGA
- Current Appraisal of Cost (CAC)
- Construction Cost Estimate (CCE)

The estimation of the total project cost in this report will be somewhere in between the high-spot estimate and the informal VGA. This option has been chosen, because the high-spot estimate method is not detailed enough, but the real formal VGA is more detailed than we can account for.

First a high-spot estimate is made. This is based on the experience of a process engineer and the estimation of prices of equipment, that has been bought in the past. The estimated equipment cost is multiplied by an experience factor and that way the total investment costs are estimated. This estimate is used for general wide-range business decisions and long-range forecasting.

The second method is the informal VGA. In this stage of the cost engineering the total equipment cost is calculated by adding the individual cost of all the unit operations in the flowsheet. The cost for the unit operations has been taken from lit. DP11. This method requires a relative detailed process flow diagram. To keep in mind, that some equipment has been overlooked a factor for miscellaneous equipment is stated. Together with the cost of all the unit operations those are the total equipment cost.

Now different factors for all steps in the building procedure are estimated on the basis of experience. By multiplying those factors with the subtotals the total project costs can be calculated. Some of the factors for the different steps in the building of the plant are for piping, instrumentation, installation, labour and special equipment. In appendices P.1 and I.1 all the factors are mentioned and specified. The magnitude of the factors has been estimated on the basis of informal VGA’s which
have been done at DuPont and have been determined after deliberation with DuPont. This estimate is used for business planning and economic study for the second or third year of the capital forecast.

The formal VGA is used for capital budgets, the first year of a three-year forecast, or for a major business decision. It may also be used in special situations in which it can be the basis of Part I of the project authorisation. This is called the "Forecast of Total Cost".

The Current Appraisal of Cost is a stage in the cost engineering which is has to made to get authorisation to get full-funds for Part I.

The Construction Cost Estimate has to be made to get authorisation to get full-funds for Part II. The total investment costs according to the estimation done by the method of DuPont is 22024 kdf/l.

10.1.1.2 The calculation with the Zevnik-Buchanan method
According to lit. Chemische Fabriek deel I, the investment in fixed capital within the battery limit \( I_B \) and the auxiliary equipment \( I_H \) form respectively 64% and 16% of the total investment.

The total investment can be calculated by the next equation:

\[
I_{\text{tot}} = I_B + I_H + I_L + I_W
\]  
(10.1)

The other two investment costs, the investment in working capital, \( I_W \), and the investment in non-materials, \( I_L \), are respectively 6% and 14% of the total investment costs for the average Dutch industrial chemical plant (lit. Chemisch Fabriek deel II).

The method of Zevnik-Buchanan provides a method to calculate \( I_B \) and \( I_H \). It is a modular exponential model. The method is based on the principle that investments are a function of both the process capacity and the process complexity. The data that is needed to calculate the investments are the number of functional unit operations \( N \), the complexity factor \( C_f \) and the Plant Cost Index \( C_I \).

The equation to calculate both the \( I_B \) and \( I_H \) is given by equation 10.2:

\[
I_B + I_H = N \cdot I_E \cdot \frac{C_f}{219}
\]  
(10.2)

The price per functional unit is a function of the complexity factor and the production in ton/year. The \( I_E \) can be read from figure III-21 from lit. HE17. The complexity factor can be calculated from the material factor \( F_m \), the pressure factor \( F_P \) and the temperature factor \( F_t \). The temperature factor can be calculated for temperatures under and above 290 K. Since the temperatures in the sulphuric acid process are both under and above 290 K two temperature factors can be calculated. The highest factor has been taken to calculate the complexity factor. The pressure factor can be read from figure III-17 from lit. HE17. The material factor can be found in table III-18 from lit. HE17. The complexity factor is calculated with equation 10.3:

\[
C_f = 2 \cdot 10^{(F_t + F_P + F_m)}
\]  
(10.3)

The Plant Cost index can be read from table III-53 from lit. HE17. The last index is from 1990. From lit. DPII the Webci-index from 1993 (128) relative to 1990 (119) can be determined. The Chemical Plant Cost index from 1990 (357.6) can be multiplied with this factor to yield the index for 1993. This can be extrapolated to 1997, assuming that the Webci-index will increase linear. The \( C_I \) for 1997 will than be 512. The results can be found in appendix 12 for the investment costs according to Zevnik-Buchanan. The course of the dollar has been assumed to be 1,80 guilders. The total investment costs will be according to this 25018 kdf/l.
10.1.1.3 The calculation with the Taylor method
The method to calculate the total investment costs is based on the fact that the investment in the
equipment within the battery limit, \( I_B \), is a function of the capacity of the process, the Chemical Plant
index and the costliness of the process (lit. HE17):

\[
I_B = 93 \cdot f \cdot P^{0.39} \cdot \frac{C_f}{300}
\]  

(10.4)

The costliness factor is a function of all the components and all the process steps in the process. Table
III-22 provides scores for the throughput, material of construction, storage time and the pressure or
temperature of the components or steps. The equation to calculate \( f \) is:

\[
f = \sum_{i=1}^{N} 1.3^s
\]  

(10.5)

The factor 93, equation (10.4), is the factor to calculate the cost in k$ in stead of k€. All values for the
scores can be found in appendix 13. The total investment according to Taylor is also calculated in
appendix 13 and amounts to 34793 kdfl. An overview of the investment costs of the three methods
can be found in table 10.1.

<table>
<thead>
<tr>
<th>Method</th>
<th>Investment costs [kdfl]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPont</td>
<td>22024.25</td>
</tr>
<tr>
<td>Zevnik-Buchanan</td>
<td>25018.28</td>
</tr>
<tr>
<td>Taylor</td>
<td>34793.16</td>
</tr>
<tr>
<td>Average</td>
<td>27278.56</td>
</tr>
</tbody>
</table>

10.1.2 The costs
For this stage of designing the total cost of a chemical product can be taken to be the sum of three
types of costs:

- Production volume dependent costs
- Investment dependent costs
- Labour dependent costs

In equation 10.6 the total costs are given:

\[
K_T = K_p + K_i + K_L
\]  

(10.6)

This is not completely true, but is it sufficient for a general calculation of the cost-price.

10.1.2.1 The production volume dependent costs
The production volume dependent cost are the cost of the raw materials, the cost of the packing, the
cost for cooling agents in the coolers, the cost for steam in the heaters and the electricity cost for the
pumps. The cost for the cooling agents has been calculated by converting the flow in kg/s to ton or m³
per year. The cost of the brine is given in dfl./m³ and the cost for cooling water has been given in
dfl./ton.
The steam cost can be calculated by converting the flow in kg/s to the flow in ton/year. The price for one ton of steam has been taken from lit. FVO-handleiding and is dfl. 35,- per ton for high pressure steam and dfl. 30,- for low pressure steam. The electricity cost can be calculated by converting the power used per second into the power used per year and multiplying this with the price per kWh. Further the amount of raw material used must be calculated and the amount of packing that will be replaced in one year. The sum of these cost form the total production dependent cost.

10.1.2.2 The investment dependent costs
The investment dependent cost can be calculated as a fraction of the total investments. The average investment cost of the Zevnik-Buchanan and the Taylor method has been used to calculate the $K_i$. The equation for the investment dependent cost is:

$$K_i = (f + i) \cdot I_{\text{tot}}$$

(10.7)

The factor $f$ is a factor for maintenance cost and so on. The factor $i$ is the capital charge for the annuities and the writing off of the investment. $I_{\text{tot}}$ is the total investment. The magnitude of $f$ depends on the depreciation and maintenance and is equal to 0.13. The magnitude of the factor $i$ has been calculated in appendix 14 and is 0.149.

10.1.2.3 The labour expense dependent costs
The labour expense dependent cost can be calculated with the following equation:

$$K_L = d \cdot L$$

(10.8)

d is a factor for uncalculated labour expense dependent cost and is equal to 2.6. $L$ is the total labour expense. The total labour expense is a function of the number of process steps, $N$, and the product capacity, $C$:

$$L = 32 \cdot N \cdot C^{0.24}$$

(10.9)

The total costs have been calculated in appendix 14.

The total income can be calculated by multiplying the product streams of HF and HCl in ton per year with the price per ton. The net profit can be calculated by subtracting the total cost from the total income. The overall results can be found in table 10.2:

<table>
<thead>
<tr>
<th>Sort</th>
<th>Amount [kdfl/yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Income</td>
<td>5130.89</td>
</tr>
<tr>
<td>$K_i$</td>
<td>558.81</td>
</tr>
<tr>
<td>$K_T$</td>
<td>7616.18</td>
</tr>
<tr>
<td>$K_P$</td>
<td>1865.71</td>
</tr>
<tr>
<td>$K_f$</td>
<td>10040.70</td>
</tr>
<tr>
<td>Profit</td>
<td>-4909.82</td>
</tr>
</tbody>
</table>

10.1.3 Economic criteria
The earning capacity of the process, based on the costs and the income, can be calculated in a number of ways. In this report the return on investment (ROI), the internal rate of return (IRR) and the pay out time (POT) will be calculated.
10.1.3.1 The return on investment
The return on investment is the expected yearly return on the investments. The disadvantage of this method is that the depreciation of the value of money and the changes of the income and profit are not taken into account. The return on investment will be taken to be 10%. This is a good value for projects in the environmental field. The ROI is the gross net profit minus taxes divided by the investment and multiplied by 100%:

\[ \text{ROI} = \frac{\text{Gross profit} - \text{taxes}}{\text{investments}} \times 100\% \]  (10.10)

10.1.3.2 The internal rate of return
By calculating the net cash flow per year, it is possible to find an interest rate at which the cumulative net present worth at the end of a project is zero. This particular rate is called the Internal Rate of Return (IRR) and is a measure of the maximum rate that the project could pay and still break even by the end of the project life. This can be put in an equation:

\[ \sum_{n=0}^{\infty} \frac{NFW}{(1 + r)^n} = 0 \]  (10.11)

\( r \) is the internal rate of return, \( NFW \) is the net cash flow per year in kdf. and \( t \) is the life-time of the project, usually 10 years. In the year 0 the cash flow is negative and is equal to the amount of investments. In the following years, it is equal to the net profit. In the last year the cash flow is equal to the net profit plus the scrap value (10% of the investments) and the working capital.

\[ \text{IRR} = 12.28\% \]

The calculation can be found in appendix 15.

10.1.3.3 The Pay Out Time
The pay out time can be defined as the minimum number of years to earn back the investment made. The initial investment is just that part of the investment, that is written off or that has been lost. This means that only the investments in fixed capital and the investments in non-materials will be taken into account.

The pay out time can be calculated by dividing the investments in fixed capital and non-materials by the exploitation remainder. The exploitation remainder can be defined as the revenues, based on an ROI of 10%, minus the total production volume dependent and the total labour dependent cost:

\[ \text{POT} = \frac{I_a + I_n + I_l}{\text{Exploitation remainder}} \]  (10.12)

From this calculation it follows that the time necessary to earn back the investment in the fixed capital and the non-materials is 2.63 years. The detailed calculations can be found in appendix 15.

Table 10.3 Overview of the economic criteria for the H₂SO₄ process

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Return on investment</td>
<td>10%</td>
</tr>
<tr>
<td>Internal rate of return</td>
<td>12.3%</td>
</tr>
<tr>
<td>Pay out time</td>
<td>2.63 years</td>
</tr>
</tbody>
</table>
10.2 The cyclohexanol process

The same procedure that has been done for the sulphuric acid process has been carried out for the cyclohexanol process. The total investments have been calculated in three manners, the costs have been calculated and the return on investment, the internal rate of return and the pay out time have been calculated.

10.2.1 The total investments

For the equations and methods with which the investment costs have been calculated is referred to paragraph 10.1.1. The detailed results can be found in appendix P1 until P3. An overview of the investment costs with all three methods is given in table 10.4:

Table 10.4 Overview of the investment costs

<table>
<thead>
<tr>
<th>Method</th>
<th>Investment costs [kdfl.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPont</td>
<td>22696.91</td>
</tr>
<tr>
<td>Zevnik-Buchanan</td>
<td>30274.23</td>
</tr>
<tr>
<td>Taylor</td>
<td>33123.77</td>
</tr>
<tr>
<td>Average</td>
<td>28698.30</td>
</tr>
</tbody>
</table>

10.2.2 The costs

The total production costs have been calculated analogous to the method in paragraph 10.2.1. The results can be found in appendix P4. An overview of the results can be found in table 10.5.

Table 10.5 Profit calculation of the cyclohexanol process

<table>
<thead>
<tr>
<th>Sort</th>
<th>Amount [kdfl/yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Income</td>
<td>5130.89</td>
</tr>
<tr>
<td>$K_1$</td>
<td>1078.00</td>
</tr>
<tr>
<td>$K_2$</td>
<td>754.71</td>
</tr>
<tr>
<td>$K_t$</td>
<td>8012.57</td>
</tr>
<tr>
<td>$K_T$</td>
<td>9845.28</td>
</tr>
<tr>
<td>Profit</td>
<td>-4714.40</td>
</tr>
</tbody>
</table>

10.2.3 Economic criteria

The return on investment, the internal rate of return and the pay out time have been calculated in the same manner for the cyclohexanol process as for the sulphuric acid process. The detailed calculations can be found in appendix P5. The results are can be found in table 10.6.

Table 10.6 Overview of the economic criteria for the cyclohexanol process

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Return on investment</td>
<td>10 %</td>
</tr>
<tr>
<td>Internal rate of return</td>
<td>12.3 %</td>
</tr>
<tr>
<td>Pay out time</td>
<td>2.63 years</td>
</tr>
</tbody>
</table>
11 Conclusions and recommendations

In this chapter the most important results will be presented and conclusions will be drawn. After a comparison between the sulphuric acid and the cyclohexanol process has been made an advice will be given which of the two processes can be chosen best to make a more detailed design of.

11.1 Important results

Hydrogen fluoride forms a maximum temperature azeotrope with water. The azeotropic composition is 38 wt% at atmospheric pressure and ambient temperature. If Hydrogen Chloride is present in low concentrations a ternary azeotrope is formed. Due to this azeotrope hydrogen fluoride can not be recovered from the sub-azeotropic feed stream by conventional distillation based on a difference in boiling temperatures.

Six processes are suitable for the recovery of HF out of the waste stream from the thermal converter. These processes are the hexane stripping, pressure swing, electrodialysis, HCl make-up, cyclohexanol extraction and the sulphuric acid extractive distillation process. The cyclohexanol extraction process is preferred to the hexane stripping process because of the lower energy requirements and reduced hazards. The pressure swing is not feasible due to the small variations of the azeotropic composition with pressure variation. The electrodialysis process is a very interesting option but discarded because of the difficulties and uncertainties during further completion and simulation of this process. Of the left processes the cyclohexanol and the sulphuric acid process are preferred and chosen as processes for a preliminary plant design. This because these two processes proofed to be able to meet the DuPont product specifications.

Both the cyclohexanol and the sulphuric acid process have been simulated with the simulation program ASPEN Plus. The feed of both the processes is 1000 kg/hr. The amount of HF in the feed is 20 wt%, those of HCl and water are 5 wt% and 75 wt% respectively.

The sulphuric acid process yielded a product stream of HF of 199.269 kg/hr HF and 0.052 kg/hr HCl. The HF has a purity of approximately 100 wt% and contains 259 ppm HCl, 18 ppm water and 217 ppb sulphuric acid. It leaves the process at 15 °C and 300 kPa (battery limit), which satisfies the requirements of DuPont. The HCl product stream contains only 18 ppm HF, less than 1 ppb of water and is acid free and has got a temperature and pressure of 15 °C and 1400 kPa respectively. Thus it can be added to the existing capacity of HCl. The waste water stream contains 0.730 kg/hr of HF. The concentration of HF in this stream is 0.1 wt%. It also contains 1.3 ppm of HCl and less than 1 ppb of sulphuric acid. The waste water leaves the process at 15 °C and 150 kPa.

The cyclohexanol process produced a HF product stream of 199.280 kg/hr of HF and 0.419 kg/hr HCl. The purity of HF is 99.8 wt% and the stream contains less than 1 ppb of water and 3 ppb of cyclohexanol. The stream leaves the process at 15 °C and 300 kPa, which meets the specifications given by DuPont. The HCl product stream contains less than 1 ppb water and cyclohexanol and 7 ppm of HF. It exits the process at 15 °C and 1400 kPa, just like in the sulphuric acid process. The waste water contains 0.720 kg/hr of HF, which equals 0.1 wt% in this stream. It also contains 1 ppm of cyclohexanol and less than 1 ppb of HCl. It leaves the process at 15 °C and 190 kPa. The waste water stream can be drained, because the concentrations remain within government restrictions.

The streams of both processes lie within the DuPont specifications concerning the loss of HF via the waste water stream and concerning the compositions of the HF and HCl product streams.
To achieve these results the sulphuric acid requires three sections interconnected by typicals and simple process equipment. These sections comprise the extraction section, the sulphuric acid recovery section and the hydrogen fluoride and hydrogen chloride separation section. The cyclohexanol process requires five sections: The extraction section, the hydrogen fluoride and hydrogen chloride recovery section, the hydrogen fluoride and hydrogen chloride separation section, the cyclohexanol recovery section and the water removal section. These sections are again interconnected by typicals and simple process equipment.

In both the processes several distillation columns are used. It can be concluded that for these columns packed bed columns are easier to construct and have a lower column height. Exception is the extraction column in the cyclohexanol process, for which the rotating disc column (better extraction performance) is used at the expense of the sieve plate and packed column.

The average investment costs for the sulphuric acid process are 27278.56 kdfl. The total production costs per year are 10040.70 kdfl and the total revenues are 5130.89 kdfl. This means that the profit will be -4909.82 kdfl.

The average investment costs of the cyclohexanol process are 28698.30 kdfl. The total production costs are 9845.28 kdfl and the revenues will also be 5130.89 kdfl. This results in a profit of -4714.40 kdfl. The investment costs of the cyclohexanol process are higher than those of the sulphuric acid process. This is logical because the cyclohexanol is a more complex process and requires more equipment.

For both processes a Return On Investment of 10 % has been taken. This is a realistic value for a project in the environmental scope. This results for both processes in an internal rate of return of 12.3 % and a pay out time of 2.6 years. An internal rate of return of 12.3 % is not very high, but it is not so low that the entire project cannot be carried out. A project which has a pay out time of 2.63 is a very viable project.

As are most waste treatment processes the project is loss-making. However this project together with the thermal converter guarantees the continuity of the DuPont site in Dordrecht. This is important because if in the future still HFC’s and CFC’s are emitted to the environment the entire site will be threatened with a shut down. By building the thermal converter unit and one of the developed processes the emissions to the air are significantly reduced and the disposed waste streams are within draining limits. This saves a levying for the waste streams and, more importantly, guarantees the continuity of the plant.

11.2 Choice between the sulphuric acid and the cyclohexanol process

There are a lot of criteria on which both the processes can be compared with each other. The criteria will be discussed and per criterion an advice will be given what process prevails in that area.

1. The cyclohexanol process is more complex than the sulphuric acid process, for it has more unit operations and more recycles. On the basis of the process complexity the sulphuric acid process will be chosen.
2. If one considers the corrosiveness of the processes it is obvious that the sulphuric acid process is more corrosive and more expensive construction materials have to be used. Taking this into account the cyclohexanol process will be a better choice.
3. When the maximum temperatures of the processes are compared it turns out that the cyclohexanol process has the highest temperature (200 °C). When HF is present in such part of the process a problem with the construction materials will occur. A Teflon lining can only be used until about 180 to 190 °C. A metal like monel or inconel will be more subjected to corrosion than a Teflon.
lining, but is more resistant to high temperatures. Another problem with this high temperature is that DuPont has to build a new steam line to provide steam with a temperature that can be sufficient to be used in the reboiler where the temperature is about 200 °C. On the basis of the temperature in the processes the sulphuric acid process will be a better choice.

4. The number of recycles influences the process control. The more recycles present the more difficult the process control is because now a change in the end of the process also influences variables to be controlled in the beginning of the process. It is obvious, that the sulphuric acid process will be preferred over the cyclohexanol process regarding the process control. The rest of the process control is the same for both the processes.

5. It is less desirable to have sulphuric acid in the HF product stream than cyclohexanol, because cyclohexanol can be easier removed than sulphuric acid by for instance blowing air through the HF stream. Sulphuric acid cannot be removed that easily and sulphuric acid contains sulphur atoms which might poison the catalyst in a process in which the HF will be applied. From this point of view the cyclohexanol process is a better choice.

6. Looking at the Safety, Health and Environment aspects of both the processes the sulphuric acid is more hazardous than cyclohexanol. On the other hand cyclohexanol is an organic chemical and therefore it is more liable to explode when present in the gas phase. It is several times in the gas phase, so the explosion hazard will be greater with the cyclohexanol process. Taking this into account the sulphuric acid process can be build in stead of the cyclohexanol process.

7. The waste water that leaves the process will have to be further treated if it contains cyclohexanol, whereas waste water that contains sulphuric acid can be neutralised if the pH is too low which is easier to do. This means that the sulphuric acid process is preferred above the cyclohexanol process.

8. The specifications were easier achieved during the simulation with the sulphuric acid process than with the cyclohexanol process. With the cyclohexanol process several artifacts had to be made to achieve the specifications given by DuPont. The results of the sulphuric acid were better than those of the cyclohexanol process. From this point of view the sulphuric acid can better be chosen than cyclohexanol.

9. The technology used in the cyclohexanol process is more complex than that of the sulphuric acid process. The equipment is more specialised and requires a training for the people at DuPont to operate for instance the liquid-liquid extraction with the rotating disc column. Also the extraction of HF with cyclohexanol is not proven for 100 % and the stripping of organics from water is not well known at the site of DuPont in Dordrecht. This means that more research will have to be done to determine if this process will really work in practice. The technology used in the sulphuric acid process is more proven and will cost less research to implement it at the DuPont site in Dordrecht. Based on this comparison the sulphuric acid process is a better choice.

10. The simulation of the cyclohexanol process is not fully optimised. In the future it could be examined to eliminate one column from the process in order to save investment costs. Since the format of the sulphuric acid process is more complete than that of the cyclohexanol process, it is better to move forward with the sulphuric acid process.

11. The amount of waste produced by both the processes is assumed to be equal, but the waste of the cyclohexanol process is more difficult to process, because it cannot be drained in the river. Facilities will have to be built to process the cyclohexanol, whereas the sulphuric acid can be easier treated by neutralising it with caustic soda if the pH is too low. so it can be drained. The cost to neutralise the sulphuric acid is also probably lower than the cost to build a distillation column to separate the waste cyclohexanol from the waste water.

12. Another argument is to choose for the sulphuric acid process is the fact, that the distribution coefficients are a big uncertainty in the cyclohexanol process. If the calculation of the coefficients turns out not to be correct, the entire process will not work and is consequently doomed to failure.

13. The investment costs of both the processes are about the same. The financial results of the cyclohexanol process are slightly better. The results don't differ that much to make this criterion the decisive factor.
The most important of the criteria given above have been included in table 11.1 and have been given ratings from ++, +, 0, - and --.

Table 11.1 Comparison table of both the processes

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Sulphuric acid process</th>
<th>Cyclohexanol process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process complexity, process set up</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Number of recycles</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Corrosiveness</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Maximum temperatures</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Construction materials</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Process control</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Extractant in product streams</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Safety, Health and Environment</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Waste water</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Simulation results</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Ease of technology applied</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Distribution coefficient</td>
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<td>-</td>
</tr>
<tr>
<td>Financial aspects</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Based on the criteria above and the ratings in table 11.1 the advice can be given to take the sulphuric acid process to the next stage of development. This because on most of the mentioned criteria the sulphuric acid is preferred to the cyclohexanol process. In short the sulphuric acid process uses less process equipment, is less complex and therefore easier to control, possesses more reliable modelling results and is based on more proven technology. The only major negative point for the sulphuric acid process is that this process operates at very corrosive circumstances. This is the consequence of a combination of the present acids with water.

11.3 Recommendations

The distribution coefficients are a big uncertainty in the cyclohexanol process, if these turn out to be incorrect the possibility exist that the process results will not be the same. Therefore more research has to be done to determine these coefficients more correctly. Experiments on either lab scale or pilot plant scale should be undertaken.

More thorough simulation research will probably lead to a more efficient process for cyclohexanol, meaning that the number of columns in this process will be possibly reduced by one.

The literature search that resulted in the possibility of an application of “electrodialysis” (lit P12, reference list) for the dehydration of the HF should also be thoroughly investigated in the future. This membrane technique is very clean and does not require any additional chemicals like in extraction.

In a more detailed design of the process pinch technology can be applied. As stated before the heat integration is not very relevant in this phase of the design. (the economic and environmental values are not very high in this process)

To future preliminary plant design groups it is recommended to give more priority to work out another process for recovery (electrodialysis), justification of the set up of the these processes, rather than trying to perfectionate the simulation of the processes to the utter perfection.
## List of symbols

### Symbols Chapter 4

<table>
<thead>
<tr>
<th>Symbols § 4.1.1</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>column diameter</td>
<td>m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbols § 4.1.1.1</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>HETP</td>
<td>height of an equivalent theoretical plate</td>
<td>m</td>
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<table>
<thead>
<tr>
<th>Symbols § 4.1.1.3</th>
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<td>μ</td>
<td>surface tension</td>
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<tr>
<td>C&lt;sub&gt;s&lt;/sub&gt;</td>
<td>capacity</td>
<td>m/s</td>
</tr>
<tr>
<td>v</td>
<td>superficial gas velocity</td>
<td>m/s</td>
</tr>
</tbody>
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<table>
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<th>System_Base_HETP</th>
<th>Efficiency of packing</th>
<th>-</th>
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<tbody>
<tr>
<td>A</td>
<td>coefficient</td>
<td>mm</td>
</tr>
<tr>
<td>n</td>
<td>amount of moles</td>
<td>mole</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>P</td>
<td>pressure</td>
<td>Pa</td>
</tr>
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<td>gas constant</td>
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<td>m</td>
</tr>
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<td>H&lt;sub&gt;reboiler&lt;/sub&gt;</td>
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<td>m</td>
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<th>Symbols § 4.1.1.4</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>P&lt;sub&gt;c&lt;/sub&gt;</td>
<td>column pressure</td>
<td>N/mm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>D&lt;sub&gt;i&lt;/sub&gt;</td>
<td>column diameter</td>
<td>mm</td>
</tr>
<tr>
<td>J</td>
<td>joint factor</td>
<td>-</td>
</tr>
<tr>
<td>f</td>
<td>design stress</td>
<td>N/mm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>e</td>
<td>wall thickness</td>
<td>mm</td>
</tr>
</tbody>
</table>

<table>
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<th>Symbols § 4.1.1.5</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>N&lt;sub&gt;m&lt;/sub&gt;</td>
<td>minimum number of stages</td>
<td>-</td>
</tr>
<tr>
<td>X&lt;sub&gt;LK&lt;/sub&gt;</td>
<td>liquid light key</td>
<td>-</td>
</tr>
<tr>
<td>X&lt;sub&gt;HK&lt;/sub&gt;</td>
<td>liquid heavy key</td>
<td>-</td>
</tr>
<tr>
<td>d</td>
<td>top</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>bottom</td>
<td>-</td>
</tr>
<tr>
<td>Y&lt;sub&gt;LK&lt;/sub&gt;</td>
<td>vapour light key</td>
<td>-</td>
</tr>
<tr>
<td>Y&lt;sub&gt;HK&lt;/sub&gt;</td>
<td>vapour heavy key</td>
<td>-</td>
</tr>
<tr>
<td>r&lt;sub&gt;LK&lt;/sub&gt;</td>
<td>relative volatility</td>
<td>-</td>
</tr>
</tbody>
</table>
symbols § 4.1.1.2.1

- \( D_c \) column diameter \( \text{m} \)
- \( V_w \) vapour rate \( \text{kg/s} \)
- \( v \) vapour density \( \text{kg/m}^3 \)
- \( u_v \) vapour velocity \( \text{m/s} \)
- \( l_t \) plate spacing \( \text{m} \)
- \( L \) liquid density \( \text{kg/m}^3 \)
- \( H_{\text{tray section}} \) height tray section \( \text{m} \)

symbols § 4.1.1.2.2

- \( u_f \) flooding vapour velocity \( \text{m/s} \)
- \( K_1 \) constant \( - \)
- \( v \) vapour density \( \text{kg/m}^3 \)
- \( l \) liquid density \( \text{kg/m}^3 \)
- \( F_{LV} \) liquid-vapour flow factor \( - \)
- \( L_w \) liquid flow \( \text{kg/s} \)
- \( V_w \) vapour flow \( \text{kg/s} \)

symbols § 4.1.1.2.4

- \( u_h \) minimum vapour velocity through holes \( \text{m/s} \)
- \( d_h \) hole diameter \( \text{mm} \)
- \( K_2 \) constant \( - \)
- \( h_{ow} \) weir crest \( \text{mm liquid} \)
- \( L_w \) liquid flow \( \text{kg/s} \)
- \( l_w \) weir length \( \text{m} \)

symbols § 4.1.2

- \( V \) volume \( \text{m}^3 \)
- \( v \) flow stream \( \text{m}^3/\text{hr} \)
- \( H_t \) hold up-time \( \text{hr} \)
- \( V_{\text{typicals}} \) volume of typicals \( \text{m}^3 \)
- \( V_{\text{equipment}} \) volume of equipment \( \text{m}^3 \)
- \( V_{\text{piping}} \) volume of piping \( \text{m}^3 \)

symbols § 4.1.4.2

- \( Q \) heat transferred per unit time \( \text{W} \)
- \( U \) the overall heat transfer coefficient \( \text{W/m}^2 \text{K} \)
- \( A \) heat-transfer area \( \text{m}^2 \)
- \( T_m \) the mean temperature difference \( \text{K} \)
- \( U_0 \) \( \text{U based on outside area of tube} \) \( \text{W/m}^2 \text{K} \)
- \( h_0 \) outside fluid film coefficient \( \text{W/m}^2 \text{K} \)
- \( h_{od} \) outside dirt coefficient \( \text{W/m}^2 \text{K} \)
- \( d_o \) tube outside diameter \( \text{m} \)
- \( d_i \) tube inside diameter \( \text{m} \)
- \( k_w \) thermal conductivity of the tube material \( \text{W/m}^2 \text{K} \)
- \( h_i \) inside fluid film coefficient \( \text{W/m}^2 \text{K} \)
- \( h_{id} \) inside dirt coefficient \( \text{W/m}^2 \text{K} \)

symbols § 4.1.4.3

- \( F_t \) temperature correction factor \( - \)
- \( R \) dimension less temperature ratio \( - \)
- \( S \) dimension less temperature ratio \( - \)
symbols § 4.1.7.4

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>P</td>
<td>power</td>
<td>W</td>
</tr>
<tr>
<td>P</td>
<td>pressure differential across the pump</td>
<td>Pa</td>
</tr>
<tr>
<td>v</td>
<td>flow rate</td>
<td>m³/s</td>
</tr>
<tr>
<td>p</td>
<td>pump efficiency</td>
<td>-</td>
</tr>
<tr>
<td>d</td>
<td>pipe diameter</td>
<td>m</td>
</tr>
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</table>

symbols § 4.2.1.1

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<th>Symbol</th>
<th>Description</th>
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</tr>
</thead>
<tbody>
<tr>
<td>dh</td>
<td>hole diameter</td>
<td>m</td>
</tr>
<tr>
<td>We</td>
<td>Weber number</td>
<td></td>
</tr>
<tr>
<td>uh</td>
<td>velocity through hole</td>
<td>m/s</td>
</tr>
<tr>
<td>dp</td>
<td>Sauter diameter</td>
<td>m</td>
</tr>
<tr>
<td>Ah</td>
<td>active surface of holes</td>
<td>m²</td>
</tr>
<tr>
<td>Ad</td>
<td>downcomer surface</td>
<td>m²</td>
</tr>
<tr>
<td>Dr</td>
<td>column diameter</td>
<td>m</td>
</tr>
<tr>
<td>Us</td>
<td>velocity of the dispersed phase</td>
<td>m/s</td>
</tr>
<tr>
<td>h</td>
<td>hold up of the dispersed phase</td>
<td></td>
</tr>
<tr>
<td>Ht</td>
<td>distance between two plates</td>
<td>m</td>
</tr>
<tr>
<td>Emd</td>
<td>Murphee plate efficiency</td>
<td></td>
</tr>
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symbols § 4.2.1.2

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>dp</td>
<td>droplet size</td>
<td>m</td>
</tr>
<tr>
<td>HTU</td>
<td>height of mass transfer stage</td>
<td>m</td>
</tr>
<tr>
<td>HDU</td>
<td>total axial height</td>
<td>m</td>
</tr>
<tr>
<td>HETS</td>
<td>Theoretical height stage</td>
<td>m</td>
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symbols § 4.2.2.1

<table>
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>HOG</td>
<td>height of overall gas phase transfer unit</td>
<td>m</td>
</tr>
<tr>
<td>n</td>
<td>slope of equilibrium line</td>
<td></td>
</tr>
<tr>
<td>Gm</td>
<td>vapour mole flow</td>
<td>mol/s</td>
</tr>
<tr>
<td>Lm</td>
<td>liquid mole flow</td>
<td>mol/s</td>
</tr>
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symbols § 4.2.2.1.1

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<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vw</td>
<td>vapour mass flow-rate per unit area</td>
<td>kg/m²s</td>
</tr>
<tr>
<td>K₄</td>
<td>parameter</td>
<td></td>
</tr>
<tr>
<td>Fₚ</td>
<td>packing factor</td>
<td>m⁻¹</td>
</tr>
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Symbols Chapter 10

symbols § 10.1.1.2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>Iₜot</td>
<td>total investment</td>
<td>kdf1</td>
</tr>
<tr>
<td>Iₘ</td>
<td>battery limit investment</td>
<td>kdf1</td>
</tr>
<tr>
<td>Iₜ</td>
<td>non-material investment</td>
<td>kdf1</td>
</tr>
<tr>
<td>Iₘ</td>
<td>working capital investment</td>
<td>kdf1</td>
</tr>
<tr>
<td>Iₘ</td>
<td>price per functional unit</td>
<td>kdf1</td>
</tr>
<tr>
<td>Cₕ</td>
<td>plant cost index</td>
<td></td>
</tr>
<tr>
<td>Cₜ</td>
<td>complexity factor</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>number of functional units</td>
<td></td>
</tr>
<tr>
<td>Tₜ</td>
<td>temperature factor</td>
<td></td>
</tr>
<tr>
<td>Sₚ</td>
<td>pressure factor</td>
<td></td>
</tr>
<tr>
<td>Sₘ</td>
<td>pressure material</td>
<td></td>
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symbols § 10.1.1.3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>capacity of the process</td>
<td>ktons/year</td>
</tr>
<tr>
<td>f</td>
<td>costliness factor</td>
<td>-</td>
</tr>
<tr>
<td>S_i</td>
<td>score</td>
<td>-</td>
</tr>
</tbody>
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symbols § 10.1.2

<table>
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_T</td>
<td>total costs</td>
<td>kdfl/year</td>
</tr>
<tr>
<td>K_P</td>
<td>production volume dependent costs</td>
<td>kdfl/year</td>
</tr>
<tr>
<td>K_I</td>
<td>investment dependent costs</td>
<td>kdfl/year</td>
</tr>
<tr>
<td>K_L</td>
<td>labour dependent costs</td>
<td>kdfl/year</td>
</tr>
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symbols § 10.1.2.2

<table>
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>f</td>
<td>maintenance cost factor</td>
<td>-</td>
</tr>
<tr>
<td>i</td>
<td>capital charge for annuities and writing off the investment</td>
<td></td>
</tr>
</tbody>
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symbols § 10.1.2.3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>uncalculated labour expense dependent cost factor</td>
<td>-</td>
</tr>
<tr>
<td>L</td>
<td>total labour expense</td>
<td>kdfl/year</td>
</tr>
<tr>
<td>N</td>
<td>number of process steps</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>product capacity</td>
<td>kdfl/year</td>
</tr>
</tbody>
</table>

symbols § 10.1.3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>ROI</td>
<td>return on investment</td>
<td>%</td>
</tr>
<tr>
<td>IRR</td>
<td>internal rate of return</td>
<td>%</td>
</tr>
<tr>
<td>POT</td>
<td>pay out time</td>
<td>years</td>
</tr>
</tbody>
</table>

Symbols in process flow sheets, appendix D and K

- C: column
- E: heat exchanger
- P: pump
- V: buffer vessel
- V: valve
- V: tank
- CC: composition control
- PC: pressure control
- RC: ratio control
- TC: temperature control
- LC: level control
- LLC: low level control
- HLC: high level control
- TSP: temperature setpoint
- RSP: ratio set point
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18. Sc. Jansen, TNO Institute of environmental science, +31 55 549 3801
Recovery of HF via the cyclohexanol extraction process

M. Cremers
I.D. Heemstra
J.M. Kleinveld
D.J. Peet

Preliminary Plant Design nr. 3194
Confidential April 1997

Stream number
Temperature (°C)
Absolute pressure (kPa)