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Conceptual Process Design

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Subject

SO_2 and CO_2 removal from flue gas

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Abstract

The emission of green house gases is becoming of ever increasing worries to the international community. The fossil fuel consumption is still increasing and therefore the emission of the green house gases. Many uncertainties exist around the negative effects arising from large concentrations of green house gases in the atmosphere. To prevent possible negative effects in the future many countries start taking action to reduce the emission of these gases a good example is off course the Kyoto protocol.

With the actions taken by the different countries new legislations are made. To be able to comply with these increasingly stricter rules the performance of the treatment installations of plants that produce large quantities of green house gases has to be improved. Large producers of green house gases are the coal fired power plants. Therefore in this project a conceptual design for a process is made that removes SO_2 and CO_2 from the flue gas of such a power plant.

The first important action taken in making the conceptual design is to define a clear task for the process. The defined task demanded that a conceptual design is made for a process that removes at least *99.3%* of the sulphur dioxide content from the flue gas. The process captures as well at least *6%* of the carbon dioxide from the flue gas. The sulphur dioxide is converted to a useful product and the carbon dioxide is just separated and the further processing is outside the scope of this project.

For the separation of carbon dioxide and the separation and conversion of sulphur dioxide different process options are investigated from literature. From the results of this literature study the process options are compared and the best options are selected for further design.
For the separation of carbon dioxide scrubbing the flue gas stream with Mono Ethanol Amine (MEA) is selected as the most realistic and feasible process.
The separation of sulphur dioxide is done by hollow fibres which show great potential in the field of selectivity consumption of energy.
For the conversion of sulphur dioxide two potentially good options were found. One biochemical process and one chemical process were selected. These processes were combined with the membrane separation section. From these combinations two preliminary bases of design have been made. The comparison between the two preliminary BOD's resulted in the selection of the biotreatment process. However after further investigation that assumptions made in integrating the membrane with the conversion sections caused too many uncertainties concerning the feasibility of this process that the chemical process is further developed.

The chemical process is based on a process developed at the international research institute ISPRA and is called Mark-13A. In this process the sulphur dioxide is together with bromine and water converted to sulphuric acid and hydrogen bromide and the sulphuric acid. The sulphuric acid is concentrated and sold. The hydrogen bromide is regenerated back to bromine with electrolysis. During this electrolysis hydrogen is formed in the same amount as bromine.

The overall process converts almost 99.8% of the sulphur dioxide and separates 6% of the carbon dioxide. A total amount of 50000 t/a technical grade sulphuric acid is produced.

From conceptual process equipment design the total investment is estimated to be around *150 M€*. The largest part of this investment goes to the sulphur dioxide separation membrane section. The meet the specified separation 177 membrane units of 1x2m are needed. However when comparing this required investment with other flue gas desulphurization units like a unit build in Bulgaria at the Maritza coal plant which costs 650 M€ the investment seems feasible.

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1 Introduction

It is well known that there is a large demand for energy that is growing every day, especially since some of the developing countries are increasing their industries at a very high rate. Most of the energy is generated by the combustion of fossil fuels and these often contain considerably high amounts of sulphur. By combusting these fossil fuels the greenhouse gases carbon dioxide (CO_2) and sulphur dioxide (SO_2) are released into the earth's atmosphere. Recently, coals have been given more attention since the oil fields tend to dry out. The desulphurisation of the flue gas is therefore becoming a more important issue. The flue gas consists in this project of the following data:

Table 1-1: Feed specifications

Flow rate	$2\ 10^6 Nm^3/h$	Composition	SO_2	$2000mg/m^3$
Temperature	$120–140\ ^0C$		CO_2	12.9vol.%
Pressure	1.1bar		H_2O	6.9vol.%
			N_2	75.2vol.%
			O_2	5.0vol.%
			HCl	$250mg/m^3$
			HF	$25mg/m^3$
			Fly ash	$75mg/m^3$

SO_2 is a rather hazardous species concerning health issues and it contributes substantially to environmental issues such as the formation of acid rain and the depletion of the ozone layer. The amount of SO_2 in flue gas of a coal-fired power plant is not very high (*$2g/m^3$*) [5], but since the volumetric flow of flue gas is very large (*$2*10^6m^3/h$*) a considerably high amount of SO_2 is still released into the atmosphere (*4ton/h*). To reduce the SO_2 emissions many countries have issued regulations on the amount of SO_2 that is allowed to be released into the earth's atmosphere. To meet these regulations several techniques have been introduced to reduce SO_2 emissions. Some of these techniques are developed to remove sulphur prior to the combustion and some are developed to remove SO_2 from flue gas.

The main current process for desulphurisation of refinery off gas and the flue gas desulphurisation of coal-fired power plants is the wet flue gas desulphurisation (wet-FGD) process. This process produces gypsum by reacting SO_2 with limestone. However, this is not a suitable solution for the future, because of the low efficiency (only 90% of the SO_2 can be removed) and the end product (gypsum) is not economically feasible anymore. The construction sector demands increasing quality of the gypsum with lower contents of contaminants (e.g. ashes), which cannot be achieved. Only three plants in the United States find this process economically feasible [20]. Table 1-2 shows the parameters for the wet flue gas desulphurisation.

One goal of this design project is therefore to design an economically feasible process and product for SO_2 in flue gas, which will meet future legislations on SO_2 emissions.

Table 1-2: Parameters wet flue gas desulphurisation

Parameter	Size
Height of absorber	*40m*
Diameter of absorber	*17m*
Desulphurisation efficiency	*90%*
Limestone consumption	$6{,}5\cdot10^{3}kg/h$
Water consumption	$2{,}8\cdot10^{3}kg/h$
Production of gypsum	$1{,}2\cdot10^{4}kg/h$

Besides a considerable amount of SO_2, very large amounts of CO_2 are emitted ($12.9vol\%=186g/m^3=373ton/h$). CO_2 is the most abundant greenhouse gas in the earth's atmosphere and it is believed that it has a large impact on the climate on global scale. Since 1997, European countries have agreed in the Kyoto Protocol on reducing the CO_2 emissions *8%* below the CO_2 emissions of 1990. This corresponds to a total reduction of 190 million tonnes of CO_2 [5]. The Netherlands is allowed to reduce the carbon dioxide emissions *6%* below the 1990 amount. With these new regulations companies can only emit CO_2 to a certain level and if they don't comply with this legislation they will be fined. The fines will be *€100/ton* of CO_2 per year so an annual amount of *€19billion* is involved. This is an enormous amount of money and therefore much research is done to find new CO_2 capture processes and possible ways of disposing it. The second goal of this design project is therefore to design a process that captures a significant part of the CO_2 produced.

This design problem therefore consists of two different parts, which should both be considered for the design. The principal, Dr. C.S. Bildea, has issued the problem of designing a plant that is able to remove SO_2 from flue gas which will meet future legislation ($<0{,}7mol\%$ SO_2 emissions) and is capable of capturing a significant part of CO_2 of the flue gas.

There are many different opportunities for the removal of SO_2 from flue gas. The two most promising are a process with bacteria that convert HSO_3^- into elemental sulphur and a process with chemical conversion of SO_2 with bromine into sulphuric acid. Both sulphuric acid and elemental sulphur are considered to be useful end products.

Sulphur, produced in the biochemical process, is an important chemical used as feedstock for e.g. sulphuric acid production. Most of the sulphur is produced through mining sulphur and only a small part comes from flue gas desulphurisation plants. Although every day more sulphur is produced by the desulphurisation of flue gas it is still not enough to satisfy the demand. One ton of pure sulphur costs *€60*, but the price of sulphur has increased the past years and is likely to keep on rising. This trend is due to a worldwide increase in the demand of sulphur especially in rapidly developing countries like China and India. Sulphur could therefore be a useful end product.

Sulphuric acid, produced in the chemical process with bromine, is also a useful product. It is used in the fertiliser industry and in many other processes such as petroleum refining, copper leaching and in the pulp and paper industry. It is by far the largest-volume chemical commodity produced as claimed by Moulijn in [6]. It has an annual production of over *130 million ton*. The price of sulphuric acid is *€70/ton*.

The biochemical process is based on two other processes, the THIOPAQ process [7] and a process described by Ebrahimi in [20]. The major advantages of this process are that it has low hazard potential, high performance and low energy consumption. The chemical process is based on the Mark-13A process described by van Velzen et al. in [8]. The major advantages of this process are the good performance, the widely available knowledge and the relatively small process streams.

Since Paques already sells the complete solution to the desulphurisation of the flue gas, it is decided that this process will not be investigated anymore. It is thought that there is no challenge in copying an existing process. It is most likely a very good solution, but not what this project is aimed at in the authors' opinion. The process chosen is therefore the chemical conversion of SO_2 with bromine into sulphuric acid. The use of bromine and the production of sulphuric acid ensure that safety is an important issue in this process. Special attention is therefore given to chapter 9 (wastes) and 10 (safety analysis).

The second part of the design consists of a carbon dioxide capturing system. The economic feasibility of such a process is related to amount of carbon dioxide that is emitted. No data concerning the current carbon emissions compared to the amount of 1990 has been found, but it is assumed that these emissions are approximately the same. The reduction of *6%* of CO_2 emission, officially based on the emission of 1990, is therefore in this project determined on the amount of the current CO_2 emission. From 2008 to 2012 each year an increased amount of carbon dioxide will have to be captured with a final reduction of *6%* in 2012. Companies exceeding the allowed carbon dioxide limit will be fined for *€100/ton* CO_2 *emitted*. But since a system of emissions rights trading will be introduced, if a reduction of CO_2 emission can be achieved, the emission rights can be sold to other companies. The price of these emission rights is expected to cost around *€20/ton*.

The captured carbon dioxide is relatively pure and can be sold. Since it is believed that the ocean will eventually take up all anthropogenic-emitted carbon dioxide, short-circuiting this process by injecting the CO_2 directly into the ocean is a possible solution. This solution however is quite similar to a current applied solution of injecting carbon dioxide into used gas fields.

The carbon dioxide capturing system has been designed for a *6%* capture of carbon dioxide. Carbon dioxide removal is not very widely applied, but the commercially most attractive option is scrubbing with an amine and this is the mostly used process worldwide. Therefore it is decided to design an amine scrubbing process, which is able to remove *6%* of the carbon dioxide from the flue gas.

This project is carried out at the section Process Systems Engineering of the faculty of Chemical Engineering at the TU Delft under the supervision of prof. Henk van den Berg and ir. John Nijenhuis as part of the masters programme in Chemical Engineering. The problem owner is dr. Sorin Bildea.

2 Process options and selection

In this chapter the different process options that were considered during the orientation phase of the project are described and it is clarified why certain processes are suitable to solve the problem and why some of the options are not. At the end of this chapter a process is chosen that is the most suitable process. This process is further developed in the remaining chapters of this report.

2.1 Problem definition

There are many different opportunities for the removal of SO_2 and CO_2 from flue gas. It is therefore important that the design problem is clearly defined. The SO_2 from flue gas has to be removed for at least *99,3%* in order to comply with future legislations. For CO_2 it is required that a significant part of the CO_2 contained in the flue gas is removed.

To obtain a better understanding and a better overview of how the problem is tackled the selection of processes and functions within the design are split into different levels. The overall view of these levels is shown in Figure 0-1 in Appendix 2-X and in the rest of the report is referred to as the process selection diagram. All Levels will be treated separately in this chapter and further chapters.

From the problem statement four different functions within the process to be designed can be identified. This is the first level of the process selection diagram. These four functions are: SO_2 separation, SO_2 conversion, CO_2 separation and CO_2 conversion. The problem statement is very clear about the first two functions, but not about the treatment of CO_2. Therefore in the first decision level a clearer definition of the problem is proposed and if necessary the functions are further specified. Since the problem statement only defines “remove a significant part of the CO_2 from the flue gas”, it has to be defined what a significant part is and what to do with this removed CO_2.

Two options where posted: convert the CO_2 to a useful product or just separate it from the flue gas stream. To make a choice between these options a literature search is performed on opportunities for CO_2 conversion. The different options are compared in Table 2-1. Table 2-1 is based on the descriptions and data given in Appendix 1. Background information on the processes can be found there as well.

Table 2-1: CO_2 conversion possibilities

CO_2 conversion	Know-ledge	Hazard	Inv. Costs	Energy	Mass streams	Size	Perfor-mance	Creative-ness	Fly ash & HF/HCl
Mineralization	+	++	-	--	--	-	+	+	+
Micro-organisms	+/-	++	--	++	+	--	-	++	+
Methanol	+	+/-	+/-	-	--	-	-	-	+/-
Epoxides	-	+	-	+	+/-	+	+/-	+	-
Trees or in greenhouses	-	+	--	++	-	-	-	+/-	--
Injection into ocean	-	-	-	-	+	+	-	-	+/-

None of the options for conversion of CO_2 into a useful product are considered viable enough, therefore it is decided that CO_2 is only to be removed from the flue gas and not converted. Another important factor is the time it will most likely take to design a process for CO_2 conversion or removal. A significant part of the CO_2 is defined as the amount necessary to comply with the Kyoto protocol, which for the Netherlands means a reduction of *6%.* The next step and level of the process selection focuses therefore on CO_2 removal and, as stated in the problem definition, SO_2 removal and conversion.

2.2 Process options; level 2

For the three basic functions defined in the first level an orientating study was performed on what types of processes are available to perform these functions. Each function was at first treated separately hence the three different blocks given in level 2.

2.2.1 SO_2 separation

After a short orientation phase an extensive literature study was performed. From this literature study four different types of processes that are potentially able to perform the SO_2 separation are chosen: membranes, adsorbing spheres, activated carbon and NH_4^+ absorption. These four different processes are not visible in Figure 0-1 and therefore the process analysis and selection block is given in more detail in Figure 0-2 in Appendix 2-X. The descriptions of the four processes are given in Appendix 2-XX. A number of different parameters are used to compare the processes. The parameters and the scores of the process on these parameters are given in Table 2-3.

With “knowledge” the amount of available knowledge on the relevant process is meant. “Inv. Costs” represents the investment costs. The mass streams are also compared and they are judged on the (assumed) size. “Size” means the estimated total combined size of the equipment. For the process selection, it is assumed that a creative process has more value for us rather than a more conventional process. Besides this, the sensitivity to fly ash, HF and HCl is also an important selection criterion.

Table 2-2: SO_2 separation possibilities

SO_2 Separation	Know-ledge	Hazard	Inv. Costs	Energy	Mass streams	Size	Perfor-mance	Creative-ness	Fly ash & HF/HCl
Membranes	+/-	++	--	+	+	+/-	+	+	--
NH_4 absorption	-	+/-	+	+	+/-	+/-	+/-	-	-
Adsorbing spheres	--	+	--	--	+/-	+	+	+	+
Activated carbon	--	++	-	+/-	+/-	--	--	+	-

From the results summarised in Table 2-2 it is decided that only the membranes are suitable to separate the SO_2 from the flue gas. The membranes are energy efficient and show very high selectivity towards SO_2, which is very important in reaching the desired removal fraction.

2.2.2 SO_2 conversion

The procedure used to find and select the most promising process bases for the separation of SO_2 was repeated for the conversion of SO_2. The literature search resulted in six different process bases that are shown in Figure 0-3 in Appendix 2-X. These are: the commonly used limestone scrubbing, the so-called Mark-13, THIOPAQ, Crystasulf, Scot&Claus, and a biotreatment process. The descriptions of these processes are given in Appendix 2-XX. The analysis of their pros and cons is given in Table 2-3.

Table 2-3: SO_2 conversion possibilities

SO_2 conversion	Know-ledge	Hazard	Inv. Costs	Energy	Mass streams	Size	Perfor-mance	Creative-ness	Fly ash & HF/HCl
Mark-13	++	-	+/-	-	+	+	+	+	-
THIOPAQ	+	++	+/-	++	-	+	++	-	++
Biotreatment	+	++	+/-	++	+	-	+	+/-	++
Scot & Claus	+	+	-	-	+/-	-	-	--	-
CrystaSulf	+	+	+	-	--	-	++	+	-
Limestone	++	+	+/-	++	+/-	+/-	-	--	-

Table 2-3 shows three processes that have good potential to perform the SO_2 conversion: the Mark-13 based process, the THIOPAQ process and the bio-treatment process.

The Mark-13 process is strong on performance, a lot of knowledge is available and it is a new and challenging process. THIOPAQ also has high performance but combines it with low energy and low hazard. The bio-treatment resembles the THIOPAQ process and has therefore the comparable advantages, but has a smaller (recycle) mass stream through the process. The THIOPAQ is a proven process that has shown great performance and can reach the SO_2 removal specifications that are required by the assignment. In our opinion the added value of performing a conceptual design is the novelty of the process that is to be designed. The THIOPAQ is already fully designed and build; therefore the redesign of this process has no added value. To be able to come to a more solid choice between the two remaining process, preliminary bases of design (from here on called preliminary BOD) are made for both processes. The BOD is given in chapter 3.

2.2.3 CO_2 separation

The literature search on CO_2 separation possibilities resulted in eight different possibilities. Table 0-4 in Appendix 2-X shows the possibilities for the removal of CO_2 from flue gas. The descriptions of these different processes are given in Appendix 2-XX

From Table 0-4 in Appendix 2-X it is clear that the different techniques for CO_2 removal do not differ significantly. Many are based on absorption principles. It is hard to find well-documented and reliable information, except for the MEA scrubber. Most of the processes, such as cryogenic distillation and MEA absorption are energy intensive. Membranes are difficult to handle with large process streams due to the required low flow velocities. In the first place three different processes are chosen, since they seem to be the most promising. These processes are: absorption in MEA, in NH_4^+ and membranes. On these three separation techniques an in-depth literature search is performed [1], [2], [4]. After this extended literature search it is decided that the MEA absorption process is the most viable process for CO_2 separation. There is much knowledge available on this process and it has good performance and low hazard. It is an expensive process due to high costs of MEA and its regeneration. It is expected however that the reduction of CO_2 will lead to an increase of income by the sale of emission rights. This will give some space for investments.

Table 2-4: CO_2 separation possibilities

CO_2 removal	Knowledge	Hazard	Inv. Costs	Energy	Mass streams	Size	Perfor-mance	Creative-ness	Fly ash & HF/HCl
MEA absorption	++	+	+	--	+/-	-	+	+/-	-
NH_4 absorption	-	+	+	-	+/-	-	+/-	+	+
Membranes	-	+	-	+	+	--	+	+	--
Cryogenic distillation	-	-	--	--	+	--	+/-	-	+
DECAB absorption	--	+	?	?	-	-	+/-	+	-
Desiccant absorption	--	+	+/-	?	+/-	-	-	+	-
Molecular sieve	--	+	+/-	?	+/-	-	-	+	-
Activated carbon	--	+	+	?	+	-	--	+	+/-

2.3 Final process selection; level 3

In the second level of the process selection diagram a process basis for the SO_2 separation and the CO_2 separation, and two process bases for the SO_2 conversion are selected. To be able to come to a more solid choice between these two processes a preliminary BOD is made for both processes. These preliminary BODs are given in Appendix 2-XXX. A short summary of these preliminary BODs is given in the next two paragraphs.

2.3.1 Biochemical SO_2 conversion process

The first step in the making the preliminary BOD is dividing the process into different functions. For the biochemical SO_2 conversion process three different basic functions are defined: feed preparation, conversion and product separation. A schematic representation is given in Figure 2-1.

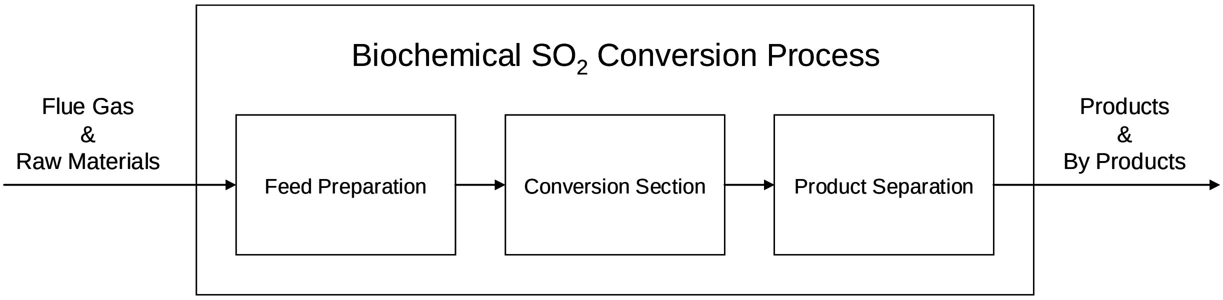

Figure 2-1: Process decomposition scheme biochemical SO_2 conversion process

In the preliminary BOD, the bio-treatment process is combined with strong features from the similar THIOPAQ process. The disadvantage of THIOPAQ is that it has a large stream due to the solvent recycle. The bio-treatment process solves this problem by using a different pH (6,5-7,5). Therefore the stream size throughout the process is significantly reduced. The first reactor used in the new combination is therefore the bio-treatment anaerobic reactor and the second reactor is the aerobic reactor of THIOPAQ. By making this combination, the number of reactors of the bio-treatment is reduced as well, which was one of the drawbacks of that process. All the important choices made concerning the contents of the three basic functions are schematically shown in Figure 2-11 of Appenidx 2-XXX.

2.3.2 Mark-13A based SO_2 conversion process

The other promising option is the process based on the ISPRA Mark-13 process. This process is also divided in three different functions that are almost similar to the functions in the biochemical process. The three different functions defined are: feed preparation, conversion and separation & finishing. The schematic representation is given in Figure 2-2.

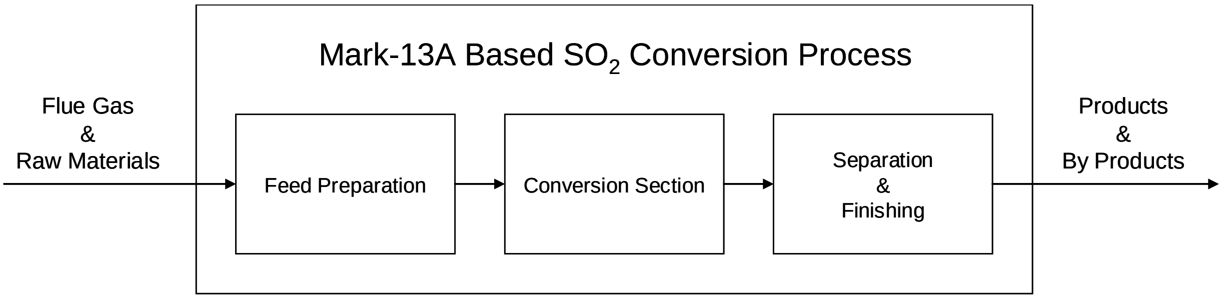

Figure 2-2: Process decomposition scheme Mark-13A based SO_2 conversion process

In the Mark-13A based process the incoming sulphur dioxide is converted with bromine and water to sulphuric acid and hydrogen bromide. The sulphuric acid is concentrated to *96%* and the hydrogen bromide is regenerated to bromine and hydrogen. The choices made within the three basic functions are schematically given in Figure 2-2 of Appendix 2-XXX

2.3.3 Comparison bio-combination and Mark-13 process

An extended comparison table has been made on the basis of preliminary bases of design for both the processes to be able to come to a better comparison. The results are shown in Table 2-5.

Table 2-5: Comparison Mark-13 and Bio-combination

	Mark-13 based process		Bio-combination	
Knowledge	++	Well known	+	Good
Hazard	-	Bromine	+	Nothing special
Energy	+/-	Hydrolysis	+	Good
Operating conditions	+	Sulphuric acid	++	Mild
Size	+/-	5 units	+/-	3 (very) large units
Mass streams	+	Fairly concentrated	+/-	Gas stream
Performance	+	>99,3%	+	>99,3%
End products	+	H_2SO_4 €70/ton	-	S^0 €60/ton
Sensitivity to fly ash, HF and HCl	-	Same for both	-	Same for both
Flexibility to change in flow rate	+	Good	+	Good
Flexibility to change in sulphur amount	+	Good	+	Good
Creativeness	+	Combination of processes	+	Combination of processes
Operational costs	-	Energy costs	+	No high pressure and temperature
Investment costs	+/-	Many large units	+/-	Large units
Margin	+	€3.5M	-	€1.3M

2.3.4 Final recommendation

From Table 2-5 it is concluded that the most promising process is the bio-combination process. The main advantages are its milder operation conditions and lower energy consumption than the other processes. The main disadvantage of the Mark-13A based process is the use of bromine. It is expected that the bio-combination process will generate the best results for the design. This process is therefore taken to the next design level where a final basis of design and the process structure were developed. To our opinion the bio-combination process is the best alternative of the investigated options. In principle the bio-combination should give high conversion is safe and produces a useful product in the form of elemental sulphur.

However after a more detailed analysis and several discussions on the process design the choice for the selected process is changed. The assumptions that were made on the very crucial part of separation of the sulphur dioxide have given rise to large uncertainties and doubts on the feasibility of this separation step. In the original membrane process Na_2SO_3 is used as a solvent. The SO_2 diffusing through the membrane forms with the solvent two molecules of $NaHSO_3$. In the THIOPAQ process the SO_2 is scrubbed with a $NaHCO_3$ solvent forming $NaHSO_3$ and CO_2. This CO_2 formed desorbs into the flue gas. The $NaHSO_3$ is converted in the first reaction section back to $NaHCO_3$. The assumption made in the bio-treatment process is that $NaHCO_3$ can replace the Na_2SO_3 solvent with a membrane configuration. In this way the expensive regeneration of the solvent Na_2SO_3 is avoided because with the use of $NaHCO_3$ the bacteria in the first reactor do the regeneration.

The uncertainties in using $NaHCO_3$ are caused by the formation of gaseous CO_2 on the solvent side of the membrane. The formation of the gaseous CO_2 disturbs the flow in the membrane fibres. Furthermore, it is not clear if this diffuses through the membrane and what will be the effect on the diffusion of SO_2. It is also highly uncertain whether the reaction between $NaHCO_3$ and SO_2 will take place because the position of the equilibrium will be influenced by the fact that the CO_2 is hardly or even not removed from the solvent. If the other solvent Na_2SO_3 is applied, biological regeneration is not possible. In absence of regeneration, continuous addition of solvent is necessary and this is considered a disadvantage. Biomass can also clog the membranes; so expensive filters need to be applied. It is possible to get around this problem, but only by use of an absorption column. Since the membrane separation is a crucial part of the process (replacing it with a absorber-scrubber would result in the original THIOPAQ process), the feasibility is very uncertain.

Therefore the decision is made to further develop the next best alternative, the Mark-13 based process. The Mark-13 based process shows a high conversion and produces two useful products, sulphuric acid and hydrogen. A drawback on the process however is the safety aspect. Due to the use of bromine special attention has to be paid on the safety aspects.

The overall process for the removal of sulphur dioxide and carbon dioxide will consist of the Mark-13 based process for the removal and conversion of SO_2 and the MEA absorption for CO_2 separation. This process is further developed and a conceptual design is made in the following chapters.

3 Basis of Design

In the previous chapter the basic concept of the process is chosen. The Mark-13 process is considered to be the best and most challenging opportunity for SO_2 removal and conversion and the CO_2 will be removed by means of absorption in monoethanolamine. The design is extended to level three and partially level four of the overall selection diagram. Equations for future calculations are presented. This chapter represents the start of the design and can therefore be seen as the basis for all the calculations and process design.

3.1 Description of the Design

This paragraph deals with the design process and focuses on the way the design problem is tackled.

The principal of the design problem is dr. C.S. Bildea and he is interested in the removal of SO_2 and CO_2 on environmental reasons. Future legislations will have to be met in order to avoid large financial fines. There are many different opportunities for the removal of SO_2 and CO_2 from flue gas. It is therefore important that the design problem is clearly defined. The SO_2 from flue gas must be removed for at least *99,3%* so future legislations will be met. For CO_2 it is required that a significant part of the CO_2 from the flue gas is removed.

The design process is divided in several different levels. The entire design process is clearly represented by Figure 2-1 of Appendix 2. The first level of the design process is the definition of the basic functions of the process. The four basic functions defined are given a clearly defined task if not present yet in this level. It is not stated in the problem definition how much CO_2 must be removed or that it should be converted into a useful product. These options are compared in Table 2-1. Since all the options for conversion of CO_2 into a useful product are not considered viable enough due to the shear volume of the gas flow, it is decided that CO_2 is only removed from the flue gas and not converted.

The second level of the design process consists of the computation and comparison of different possibilities for the three remaining basic functions. The different possibilities for the SO_2 separation, the SO_2 conversion and the CO_2 separation are given in Table 2-2, Table 2-3 and Table 2-4. From these tables is decided that a preliminary basis of design is made for the two most promising processes, the bio-treatment process and the mark-13 based process, which are combined with membranes for SO_2 separation and a MEA scrubbing process for the CO_2 separation.

From Table 2-5 it was concluded that the most promising process is the bio-combination process. Unfortunately the use of the SO_2 membrane separation turned out to be unworkable, as stated in paragraph 2.3.4, and the second best option, the mark-13A based process, is further developed and designed. For the treatment of CO_2 is chosen for a MEA absorption column, since this technology is the most developed, has good performance and low hazard.

The resulting process will remove *99.3%* of the sulphur dioxide present in the feed. No other components will be converted. The process will produce concentrated liquid sulphuric acid at technical grade (*96wt%* pure). Per mole of sulphur dioxide converted the process will produce one mole of hydrogen. The hydrogen formed is used for energy production. The bromine is regenerated by electrolysis. No wastewater will be produced since all the chemicals in the process are regenerated and recycled to the reactor. A significant part of the CO_2 will be separated from the flue gas. A significant part is chosen to be *6%*. With this reduction future calculations will be performed.

In the design changing feedstock is taken into account. The amount of SO_2 depends on the type of coals used in the coal-fired power plant. The reactors are designed in such a way that they can handle a decrease of *50%* in flue gas and an increase of *20%* of sulphur dioxide content. This does not influence the quality of the product due to an excess of bromine is used and buffer vessels are placed to be able to control the bromine feed.

The biggest competitor for flue gas desulphurisation installations is Paques with their process based on the biological conversion of SO_2 to elemental sulphur (THIOPAQ). This process has low energy consumption and will therefore be less expensive than the process applied in this design. A disadvantage of the THIOPAQ process can be that employees and operators are not well known with biological operations and this might cause problems with the maintenance. An advantage of the Mark-13 process is the small flow streams that ensure that the reactors and pipes are small.

The biggest problems expected are the dimensions of the membranes and the toxicity of the bromine. The membranes' size is very large because the maximum flow they can handle is low (*~1m/s*) and this must result in multiple membranes in parallel. To solve the bromine problem an extensive safety analysis is carried out, which resulted in strict regulations and recommendations. This process is chosen because most of the data is available or easily retrievable, so no problems are expected.

3.2 Process Definition

This paragraph deals with the Mark-13 process. It gives background information on the calculations with equations and explains the design process for the separate design blocks (SO_2 and CO_2 treatment).

3.2.1 Process Concept Chosen

In chapter 2 the Mark-13A process for SO_2 removal is selected to further develop and design together with a MEA scrubbing process for the CO_2 removal. In this paragraph a more in depth description of this SO_2 and CO_2 process is given. The overall process will be described in two parts, first the desulphurisation section and secondly the carbon dioxide removal part.

Sulphur Dioxide Removal

The basis for this flue gas desulphurisation is based on the ISPRA Mark-13A process, which was extensively investigated by Van Velzen and Langenkamp in [8],[9],[10] and [11]. This regenerative process is based on a hybrid cycle that converts sulphur dioxide to sulphuric acid and hydrogen. In this process the following two reactions form the basis:

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr \tag{3-1}$$

$$2HBr \rightarrow Br_2 + H_2 \tag{3-2}$$

The conversion section of the ISPRA Mark-13A process takes a highly concentrated sulphur dioxide gas stream. Because the flue gas stream itself is dilute in sulphur dioxide a flue gas pre-treatment is needed. The pre-treated gas stream is fed to two reactors in series. In these reactors the sulphur dioxide reacts with bromine and water to sulphuric acid and hydrogen bromide at around *320K–370K*. The second step of the process is the regeneration of the hydrogen bromide. With an electrolysis reaction hydrogen and bromine are formed. The bromine is then fed back to the first step in the process.

The overall process yields two useful products, sulphuric acid and hydrogen, as can be seen from the two reaction equations 3-1 and 3-2. The process will remove *99.3%* of the sulphur dioxide present in the feed. No other components will be converted. The process will produce concentrated sulphuric acid with a quality of *96wt%*, because the sulphuric acid is concentrated in a distillation column after the reaction. Per mole of sulphur dioxide the process will produce one mole of hydrogen. No wastewater is produced since all the chemicals in the process are regenerated and recycled to the reactor.

From the description in paragraph 3.2.1 the process can be decomposed in three different functions, the flue gas pre-treatment, the conversion section and a separation and finishing section where the products and raw materials are separated and either recycled or finished to a valuable product. These different functions are shown schematically in Figure 3-1.

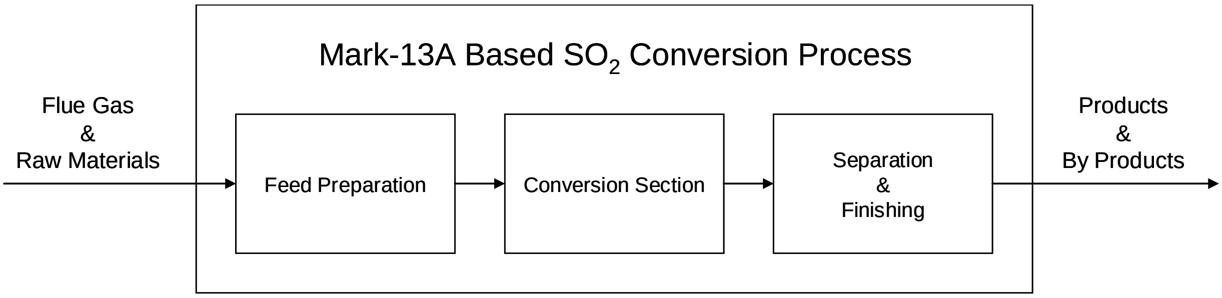

Figure 3-1: Mark-13A based SO_2 conversion process decomposition

The three different functions within the process can be performed with different methods. To make valid choices about which method to use the alternative process configurations diagram shown in Figure 3-2 is used. In this diagram all the alternative methods are shown and the selection for each method is described per level in this paragraph.

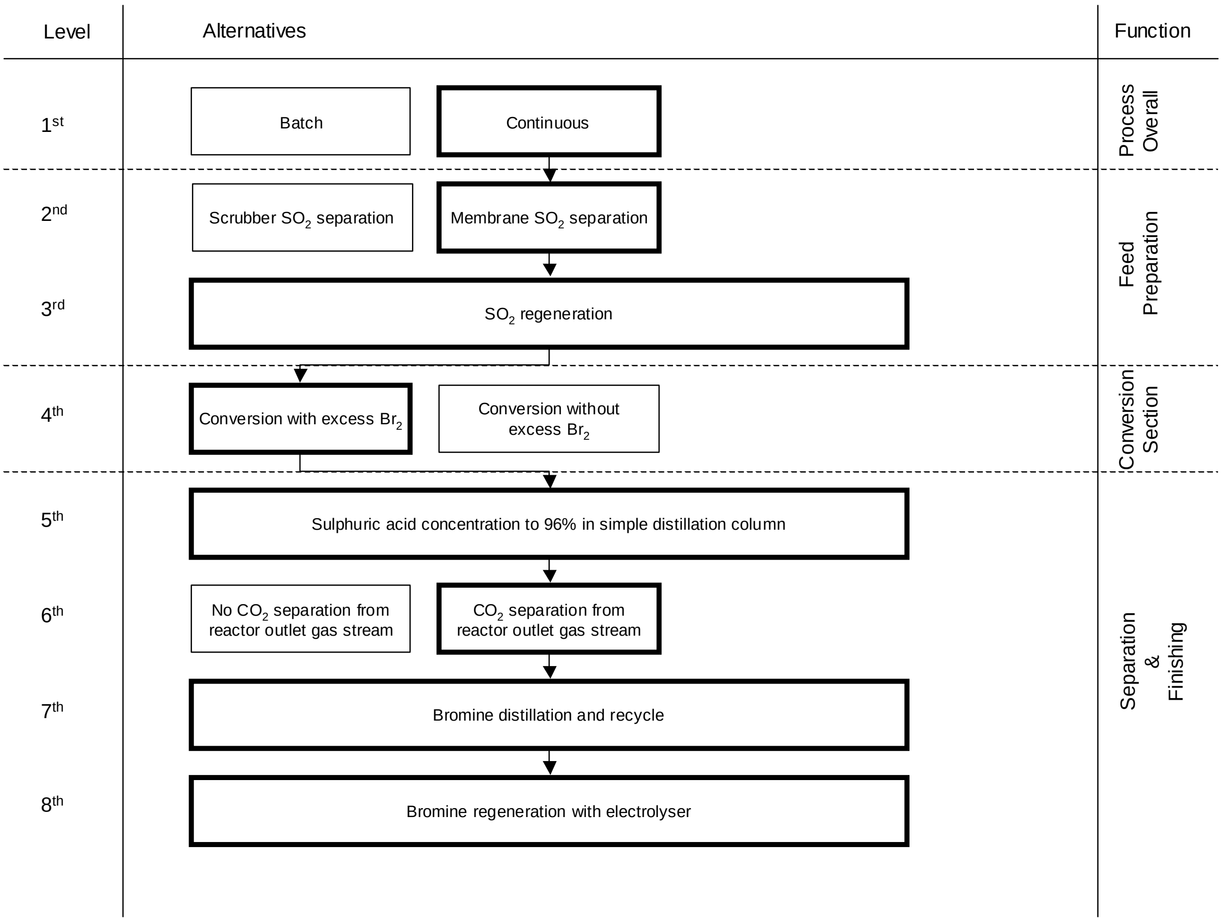

Figure 3-2: Alternative process configurations for the Mark-13A based SO_2 removal process

Level 1

The first level represents the overall decision between batch and continuous operation in the design process. A number of rules of thumb for this decision are given in Douglas [14]. The most important decision parameter for the desulphurisation of flue gas is the capacity. Douglas uses a capacity larger than *10Mlb/yr* or around *5Mkg/yr* as a criterion for continuous operation. Since the amount of sulphur dioxide to be processed is around *32Mkg/yr* continuous operation is the more convenient mode of operation.

Level 2

The second level represents the first step in the desulphurisation process, the feed preparation. Three different options are identified: separation of the sulphur dioxide from the flue gas stream with a membrane, with a scrubber or no separation of the sulphur dioxide at all so using the complete flue gas stream. The last option is not suitable since the conversion section is originally developed for a highly concentrated sulphur dioxide stream and this is not the case then. No separation will also result in pumping significant amounts of useless gas through the process, which causes the equipment to be very large. For this process the membrane SO_2 separation is selected over the scrubber. The criterion for this selection is the higher selectivity of the membranes towards SO_2 as described by Nii et. al. [2]. A schematic overview of the used set-up is given in Figure 3-3.

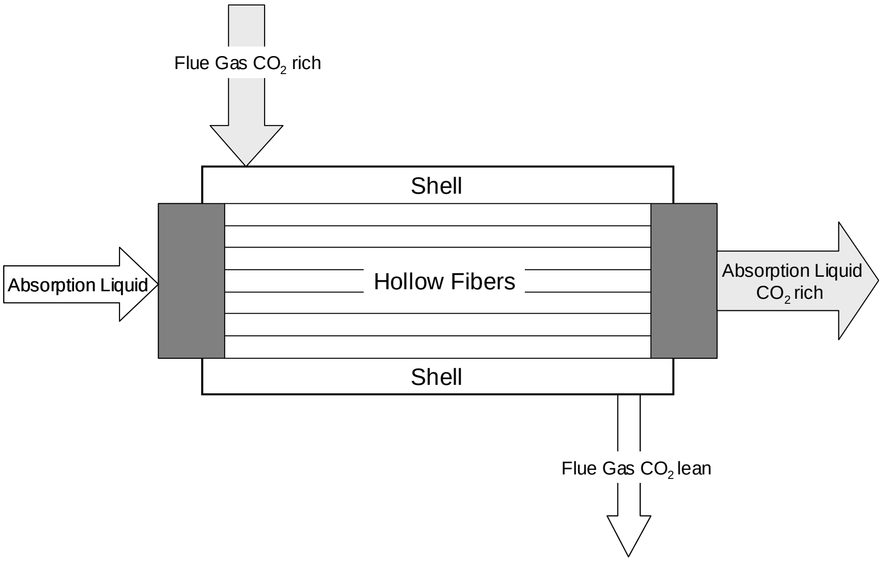

Figure 3-3: Schematic membrane unit overview

Level 3

When separating the SO_2 from the flue gas the SO_2 gets dissolved in a solvent, because the conversion section takes in a highly concentrated SO_2 gas stream the dissolved SO_2 has to be regenerated. There is only one method known to regenerate the SO_2 from the solvent and that is by means of heating (e.g. with steam).

Level 4

The highly concentrated SO_2 stream from the feed preparation section is converted to sulphuric acid, the reaction is given in equation 3-1. This reaction can be performed with or without an excess bromine inlet in the reactor. The advantage of not having an excess bromine inlet is that a bromine free reactor outlet is obtained. The biggest disadvantage of not having excess bromine is that when fluctuations in the SO_2 gas stream occur part of the SO_2 is not converted and therefore the specifications are not met. Since part of the assignment is to be able to handle fluctuations in the SO_2 loading a conversion section with an excess of bromine has been chosen.

Level 5

Level five represents the first step of the separation and finishing section, the product upgrade. The concentration of sulphuric acid is done with an absorber-stripper column. This method is taken directly from the original Mark-13A process [8]. No alternatives are considered because of the simplicity, effectiveness and possibilities of heat integration with the flue gas inlet stream.

Level 6

Level six represents the second step of the separation and finishing section, the cleaning of the outlet gas stream of the reaction section. The outlet gas stream from the conversion section contains some CO_2 that is not converted in the process. This CO_2 will build up in the system through the recycle stream. Therefore the CO_2 has to be removed to prevent accumulation of the CO_2 in the system. This is done with a similar membrane as the SO_2 separation only with a different solvent.

Level 7

Level 7 represents the third level of the separation and finishing section, the recycle of the un-reacted bromine. The un-reacted bromine from the conversion section is recycled, because bromine is a toxic substance and it is not allowed to be released in the environment. For the separation of this bromine a simple distillation column is used. This distillation column is used in the original Mark-13A process [8] as well. Again no alternatives are considered because of the simplicity, effectiveness of this method.

Level 8

Level eight represents the fourth and last step of the separation and finishing section, the regeneration of the hydrogen bromide to bromine. This regeneration is performed with an electrolyser as in the original Mark-13A process. Since the purity of the produced hydrogen is high enough it is used for energy production. Together with the conversion section the HBr electrolysis forms the backbone of both the desulphurisation process described in this paragraph and the original Mark-13A process.

Carbon Dioxide Removal

In Chapter 2 a monoethanolamine (MEA) scrubber is selected as the most suitable option to remove a significant part of the CO_2 from the flue gas. Figure 3-4 shows alternative process configurations for the removal of CO_2. In this diagram all the alternative methods are shown and the selection for each method is described per level in this paragraph.

Level 1

The first level represents the overall process choice between batch or continuous. As for the SO_2 process, here is also chosen for the continuous process since the flow rate of the flue gas is too large to deal with in a batch reactor.

Level 2

The second level represents the feed pre-treatment stage. This requirement is met by the SO_2 removal/conversion process.

Level 3

The third level represents the most important choice for the CO_2 removal. Here is decided that absorption is the best solution because the membrane separation costs too much energy to be feasible.

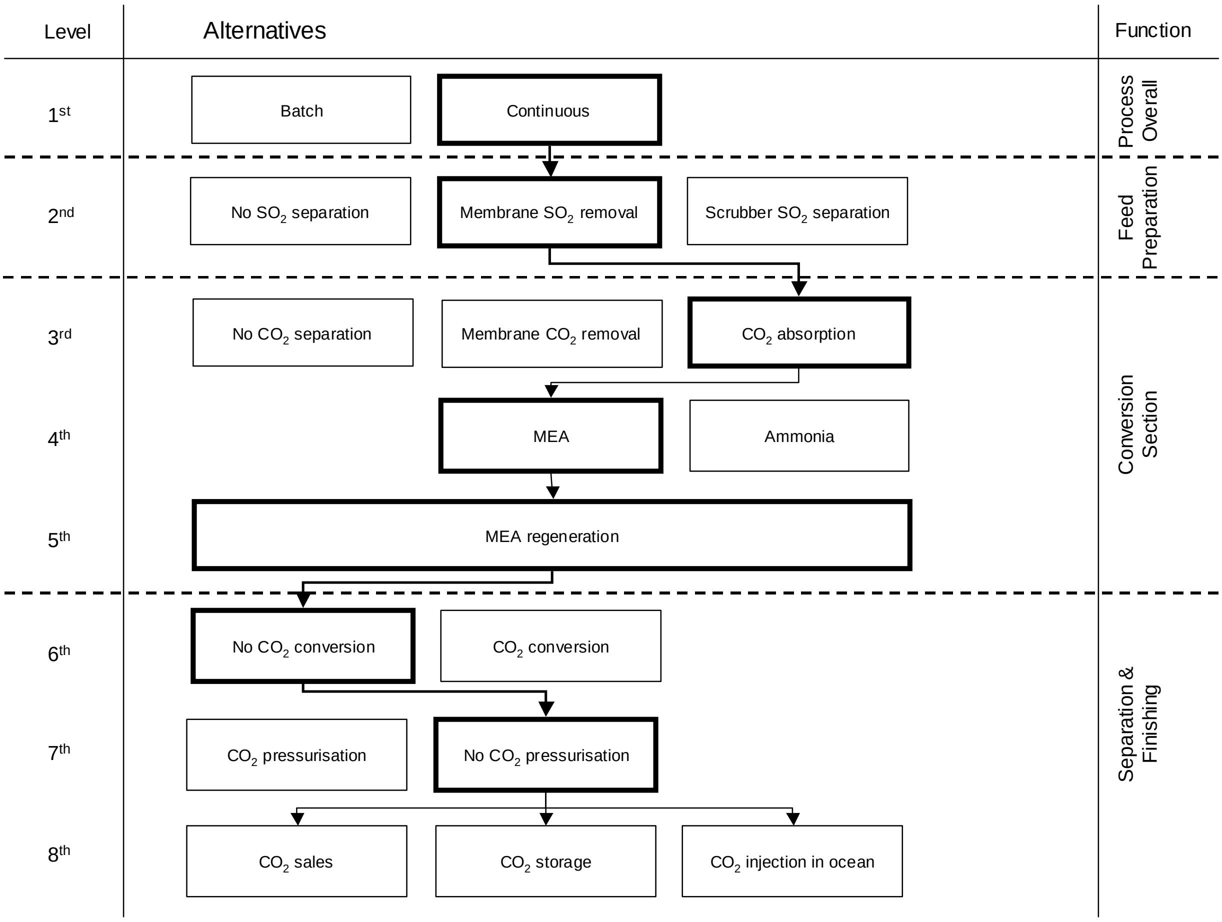

Figure 3-4: Alternative process configuration for the removal of CO_2

Level 4
The fourth level represents the second level of the conversion section. Here the type of absorbent is chosen. Monoethanolamine is chosen over ammonia, because little information is found on this absorbent. MEA is more expensive, but still the more desirable solution.

Level 5
The fifth level represents the regeneration of the MEA. A simple stripper is chosen for this process, because it is easy to model.

Level 6
The sixth level represents the choice between converting CO_2 in another product or not. It is decided in chapter 2 that this is not done to limit the scope of the project.

Level 7
The seventh level represents the collection of the CO_2. It is chosen not to pressurise the CO_2 since this is considered to be outside the scope of our design process.

Level 8

The last level represents the final solution to what to do with the CO_2. There are several possible solutions, such as selling it to potential customers, storage and injection into the ocean. The decision on this level is not included in this project because it is considered to be outside the scope of the project.

3.2.2 Block Scheme

On the basis of the choices made in the previous paragraphs a block scheme is constructed. This block scheme is given in Figure 3-5.

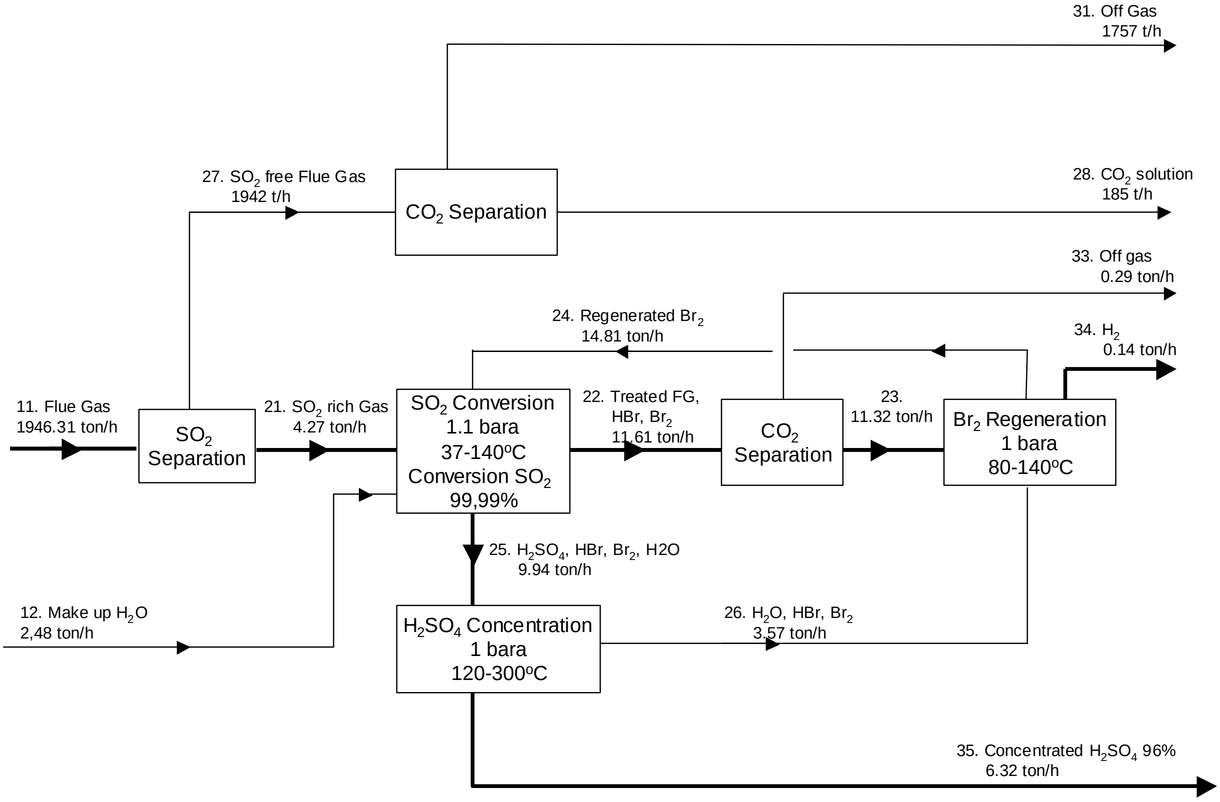

Figure 3-5: Block scheme process

The first block of the process is the SO_2 separation from the flue gas stream. The SO_2 separation block includes a membrane to separate the SO_2 from the flue gas stream and a regeneration section to regenerate the membrane solvent. Before the sulphur dioxide from the flue gas can be converted it has to be separated from the flue gas stream. This separation is done with a hydrophobic Microporous Teflon Hollow Fibre membrane that has a high selectivity towards sulphur dioxide due to the specific solvent used as shown by S. Nii et. al. in [2]. This solvent is a sodium sulphite solution of *0.1M*. Besides sulphur dioxide it will also separate *0.048%* carbon dioxide from the flue gas stream. In this system the following reactions in the liquid film are considered:

$$SO_2 + SO_3^{2-} + H_2O \leftrightarrow 2HSO_3^- \tag{3-3}$$

$$CO_2 + SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + HCO_3^- \tag{3-4}$$

$$SO_2 + HCO_3^- \leftrightarrow 2HSO_3^- + CO_2 \tag{3-5}$$

The equilibrium constants K_{3-3}, K_{3-4} and K_{3-5} at infinite dilution and the reaction rates for the reactions 3-3, 3-4 and 3-5 are given in Table 3-1. It is clear that reaction 3-3 proceeds much faster than the others; its reaction rate constant is much higher.

Table 3-1: Equilibrium constants for the reactions in the liquid film SO_2 absorption, taken from [2].

Reaction number #	Equilibrium Constant K (mol cm^{-2} s^{-1} Pa^{-1})	Reaction rate (m^3 mol^{-1} s^{-1})
3-3	*$2.76x10^5$*	*$\sim10^5$*
3-4	*7.12*	*$2.39x10^{-2}$*
3-5	*$3.08x10^4$*	-

In the simultaneous membrane absorption of SO_2 and CO_2, the SO_2 dissolved in the liquid reacts instantaneously with SO_3^{2-} and is depleted in the liquid boundary film. Figure C-5 in Appendix 3 shows the absorption rates of SO_2 and CO_2 against the liquid velocity, u_L. The filled symbols represent SO_2 and the open symbols represent CO_2. It is clear that the CO_2 flux (J_{CO2}) increases considerably with increasing u_L, whereas the SO_2 flux (J_{SO2}) is hardly influenced by u_L as long as SO_3^{2-} ion in the liquid boundary is not depleted. Thus, for flue gases containing a much lower partial pressure of SO_2 than of CO_2 it is expected that the selective removal of SO_2 with respect to CO_2 is only possible in hydrophobic hollow-fibre membranes under the conditions that the liquid flow rate is low. In other words the SO_3^{2-} concentration near the gas-liquid interface is low.

The microporous hydrophobic Teflon HF membranes are tested and proved to execute the separation by Nii in [2]. The inner diameter d_i=*0.1cm*, the outer diameter is d_o=*0.18cm.* The pores have a maximal diameter of *2µm* and a porosity ε of *0.5*. For the calculation of the membrane separation, the film theory can be applied, because under laminar flow no liquid can escape through the pores of the membrane.

The absorption flux for the permeate gas is expressed as J [mol cm^{-2}s^{-1}] in equation 3-6, taken from Nii in [2]:

$$J = k_G(p - p_1) = k_M\varepsilon(p_1 - p_2) = k_L(C_2 - C) \tag{3-6}$$

The pressure is given by p_x in [Pa] with 1 for the outer surface of HF and 2 for the gas-liquid interface. The concentration C is given in [mol cm^{-3}]. k_G in [mol cm^{-2} s^{-1} Pa^{-1}] and k_L in [cm s^{-1}] are the mass-transfer coefficients for the gas and liquid boundary films, respectively.

k_M is the membrane-transfer coefficient in [mol cm^{-2} s^{-1} Pa^{-1}] given by equation 3-7, taken from Nii in [2]:

$$k_M = \frac{D_G}{\delta RT\tau} \tag{3-7}$$

Where D_G is the diffusion coefficient in the gas phase in [$cm^2\ s^{-1}$], δ the membrane thickness in [cm] and τ is the tortuosity in [-].

Henry's law reads $p=HC$ with H representing Henry's constant in [Pa $cm^3\ mol^{-1}$], so the molar flux is rewritten in terms of the partial pressure as equation 3-8, taken from [2]:

$$J = K_G(p - p^*) \tag{3-8}$$

K_G is the overall gas-phase mass-transfer coefficient in [mol $cm^{-2}\ s^{-1}\ Pa^{-1}$], expressed as the sum of the three transfer resistances, taken from [2]:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{\delta RT\tau}{D_G\varepsilon} + \frac{H}{k_L} \tag{3-9}$$

The mass transfer coefficient in the liquid film k_L can be evaluated from equation 3-10, found in [2]:

$$\frac{k_L d_i}{D_A} = 1.62 \cdot \left[\left(\frac{d_i}{L}\right) \cdot R_e \cdot Sc\right]^{0.33} \tag{3-10}$$

Equation 3-10 uses the module length L in [cm], the Reynolds number (Re) and the Schmidt number (Sc). Values of k_G and k_M are determined using SO_2 in aqueous alkaline solution. A gaseous feed of *0.2%* SO_2 (in N_2) is brought in contact with *1.2 M* NaOH. SO_2 reacts instantaneously with the OH^- ion at the gas-liquid interface inside the HF, thus the overall coefficient K_G becomes

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k_M\varepsilon} \tag{3-11}$$

After absorbing the sulphur dioxide and a little carbon dioxide in the solvent the mixture has to be regenerated. By heating with steam the reactions given in equations 3-3 to 3-5 occur in opposite direction. The resulting gas stream contains mainly sulphur dioxide and around *6%* carbon dioxide. This gas stream is then further processed.

SO_2 Conversion

The second block of the block scheme in Figure 3-5 is the SO_2 conversion section. In the SO_2 conversion section reaction 3-1 is taking place. This reaction is carried out at ambient pressure and at temperatures ranging from *40^oC* to *80^oC*. The design equations for the reactors in this conversion section are given below, equation 3-12 to 3-16.

The first equation is the definition of the relative sulphuric acid concentration. The sulphuric acid concentration has a large influence on the sulphur dioxide conversion in this process; therefore the following definition in equation 3-12 for the relative sulphuric acid concentration (*C*) is of great importance for the design of the process. For this special case the numbers between the square brackets are the mass flow rates of the species. Equation 3-12 is taken from van Velzen in [11].

$$C = \frac{[H_2SO_4]}{[H_2SO_4]+[H_2O]} \; [wt/wt] \tag{3-12}$$

Another important design parameter in this process is the number of overall gas transfer units (N_{og}). The relation for this number is given in equation 3-13, taken from [11], whereby the Y is the sorbent mol fraction in the gas phase.

$$N_{og} = \ln \frac{(Y - Y_{eq})_{in}}{(Y - Y_{eq})_{out}} \tag{3-13}$$

Table 3-2: Equilibrium sorbent mol percentages in the gas phase for relative H_2SO_4 concentrations, taken from [11].

Relative H_2SO_4 concentration	Y_{eq} (%)
0.747	*2.89*
0.641	*0.00*

An alternative expression for the number of overall gas transfer units is found from the mass balance and is given in equation 3-14, taken from [11].

$$N_{og} = \frac{K_g azAP}{G} \tag{3-14}$$

The cross-sectional area is given by A in [m^2], the height of the column as z in [m] and G represents the gas flow rate in [kgmol h^{-1}]. Combining the overall gas phase transfer coefficient (K_g) with the interfacial area (*a*) yields the overall absorption coefficient ($K_g a$). This overall absorption coefficient is divided in a diffusion part and a reaction part; the relation between these parameters is given in equation 3-15, taken from [11].

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{1}{R} \tag{3-15}$$

The value for $k_g a$ is determined by van Velzen et al. in [8] for *5mm* Raschig rings to be *50kmol* m^{-3} h^{-1} at *4cm/s*. The reaction rate in the reactor is given in equation 3-16, taken from [8].

$$R = K_1(0.82 - C)^2 \tag{3-16}$$

The value for K_1 was experimentally determined by van Velzen et al. in [8] and found to be *1.24x10*^{3}*kmol* m^{-3} h^{-1}; C and the constant are dimensionless.

Sulphuric Acid Concentration

The third block in the block scheme in Figure 3-5 is the concentration of the sulphuric acid to make it a more valuable product. The sulphuric acid is concentrated to a quality of *96wt%* (technical grade) in a simple distillation column. The ambient pressure column is fed with a concentrated sulphuric acid solution saturated with hydrogen bromide and un-reacted bromine from the conversion section. The bottom temperature is maintained at a temperature around 295^oC to guarantee the product composition. The product only contains technical grade sulphuric acid and traces of hydrogen bromide. The top temperature will be around 120^0C. The distillate contains the remaining water, bromine and hydrogen bromide.

CO_2 separation (2)

The fourth block in the block scheme of Figure 3-5 is CO_2 separation (2). The stream coming from the top of the reaction section consists of HBr, Br_2 and *6%* CO_2. This CO_2 must be removed because otherwise it builds up in the process. Normally a bleed would be applied, but since the bromine is very toxic, this is not desirable. Only the CO_2 is therefore removed. A membrane is the best option due to its higher selectivity. Also the present HBr makes the process complicated and ensures that a flash operation is not possible. For the design of this membrane the same equations are used as for the SO_2 removal from the flue gas (equation 3-6 to 3-11). Figure C-20 in Appendix 3, taken from Nii in [2] shows different solvent for the absorption of CO_2 via a membrane. From this figure it is decided that MEA is the best absorbent for CO_2. It can remove *95%* of the CO_2 present, as stated in [2] by Nii.

Bromine Regeneration

The fifth block in the block scheme in Figure 3-5 is the regeneration of the bromine. The bromine in the gas stream leaving the conversion section and the HBr in the stream leaving the sulphuric acid concentration section are separated in a combined stripper/absorber column. The bromine is stripped from the gas and the HBr is absorbed in water. The water/HBr solution is removed at the bottom. The bottom conditions of this column is maintained at ambient pressure and around 130^0C to guarantee a bromine free product in the bottom. This bottom product is sent to the hydrogen bromide electrolysis. In the electrolyser the reaction given in equation 3-2 is taking place. This reaction is carried out at a temperature around 70^0C.

CO_2 Separation (1)

The last and sixth block in Figure 3-5 is the CO_2 treatment. The flue gas stream leaving the desulphurization is sent to the CO_2 separation. As stated in paragraph 3.2.1, the separation is a MEA scrubbing process. This MEA scrubbing process consists of two parts: a scrubber and a regeneration section. In the first section a stream containing carbon dioxide, water, oxygen and nitrogen and a small amount of sulphur dioxide is sent to an absorber, which contains usually a *30%* MEA in water solution. This stream is contacted with the MEA solution and the MEA reacts with carbon dioxide forming a CO_2 rich solution.

In the regeneration section this rich solution is sent to a stripper and is first heat exchanged with the hot stream coming out of the stripper. In the stripper the rich solution is heated causing the desorption of carbon dioxide from the solution. The CO_2

released by the stripper is collected and pure enough for transport or sale. The CO_2 lean stream is sent back to the scrubber to strip carbon dioxide from the flue gas again. The exhaust of the absorber contains significantly less carbon dioxide than the flue gas that entered the absorber.

For designing such a scrubber system equilibrium constants and rate constants are needed. The following reactions given in equation 3-17 to 3-26 are likely to occur, while carbon dioxide dissolves and reacts with the MEA-solution [2].

Ionisation of water:

$$2H_2O \xleftrightarrow{K_1} OH^- + H_3O^+ \tag{3-17}$$

Dissociation of dissolved CO_2 through carbonic acid:

$$CO_2 + 2H_2O \xleftrightarrow{K_2} HCO_3^- + H_3O^+ \tag{3-18}$$

Dissociation of bicarbonate:

$$HCO_3^- + H_2O \xleftrightarrow{K_3} CO_3^{2-} + H_3O^+ \tag{3-19}$$

Zwitterion formation from MEA and CO_2 reaction:

$$CO_2 + RNH_2 \xleftrightarrow{K_4} RNH_2^+COO^- \tag{3-20}$$

Carbamate formation by deprotonation of the zwitterion:

$$RNH_2^+COO^- + RNH_2 \xleftrightarrow{K_5} RNH_3^+ + RNHCOO^- \tag{3-21}$$

$$RNH_2^+COO^- + H_2O \xleftrightarrow{K_6} H_3O^+ + RNHCOO^- \tag{3-22}$$

$$RNH_2^+COO^- + OH^- \xleftrightarrow{K_7} H_2O + RNHCOO^- \tag{3-23}$$

Carbamate reversion to bicarbonate (hydrolysis reaction):

$$RNHCOO^- + H_2O \xleftrightarrow{K_8} RNH_2 + HCO_3^- \tag{3-24}$$

Dissociation of protonated MEA:

$$RNH_3^+ + H_2O \xleftrightarrow{K_9} RNH_2 + H_3O^+ \tag{3-25}$$

Bicarbonate formation:

$$CO_2 + OH^- \xleftrightarrow{K_{10}} HCO_3^- \tag{3-26}$$

From [9] the necessary equilibrium constants and rate constants for these reactions are obtained and with that information the absorber and stripper are designed, because for designing absorbers equilibrium constants are needed. The equilibrium equation is given in equation 3-27, taken from [2].

$$\ln K = \frac{a_1}{T} + a_2 \ln T + a_3 \qquad (3\text{-}27)$$

The results for theses constants are given in Table 3-3.

Table 3-3: Equilibrium constants for MEA scrubber taken from [9]

	a_1	a_2	a_3	Temperature range (K)
K_1 (mol/L)^2	*-13445.9*	*-22.4773*	*140.932*	*273-498*
K_2 (mol/L)^2	*-12092.1*	*-36.7816*	*235.482*	*273-498*
K_3 (mol/L)^2	*-12431.7*	*-35.4819*	*220.067*	*273-498*
K_8 (mol/L)^2	*-3090.83*	*0*	*6.69425*	*298-413*
K_9 (mol/L)^2	*-5851.11*	*0*	*-3.3636*	*298-413*

This presentation however does not take everything into account. There has to be a make-up stream for MEA, because it will irreversibly react with any sulphur containing components (SO_x); two moles of MEA are needed per mole of SO_x. To minimise the expensive MEA consumption the desulphurization section is put before the CO_2 removal section. Furthermore the carbon dioxide will also cause some attrition. *1,6kg* MEA should be added per ton of removed carbon dioxide. So if *6%* of all carbon dioxide is removed *34kgMEA/hr ton of* CO_2 should be added for make-up.

3.2.3 Thermodynamic Properties

Table 3-4 shows the most important thermodynamic properties of the most used components in this process. The melting temperature and boiling temperature are important for the determination of the state. The heat capacity and the heat of vaporisation are necessary for calculation of the heat balances, heat exchangers and safety analysis (Chemical Exposure Index in chapter 10). Appendix X shows all used tables with thermodynamic properties.

Table 3-4: Most applied thermodynamic properties for the most used components, taken from [X]

Component	Melting temperature T_m (^oC)	Boiling temperature T_b (^oC)	Heat capacity C_p (J mol^{-1} K^{-1})	Heat of vaporisation H_{vap} (kJ mol^{-1})
SO_2	*-76*	*-10*	JH	-
CO_2	*sublimation*	*-79*	JH	-
H_2	*-259*	*-253*	JH	-
Br_2	*-7.2*	*58.8*	*37.52*	*29.16*
HBr	*-86*	*-66.4*	*29.08*	*11.25*
MEA	*10.3*	*172*	*211.40*	*54.99*
Water	*0*	*100*	*JH*	-
H_2SO_4 (98%)	*3*	*330*	*146.44*	*46.84*

Other important properties are the Txy-diagrams of the components. The thermodynamic models taken from Aspen Plus, version 11.1, are compared with experimental data found. Problems arise when electrolytes (HBr, HCl and HF) are taken into account. Aspen is not capable of correctly modelling electrolytes in solution. This causes problems for the equipment design in chapter 8. Appendix XXX shows the difference clearly between the experimental data found and the model of Aspen.

3.2.4 Pure Component Properties

Table 3-5 shows the pure component properties for the most used components. This table provides the basis for the safety analysis in chapter 10. More pure component properties are given in table 1-3 in Appendix XX.

Table 3-5: Pure component properties for the most used components, taken from [chemiekaarten]

Component name		Technical data				Medical data	
Systematic	Formula	Molecular weight (g/mol)	Boiling point (^oC)	Melting point (^oC)	Density of Liquid (rel. to water)	MAC-value (mg/m^3)	LD_{50} (mg/kg) for a rat
Sulphur dioxide	SO_2	*64.1*	*-10*	*-76*	-	*5*	*3120*
Carbon dioxide	CO_2	*44*	*-79*	*Subl.*	-	*9000*	-
Hydrogen	H_2	*2*	*-253*	*-259*	-	*33*	-
Bromine	Br_2	*159.8*	*58.8*	*-7.2*	*3.1*	*0.7*	*2600*
Hydrogen Bromide	HBr	*80.9*	*-66.4*	*-86*	*1.5*	*6.7*	*11840*
Monoethanol-amine (MEA)	C_2H_7NO	*61*	*172*	*10.3*	*1.015*	*2.5*	*1720*
Sulphuric acid	H_2SO_4 (98%)	98.1	330	3	1.8	1	2140

3.3 Basic Assumptions

3.3.1 Plant capacity

The feedstock of the process consists of flue gas, which is cleaned from fly ash and from the acids HCl and HF. Two products are formed, technical grade sulphuric acid (*96wt%*) and hydrogen. One waste stream is produced which is the sulphur dioxide cleaned flue gas. Besides product and waste streams two other important base chemicals are present within the battery limit, bromine and sodium sulphite. These chemicals are regenerated within the battery limits and no amounts of these compounds have to be added during operation. They also do not show up in Table 3-6 that is a summary of all the in- and outgoing streams in tons per year. Low-pressure steam and cooling water are the utilities used in the process. They are also taken into account in Table 3-6. The plant capacity is the total amount of flue gas that can be handled by this process, *$1.56\cdot10^{7}$ ton/year*. It is assumed that the plant runs 8000 hours per year.

Table 3-6: In- and outgoing streams per year

In	Streams (ton/year)	Out	Streams (ton/year)
Flue gas	$1.56\cdot10^{7}$	Treated flue gas	$1.46\cdot10^{7}$
Water	$6.00\cdot10^{5}$	Water	$5.84\cdot10^{4}$
MEA	$1.84\cdot10^{3}$	MEA salts	$3.17\cdot10^{3}$
		CO_2	$1.80\cdot10^{5}$
Low-pressure steam	$4.33\cdot10^{5}$	Sulphuric acid	$4.88\cdot10^{4}$
Cooling water	$6.06\cdot10^{5}$	Hydrogen	$9.95\cdot10^{2}$
		HCl	$4.00\cdot10^{3}$
		HF	$4.00\cdot10^{2}$
		Fly ash	$1.20\cdot10^{3}$

3.3.2 Location

The location of the plant will be near a *600MW* coal fired power plant. The country is not of direct importance. Since it is expected from the safety analysis that the toxicity of bromine is significant, the plant should be located as far as possible from inhabited areas.

3.3.3 Battery limit

In Figure 3-6 a schematic representation of the battery limit of the process is shown. The scheme is based on the amounts in Table 3-6.

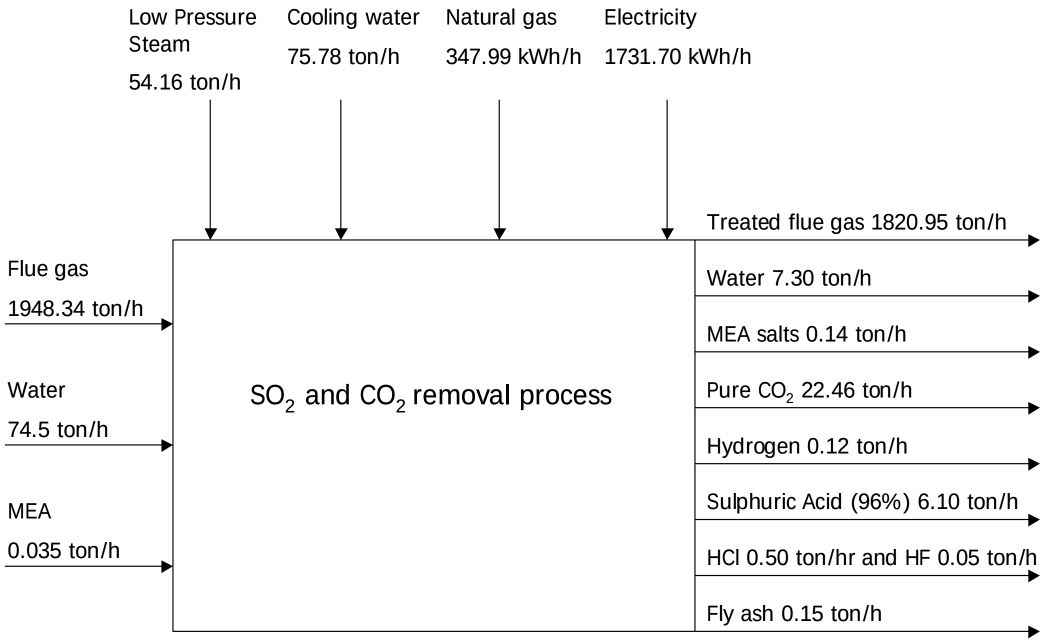

Figure 3-6: Schematic representation of the battery limit of the process

The most important equipments within the battery limit are the separation membranes, the two sulphur dioxide conversion reactors, the sulphuric acid concentrator, the bromine distillation column and the electrolyser. The most important equipments outside the battery limit are the steam generation for regenerating the membrane solvent and the electricity plant for the electrolyser. The battery limit does not include storage of any product and the CO_2 is not compressed, so sold or further treated under the same conditions it comes from the MEA stripper.

3.4 Economic Margin

The prices of raw base chemicals used in this chapter come from the website called http://ed.icheme.org/costchem.html. The prices on this website are estimates from prices for educational use only. There is no guaranty that the chemicals can be purchased for these prices especially not since this website was last updated in February 2002.

Table 3-7 shows the prices applied in the design for the determination of the economical feasibility, carried out in chapter 11.

Table 3-7: Prices and total income or expenditure of the chemicals

Component	Price (€/ton)	Total (€) Income	Total expenditure
Sulphuric acid	*70*	*3.56 million*	
Water	*0.10*	*5842.97*	*60000,-*
MEA	*408.35*		*0.75 million*
CO_2	*100*	*18 million*	
Low-pressure steam	*12.71*		*5.5 million*
Natural gas	*0.026*		*72766.69*
Cooling water	*0.027*		*16506.08*
Electricity	*0.078*		*1.09 million*

The margin in the process depends on whether the produced hydrogen is sold or used as an energy source for the electrolysis. Because of the relative high purity hydrogen produced it is decided to use the hydrogen as energy source for the electrolysis. The margin of this process is therefore around *€3.5M*.

In chapter 2 of Douglas [14] a number of rules of thumb are given for the determination of the start up costs, the working capital and the salvage value. These rules are given in the equations below.

$$Working\_Capital = 0.15 \cdot Total\_Investment \tag{3-28}$$

$$Salvage\_Value = 0.03 \cdot Total\_Investment \tag{3-29}$$

$$Start\_Up\_Costs = 0.10 \cdot Total\_Investment \tag{3-30}$$

The basis of the method is that the present value of the money invested in the plant is equal to the present value of the money earned in the upcoming years. This basis is represented in equation 3-31.

$$PV\_Cash\_Flow + WC + SV = PV\_Total\_Investment + WC + SUC \qquad (3\text{-}31)$$

With these rules and rearranging the method described on page 59 in Douglas [14] the total investment possible for this process is calculated. Assuming a life span of 10 years for the plant, a building time of 4 years and a Discount Cash Flow Rate Of Return (DCFROR) of *10%* the total investment possible is around *€14.7M*. The Excel sheet used for these calculations is given in Appendix 3.

For this design process the operation is not assumed to be profitable; the flue gas cleaning is the main goal. The task is to design an efficient removal process for SO_2 and CO_2, because regulations say so. If the flue gas is not clean enough, fines will be the result. Profits will be made on the energy production by the power plant.

3.5 Conclusions of Basis of Design

In this chapter, the basic data for the design is presented. All the data given here are used for the calculations in the following chapters. In chapter 2 it is decided that the most feasible and challenging process for conceptual design is the process based on the Mark-13 process. This chapter expands this design. Choices are made for the type of reactors and type of separations, shown in Figure 3-2 and Figure 3-4. Figure 3-5 represents the block scheme for the different functions in the design.

The most applied thermodynamic properties for the components in the process are searched and presented in this chapter. The heat capacity and the heat of vaporisation are used for the heat balance in chapter 7 and in the safety analysis.

The characteristics of the pure components are given in Table 3-5 and from it can be concluded that safety analysis is an important topic for this process. The battery limit diagram shows the total streams going in and out of the process. The utilities necessary are determined and are also presented in the battery limit diagram in Figure 3-6.

The last part of this chapter deals with the economic margin. There is concluded that the process is not profitable, but this is not a problem since the goal of this project is to design a waste stream cleaning process. The profit is made by the energy production of the power plant. Too much SO_2 and CO_2 emissions result in severe financial fines that exceed the costs of the cleaning process.

4 Thermodynamic Properties

In this chapter the relevant thermodynamic properties and models that will be used in the conceptual design are given.

4.1 Heat Capacities

The relevant heat capacities needed for the conceptual design are given in this paragraph. For the calculation of heat capacities for gases, equations 4-1 and 4-2 are used.

$$C_P^{ig} / R = A + BT + CT^2 + DT^{-2} \tag{4-1}$$

$$C_P^{ig} / R = A + BT + CT^2 + DT^3 + ET^4 \tag{4-2}$$

The parameters for equation 4-1 are given in Table 0-1 and the parameters for equation 4-2 are given in Table 0-2 of Appendix X.

The heat capacities for liquids are calculated using equation 4-3.

$$C_P / R = A + BT + CT^2 + DT^3 \tag{4-3}$$

The parameters in equation 4-3 can be found in Table 0-3 of Appendix X.
The heat capacities for solids are calculated with equation 4-4.

$$C_p / R = A + BT + DT^{-2} \tag{4-4}$$

The parameters for equation 4-4 are shown in Table 0-4 of Appendix X

4.2 Standard Enthalpies of Formation

To calculate the enthalpy change at elevated temperatures and constant pressures, equation 4-5 is used.

$$\Delta H = \Delta H^{\circ}_{f_{298}} + \int_{298}^{T} C_P \cdot dT \tag{4-5}$$

The values for the heat capacity are given in the previous paragraph; the standard enthalpies of formation are given in Table 0-5 of Appendix X.

4.3 Solubility and Density

Solubility and density data of the different components can be found in Table 0-6 in Appendix X

4.4 Critical Constants and Boiling Points

The boiling points and critical temperature and pressures of the different components are shown in Table 0-7 in Appendix X.

4.5 Heat of Evaporation

The heat of evaporation is calculated with equation 4-6. The parameters needed are given in Table 0-8 in Appendix X.

$$H_{vap} = A\left(1 - \frac{T}{T_c}\right)^n \tag{4-6}$$

4.6 Pure Component Properties

A list of pure component properties is given in Appendix XX. Properties like molecular mass, melting and boiling points, densities, flammability data and toxicity data are given in this list.

4.7 Thermodynamic Model

For simulation of the different units in Aspen Plus, a thermodynamic model has to be selected that is most suitable for the operating conditions in the unit and the component present in this unit. Since all units in the process contain one or more electrolytes the ELECNRTL model was chosen as the most suitable model after consulting Dr. Ir. Th. W. de Loos.

The validity of this model for the different mixtures present in the process was verified by comparing the Txy diagrams generated with Aspen Plus and experimental Txy data. This verification is done for the binary mixtures of water with hydrogen bromide, hydrogen chloride and hydrogen fluoride. Unfortunately no experimental data could be found on water sulphuric acid mixtures. The different Txy diagrams containing both the simulated and experimental data are shown in Figure 0-1, Figure 0-2 and Figure 0-3 of Appendix XXX.

From all three figures it is clear that even with the little data available on water/hydrogen bromide and water/hydrogen chloride, the ELECNRTL does not give an adequate description of the Txy diagram. This means that when using Aspen Plus for simulations with water and one of these three components present, special attention should be paid to the results since they might deviate strongly from the results that can be realistically expected.

5 Process Structure and Description

In this chapter, unit operations and equipment are selected. A process overview is given in a process flow scheme and all stream data is collected in the stream summary. A process description accompanied with selection reasons is given. Furthermore, details regarding required utilities, heat exchangers and pumps will be provided in the accompanying texts and specification sheets.

5.1 Criteria and Selections

5.1.1 Design performance criteria

The design performance criteria are found in [5]. A total sulphur removal of *99.3%* has to be achieved and a significant part of the carbon dioxide has to be removed. A total carbon dioxide removal of *50%* has been established as a design criterion. Furthermore the process should be flexible enough to handle steady-state changes in the flue gas load (turndown ratio of *50%*) and in SO_2 loading (by *25%*) as well as faster dynamic variations in the feed stream (~*5%* flow change/hr and *10%* SO_2 content/hr).

5.1.2 Unit operations/equipment selection

In Figure 3-5 the following tasks are identified: feed pre-treatment, SO_2 separation, sulphuric acid production, sulphuric acid concentration, CO_2 removal, bromine regeneration, and CO_2 separation. For each task it is decided how this step will be performed. Furthermore, the position in the flow scheme is determined.

The feed pre-treatment consists of the removal of fly ash, and the removal of HCl and HF. Fly ash removal is necessary since membrane units can get easily clogged by ashes. It is not strictly required to place the HCl and HF removal before the SO_2 separation section, it is however required to be positioned before the CO_2 separation section in order to prevent deterioration of MEA. For this reason the decision is made to place both feed pre-treatment units before the SO_2 separation.

Fly ash removal

Since in this process a membrane unit will remove SO_2, an elaborate fly ash removal is necessary. Three removal options were investigated: contacting with water (Venturi and cloud chamber scrubber), use of a cyclone and the use of an ElectroStatic Precipitator (ESP). For the removal of the acidic gases HF and HCl water absorption is the most promising option. This leaves room for a combination of the two tasks, since both treatments have the possibility of contacting with water. A problem of this solution is that the wastewater has to be thoroughly cleaned from fly ash, since it is not allowed to dump this slurry. Therefore a combination of these tasks is not considered a viable option. A cyclone cannot remove sufficient fly ash and therefore an ESP was chosen for the removal of fly ash. The ESP removes the fly ash to a level of below *25ppm* and has a very high energy efficiency

HF/ HCL removal section

In the flue gas feed some HF and HCl is present. For the removal of these acidic gases, water absorption in a single column is the most promising solution due to its high removal rates and low complexity, and therefore this option is chosen.

SO_2 separation

To separate sulphur dioxide from a flue gas stream, two options are in general available: absorbing with a solvent (scrubbing) or membrane separation. Several criteria are evaluated to make the final choice between these techniques. The most important criterion is the design specification of *99.3%* sulphur removal. Conventional limestone scrubbers can reach an efficiency of *95%* [39]. When sulphur removal at higher levels is desired, a much larger limestone scrubber than the ones that are currently built would be needed. Moreover, the produced gypsum cannot be used in construction works or in landfill due to impurities. A membrane separation however, can achieve much higher efficiencies and the used solvent can be easily regenerated. As a result, a membrane separation unit for SO_2 removal was chosen. In the membrane unit, SO_2 and small amounts of CO_2 permeate in an aqueous SO_3^{2-} solution. The loaded solvent is subsequently pumped into a regenerator vessel where the solvent is regenerated by thermal treatment (this desorbs the SO_2 and CO_2). A separate stream coming from a S/L separator removes any insoluble salts that might be formed.

Reaction section

The sulphur dioxide is converted into hydrosulphuric acid in a slightly modified form of the Mark #13 process. This process is chosen for the usefulness of its end products, H_2SO_4 and H_2, and consists of two trickle-bed reactors in series packed with Raschig rings. The SO_2 and CO_2 gas stream is mixed with gaseous bromine, which is fed to the top of reactor 2. The liquid effluent of reactor 1, which already contains some hydrogen sulphate is also fed in the top of this reactor. The formed H_2SO_4 in both reactors (L) is pumped to the product separation unit.

The remaining gas, which still contains a significant amount of SO_2 and all the CO_2 is then fed in the top of reactor 1. Here it comes into contact with a mixture of fresh and recycled water. The bromine and water used in this section are fed from buffer vessels that are used to be able to control potential fluctuations in the gas load and its composition without having excessively large recycle streams.

Sulphuric acid purification section

The reactor effluent contains sulphuric acid, considerable amounts of water, bromine and hydrogen bromide. To separate the produced sulphuric acid from the other components, a simple distillation column is chosen due to the simplicity and effectiveness of this unit. The formed H_2SO_4 is separated from a watery mixture of bromine (trace) and hydrogen bromide, which is sent back to the water mixture vessel. The separated H_2SO_4 is concentrated to a *96%* pure mixture (technical grade) that contains some water and hydrogen bromide as impurities.

Carbon dioxide removal section

In the separation of sulphur dioxide from the flue gas, a small amount of carbon dioxide also comes through the membrane. This CO_2 has to be removed from the system to prevent accumulation. A membrane unit similar in operation as the unit used for the SO_2 removal can perform the removal of CO_2 from the reactor effluent, which consists of a mixture of carbon dioxide, bromine, hydrogen bromide and a trace of water very effectively. In this unit, MEA is used as solvent rather than a SO_3^{2-} in solution. In a regenerator the MEA is recovered and the pure CO_2 is collected. The off gas coming from this section is pumped to the bromine regeneration unit. A separate stream coming from a S/L precipitator removes insoluble MEA salts that might be formed

Bromine regeneration section

From an environmental and economical perspective, bromine is recycled in the process. Therefore all hydrogen bromide that comes from the reactor is to be regenerated. The gaseous stream that comes from the CO_2 removal membrane unit is sent to the unit that strips off the bromine and absorbs the hydrogen bromide. The absorbed hydrogen bromide leaves via the bottom of the column. This unit can be considered as being a simple distillation. The hydrogen bromide has to be converted to bromine before it can be reused, and is therefore sent to an electrolysis unit where the dissolved hydrogen bromide is converted into bromine and hydrogen. Hydrogen escapes as a gas, which is compressed and used for energy production. The formed bromine remains in an aqueous solution together with unreacted hydrogen bromide and is recycled to the absorber.

Carbon dioxide separation section

The desulphurised flue gas stream is sent to the CO_2 separation section. This separation is performed by absorption of CO_2 in MEA in an absorber. The flue gas, together with MEA make-up (when required) is brought into the column where *6%* of the CO_2 present is absorbed in MEA. The loaded solvent is subsequently sent to the MEA regeneration unit (scrubbing column), where CO_2 desorbs upon heating. The lean solvent is pumped back to the absorber after passing through a heat exchanger, where it gives some of its heat to the loaded MEA coming from the absorber. The treated flue gas stream escapes over the top of this column to a stack where it is released into the environment. The separated CO_2 is combined with the CO_2 coming from the CO_2 membrane removal.

Overall process conditions

The process conditions can be classified as being mild due to the low pressures and low temperatures used in the various units. The reaction sections and the regeneration sections of the various separation units operate at significantly higher temperatures when compared to the rest of the process (around *100°C* in opposition to approximately *20–30°C*). The pressure of the entire process is *1.1atm* for the incoming gas streams and *1atm* for the liquid and all in-process gas streams. At the membrane inlets, much higher pressures might be applied in order to overcome the pressure drop of the membrane hollow fibres.

5.2 Process Flow Scheme (PFS)

The process flow scheme, together with a detailed walkthrough can be found in appendix 5.

5.3 Process Stream Summary (PSS)

The complete process stream summary can be found in Appendix 6. The enthalpies of all streams are calculated by the summation of all enthalpies of all components. For the calculation of the enthalpies the thermodynamic data (C_P values) from chapter 4 are used.

5.4 Utilities

The summary of utilities and a brief description of the calculation methods as were used can be found in Appendix7.

5.5 Process yields

To evaluate the performance of this process option, it can be very useful to consider the consumption of feed, utilities, and process chemicals per ton of product. Process yields lead to better understanding of the process. With the total in- and outgoing streams and the utilities calculated, the process yields with respect to the sulphuric acid production can be calculated.

Table 5-1: Yields of process streams with respect to sulphuric acid

Process streams							
Name	Ref Stream	kg/s		ton/h		ton/ton sulphuric acid	
		IN	OUT	IN	OUT	IN	OUT
INGOING STREAMS							
flue gas	<101>	541.21		1948		307	
MEA make up	<102>	0.01		0.03		0.004	
water make-up	<103>	0.69		2.49		0.392	
bromine make-up	<104>	0		0		0	
water to hcl scrubber	<105>	20.00		72		11.3	
SO3 make up	<106>	0		0		0	
small MEA make-up	<107>	0.002		0.009		0.001	
OUTGOING STREAMS							
treated flue gas	<901>		552		1986		313
MEA insoluble salts	<902>		0.04		0.13		0.02
pure CO2	<903>		6.3		22.7		3.6
hydrogen	<904>		0.03		0.12		0.02
MEA salts	<905>		0.003		0.01		0.002
sulphuric acid product	<906>		1.77		6.4		1
SO3 salts	<907>		0		0		0
water from hf hcl removal	<908>		1.96		7.1		1.11
fly ash	<909>		0.04		0.15		0.02
total		561.9	561.9	2022.9	2023.0	318.3	318.3

In Table 5-1 the size of all in- and outgoing streams are tabulated in kg/s and ton/h. It can be seen that there is a slight difference between the in- and outgoing streams in ton/h. This is probably because of a minor miscalculation, but since this is such a small fraction it can be ignored as being important. A remarkable thing is the fact that 3.6 times as much carbon dioxide is removed from the stream than sulphuric acid is produced. Another remarkable fact is that the only about *2wt%* of the original flue gas stream is removed from the flue gas but this does meet the specification of a *6%* reduction of the carbon dioxide emission and almost complete removal of sulphur dioxide.

The yields can also be calculated for the utilities. This leads to the following table:

Table 5-2: Yields of utilities with respect to sulphuric acid

Utilities							
Name	Ref Stream	kg/s	kW	ton/h	kWh/h	t/t H2SO4	kWh/ t H2SO4
LP steam		15.0		54.2		8.5	
Natural gas			348		348		55
Cooling water		21.0		75.8		11.9	
Electricity			5170		5170		813

From Table 5-2 can be concluded that per ton of produced sulphuric acid *8.5ton* of steam is needed and *11.9ton* of cooling water. This is a considerable amount, however in Appendix is shown that if heat integration would be performed on certain units these amounts would certainly be reduced.

Limestone scrubbing in general produces *3ton* of gypsum per ton of SO_2 removed. Since *3,972ton* of sulphur dioxide is removed per hour, this leads to *11,916ton* of gypsum produced. Since the local market for gypsum is limited and the gypsum often is polluted, it is land filled. When the SO_2 is converted in a useful product, this waste stream is prevented.

In this process a number of wastes are produced: insoluble MEA salts, wastes from the HF/HCl absorber and fly ash. Together these amount to *7.39ton/h*. However, the wastewater coming from the HF/ HCl absorber can be treated and recycled. Thus, when this stream is omitted from the rest of the wastes, only *0.29ton/h* is produced. When the assumption is made that in conventional processes fly ash removal is also required, the wastes specific for this process amount to *0.14ton/h*, which is significantly less than the wastes produced in limestone scrubbing.

Concluding it can be said that this process certainly behaves better than limestone scrubbing from a waste point of view. Although this process might be more elaborate and energy consuming, the benefit is that useful products are formed from the captured SO_2. Furthermore, in this process also significant amount of CO_2 is removed. When data on other SO_2 removal processes is available, the process yields could be compared with each other in order to come to a more elaborate assessment of the performance of this process. The comparison then could be made with the SCOT, THIOPAQ and the CrystaSulf processes.

6 Process Control

The overall process in figure X uses different types of reactors, namely three absorbers, one stripper, two membrane units, a distillation column and the SO_2 conversion section with two reactors. In general, for the same type of reactors, the same type of control is applied. This chapter is therefore divided per type of reactor.

All these reactors need to be controlled in order to maintain the requirements. For this project, only simple control is necessary, so complicated and difficult structures are not taken into account. The easiest applicable controllers are ratio controllers, temperature controllers, pressure controllers and flow controllers. These are therefore the only ones applied.

6.1 Configuration of control systems

6.1.1 HF / HCl Absorber

Absorbers are used to separate HF and HCl from the incoming flue gas and to regenerate the bromide. The applied control configuration is shown in Appendix F. There is a pressure sensor on the flue gas stream coming in and a flow controller on the water stream coming in. The amount of water, which is to be added, needs to be related to the size of the flue gas stream. A sort of ratio controller, which is between this pressure sensor and flow controller, performs this action. Depending on the size of the flue gas stream, water is added. A pressure controller controls the flow of the product leaving the top. The liquid level in the bottom of the column is controlled by a level controller, which is connected to a valve on the outlet of the bottom product.

6.1.2 Membrane units & heated regenerator

The membrane units are very sensitive to the flow rate. Therefore this parameter must be controlled at best. A pressure control on the outgoing stream will perform this action. The absorbed gas then leaves the membrane unit in a solution, of which a flow controller controls the flow rate going to the regenerator. The amount of gas released in the regenerator is dependent on the temperature of the heating fluid. The temperature in this reactor must therefore be controlled as well. This action is performed by a temperature controller, which is connected to a valve in on the process steam stream. In the heated regenerator, a liquid level controller is placed, because heater must not dry out. The bottom product of the regenerator needs to be cooled down and this will be done in a cooler. A temperature controller controls the amount of cooling water, which needs to be fed through the cooler. Appendix F shows the configuration of a membrane unit.

The configuration mentioned in Appendix F cannot only be applied to the membrane units, which split of sulphur dioxide from the flue gas stream (S02 and V01), but also to the membrane units, which split of carbon dioxide from the sulphur dioxide stream (S03 and V04). Those units are controlled in exactly the same way as the units in Appendix F. The only difference is that the stream names differ and the names of the units are different.

6.1.3 MEA absorber and MEA stripper

The monoethanolamine absorbs CO_2 and this is regenerated in a scrubber. For this combination of reactors, the control structure is designed as in Appendix F.

A pressure controller on the top of the absorber controls the flow of the outlet gas. On the bottoms of both the columns (absorber and regenerator) level controllers are placed for two reasons. The first reason is to maintain an acceptable amount of liquid in the bottom of the columns. The second reason is that, if the level controllers are very well configured, they will be able to control the amount of MEA in the columns and it is not dependent of the size of the flue gas stream entering the absorption column. In order to do so the maximum size of the flue gas stream needs to be calculated. Then the level controllers must be set in such a way, that the flow in the columns will always be able to cope with the amount of flue gas fed to the stream. If less flue gas enters the column this doesn't matter; it will only lead to more carbon dioxide absorption.

A drawback of this configuration is that, if the flue gas flow will increase, this system might not be able to cope with this change and the system might become instable. So the proposed configuration is just a recommendation to control the current system. If the plant were to be really designed, this control structure would have to be evaluated for suitability to for example a possible scale-up. Control of recycle streams is always quite complex and since a time constraint is applied to the project there was no time to fully develop a configuration, which is completely free of failures.

The two streams connecting the two columns are integrated through a heat exchanger on which no control needs to be applied. The product over the top of the scrubber is mostly CO_2, but some MEA (and / or water) will come with it. To cool this stream down a cooler is necessary and to determine how much cooling water needs to be fed to the cooler a temperature controller is applied. The pressure controller in the condenser adjusts the outlet of carbon dioxide. Some of the MEA is reheated in the bottom of the column in order to maintain the temperature. This temperature controller regulates the amount of heating fluid. The liquid level in the bottom is maintained by a level controller to ensure that the column does not dry out.

6.1.4 Distillation column (Sulphuric acid concentrator)

In Appendix F is shown how the control structure of the distillation column has been configured.

The flow of the condenser is liquid and therefore the reflux ratio is controlled instead of the temperature of the top of the column. The level controller of the condenser is connected to the outlet stream of the top of the column. The pressure controller is responsible for the flow of the cooling liquid in the top.

In the bottom of the column a level controllers controls the level of the liquid in the column and a temperature controller makes sure the bottom of the column has the right temperature for the distillation/concentration.

6.1.5 Reaction section

The reaction is the core of the process, so this needs to be controlled very well. Two buffer vessels are situated in the process, so that the variation in the flows can be easier dealt with. Appendix F shows the control configuration of the reaction section.

The buffer vessels are controlled with level controllers by a make-up stream. The bromine needs to be evaporated in a evaporation vessel. To do so temperature control is applied. The inlet flow of the reaction section consists of two gaseous streams. They are controlled with a flow ratio controller. Level controllers control the liquid in the bottoms of the reactors and pressure controllers are controlling the gas streams.

6.1.6 Bromine stripper

The last part of which a control structure needs to be designed is for the bromine stripper and electrolysis cell section. Appendix F also shows the control configuration for the bromine stripper and electrolysis cell.

The bottom of the stripper and the electrolysis cell are on level control. The heaters and coolers in this section are both on temperature control. In the electrolysis cell there is a pressure controls with which the release of hydrogen is controlled. The condensation vessel on the top of the bromine stripper is on flow control to make sure only bromine is recycled. In the bottom of the vessel water (and some bromine) is sent back to the bromine stripper.

6.2 Conclusion

The control configuration of the separate units have been implemented in the overall process scheme. Because of a lot of recycle streams exist in this process control is fairly complicated and if the production would have to increase problems might arise with this control structure. However for this specific problem the control structure will suffice. The overall block scheme is shown in figure X1 in appendix X2.

7 Mass and Heat Balances

7.1 Mass and heat balances of units

After completion of the flow sheet for each unit a mass and heat balances needs to be constructed in order to see whether the system is consistent and no mass or heat is created or converted into nothing.

The mass and heat balances of all units can be found in Appendix F along with an explanation on how these balances are constructed.

Some units have some minor differences in in- and outgoing mass streams. It is most likely that these deviations are made by some slight calculation errors. The

7.2 Total mass streams

From Appendix F yields can already be concluded that the total in- and outgoing mass streams are equal so the total mass balances are correct. Totally *561.90kg/s* enters the system and totally *561.93kg* leaves the reactor every second. This is such a small difference on such a high mass flow rate that, apart from a minor miscalculation somewhere, that can be concluded that the mass balances are overall right. So data consistency has been proven.

8 Process and Equipment Design

8.1 Fly Ash Removal

The reduction of particulate emissions from coal burning units is essential due to the large amounts of fly ash produced (±*150kg/h*), which could be harmful for human health, the environment and can cause operation problems in downstream processing. Although there are several options for controlling particulate emissions, the main method nowadays in electric power plants for collecting fly ash is through electrostatic precipitators, ESP. The fly ash composition from a coal-fired power plant is given in X in Appendix 9. The fly ash has a mean particle size of *12μm* and only *10%* of ash is larger than *45μm*.

8.1.1 Types of Fly Ash Collectors [2]

As mentioned above there are several technologies available to remove fly ash from flue gases. To compare the different types, it is worth to give a short description of each type along with the advantages and disadvantages and the common operating problems and if possible the solution to these problems. The types of fly ash collectors considered are: wet scrubbers, fabric collectors, inertial separators and electrostatic precipitators. The four collectors types are compared in Appendix 9 because they vary widely in design, effectiveness, operation, space requirements, construction, and capital, operating, and maintenance. Each type has some unique advantages and disadvantages. The selection of the collector is based the factors given in Table X in Appendix 9.

An ESP is used to remove the fly ash from the flue gas because of the properties of the ESP. It has the highest collection efficiency; it removes almost all particles from *0.25μm* and up, lowest pressure drop and therefore lower operating costs. One ESP unit can handle our flue gas flow because the flue gas does not contain combustible gases so there is no explosion risk. The ESP requires less energy and minimal maintenance requirements.

8.1.2 Electrostatic precipitator

Electrostatic precipitators use electrostatic forces to separate dust and fly ash particulates from exhaust gases. Because ESPs act only on particulates that have to be removed, so minimally hinder flue gas flow, they have very low energy requirements and operating costs. In an ESP, an (intense) electric field is maintained between high-voltage discharge electrodes and grounded collecting electrodes. The airborne particles receive a negative charge as they pass through the ionized field between the electrodes. These charged particles are then attracted to a grounded or positively charged electrode and adhere to it as depicted in Figure 8-1.

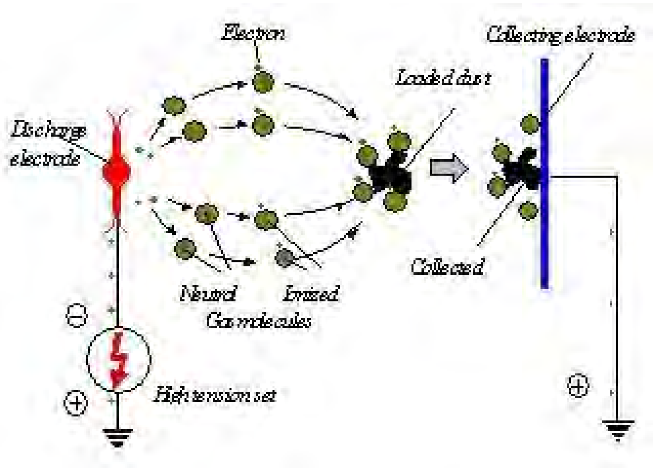

Figure 8-1: Method of operation [4]

The majority of electrostatic precipitators used in industry are the plate type. Collecting plates are parallel to the gas flow and are 8-18 inches apart with discharge electrodes. Vibrating the collecting electrodes either periodically or continuously removes the collected material on the electrodes. Cleaning can be done without interrupting the airflow. In table H-6 in Appendix H the main advantages and disadvantages of ESP are summarised based on the data found in [41], [42] and [43].

8.1.3 Design specifications

To design a precipitator that can be used for the particular case some operating parameters, energy requirements and space requirements are defined.

The specific collection area (SCA) is defines the ratio of collection surface area to the gas flow rate into the collector.

$$\text{SCA} = \frac{\text{total collection area in m}^2}{\text{gas flow rate (1000 m}^3/h)} \tag{8-1}$$

In general range of SCA is between $11m^2$ and $45m^2$ per $1000m^3/h$. $30m^2$ is taken per $1000m^3/h$. The total collection area is then $60.000m^2$.

The aspect ratio relates the length of an ESP to its height. This is an important parameter to prevent large amounts of collected dust from being carried out of the ESP before reaching the hopper.

$$\text{AR} = \frac{\text{effective length, m}}{\text{effective height , m}} \tag{8-2}$$

The effective length of the collection surface is the sum of the plate lengths in each consecutive field and the height is the height of the plates. Effective plate lengths must be at least *10.7m* to *12.2m* to prevent dust loss. Most ESPs though have more than one field depending on the collecting efficiency. To reach a high collecting efficiency, higher than *99%*, the aspect ratio should be greater than *1.0*. We take *1.5* as the aspect ratio.

For high collection efficiency, corona power is usually between *59W* and *295W* per $1000m^3/h$. Here a corona power of *100W* per $1000m^3/h$ is applied, which requires *0.2MW* of power to run the ESP.

In Table 8-1 a summary is given of the design specifications of the ESP used in this project.

Table 8-1: Design parameters of the precipitator

Parameters	Values
Collecting efficiency	*99.9%*
SCA	$30m^2$
AR	*1.5*
Power	*0.2mW*
Inlet temperature	*130°C*
Outlet temperature	*130°C*

It is an opportunity to install a baghouse collector behind the ESP when the particles getting through the ESP reach a critical value. This is not done in this process. The HF and HCl from the flue gases have to be removed by a wet scrubber, because these components can be harmful during downstream processing. They can diffuse through the membrane and accumulate in the system because we have no bleed stream to prevent loss of HBr and Br_2.

8.2 Acid gas scrubber

To remove HF and HCl from the flue gas coming from the ESP a conventional wet scrubber is designed to fulfill the specifications. HF and HCl are removed to prevent the accumulation of these compounds in the system and due to the environmental restrictions it is not allowed to dump them into the air or surface water.

8.2.1 Selection

There are two technologies based on scrubbing that could be used to remove HF and HCl, wet scrubbing and dry scrubbing. In a spray dryer, a slurry of alkaline reagent is atomised into the hot flue gas to absorb pollutants. The resulting dry material is collected in a down stream particulate control device, typically an ESP. At this point dry scrubbing is banned not only because the ESP is placed upstream to the scrubber but also because dry scrubbers are especially used for flue gas desulphurization that is not desired until this point. In this process SO_2 is separated from other gases to process it in the reactor and convert it to a valuable product, e.g. sulphuric acid. Beside a clean CO_2 stream is needed without HF and HCl.

In the scrubber HF and HCl are absorbed physically and chemically to the absorbent, water in this case, and are removed from the gas stream. The water flow containing HF and HCl should be dealt with as wastewater stream and is sent to a wastewater treatment unit, which is beyond the scope of this project. In the wet scrubber, water is sprayed into the flue gas in an absorber vessel. The gas phase and the particulates that passed the ESP are contacted directly with water and are dissolved or diffused (scrubbed) into the water. A wet slurry waste is produced. Concentration of solid particles is too small to be of any importance and is therefore ignored.

Water is used as absorbent because only HF and HCl are removed and SO_2 is kept in the gas stream. In table I-1 in Appendix I the main advantages and disadvantages of the wet scrubber are mentioned.

8.2.2 Design specifications

The absorber is designed using RadFrac in Aspen plus. ELECNRTL is the model used because the solution consists of electrolytes; HCl is totally dissociated while HF stays unionized in the solution. The absorber used has 6 trays and no condenser nor reboiler. The absorber is depicted in figure I-1 in Appendix I. Water is sprayed above the top tray and flue gas stream form the ESP is introduced at the bottom tray. The two streams are contacted in counter-current manner. Mass and heat balances of the streams are given in the chapter 7 on mass and heat balances.

To calculate the tower dimensions we use the equations used to calculate the height and diameter of the distillation column and gas absorbers [42]. The specifications of the absorber are summarised in Table 8-2.

Table 8-2: Specifications of the absorber

Number of trays	*6*
HF removal	*±100%*
HCl removal	*±100%*
Temperature (°C)	*50,7364*
Pressure (bar)	*1,1*
Height (m)	*8.4*
Diameter (m)	*2.75*

Removal of 100% is not feasible, but these are the values attained by Aspen and the literature predicts values up to 97% [14].

The gas stream leaving the absorber is directed to a contactor membrane, whereas the waste stream drawn from the bottom of the absorber, which contains water and the absorbed HF and HCl goes to a waste water treatment unit.

8.3 Membranes to separate SO_2

8.3.1 Selection

Conventional capture technologies based on variety of physical and chemical processes including absorption, adsorption, cryogenic and membranes, involve energy problems that has negative effect of the energy efficiency and the economics of the power stations. In principal SO_2 removal can be achieved by gas-liquid contactor, but the large amounts of gas produced by thermal power plants rises in the range of a few million N m^3/h. To treat such a large amount by a conventional contactor, a large cross-sectional area of the column is needed to prevent flooding, resulting in too much absorbent liquid. This causes an increase in regenerator duty and operating costs.

The most effective way of providing a large surface area of contact between phases and improving the operability at the liquid flow rates is by using a hollow fibre (HF) module. Because the membrane activity is based on the conventional absorption, membrane based absorption can be applied to the most systems treated by conventional gas absorption technology. In Table J-1 one can read the advantages and disadvantages of membrane based absorption compared to the conventional absorption.

Hydrophobic microporous Teflon hollow fibre membrane modules are used to remove SO_2 from the flue gases leaving top of the HF-HCl absorber. A microporous membrane means dealt is with a contactor rather than a semi-permeable membrane. Adjusting flow conditions, the temperature and the pressure of the absorbent creates the selectivity towards SO_2 removal in the present of large amounts of CO_2. The absorbent solution used is an aqueous solution of Na_2SO_3, flowing on the lumen side of the HF in laminar flow, while the flue gas flows on the shell side see Figure 3-3.

In this membrane simultaneous absorption of SO_2 and CO_2 in Na_sSO_3 solution takes place. In this system the following reactions in the liquid film are significant:

$$SO_2 + SO_3^{2-} + H_2O \rightleftharpoons 2HSO_3^- \qquad (8\text{-}3)$$

$$CO_2 + SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HCO_3^- \qquad (8\text{-}4)$$

$$SO_2 + HCO_3^- \rightleftharpoons HSO_3^- + CO_2 \qquad (8\text{-}5)$$

Reaction 8-6 proceeds much faster than the others. In the simultaneous membrane absorption of SO_2 and CO_2, the SO_2 dissolved in the liquid reacts instantaneously with SO_3^{2-} and is depleted in the liquid boundary film. Thus, for flue gases containing a much lower SO_2 than CO_2 partial pressure, it is expected that the selective removal of SO_2 with respect to CO_2 be attained in the present membrane absorption under the condition that the liquid flow rate is low.

8.3.2 Design specifications

The objective is to remove SO_2 as much as possible. The result is that *17.3mol/s* SO_2 (equals *99.8%*) and *1.14mol/s* CO_2 (equals *0.048%*). The dimensions of the membranes are given in Table 8-3. The flow conditions of the absorbent at the lumen side of the membrane are given in Table 8-4.

Table 8-3: Membrane dimensions

Membrane dimensions		
Outer diameter	do (cm)	*0,18*
Inner diameter	di (cm)	*0,1*
Length of membrane	L (cm)	*200*

Table 8-4: Flow conditions of the absorbent

Flow conditions		
Liquid flow rate	u_L (cm/s)	*0,4*
Gas flow rate	u_G (cm/s)	*11,5*
Flux of CO_2 through membrane	J_{co2} (mol/cm2.s)	*2,0E-09*
Flux of SO_2 through the membrane	J_{so2} (mol/cm2.s)	*3,0E-08*
Temperature	T (K)	*298*

To treat the flue gas of this amount a large surface area is needed, in other words, an enormous amount of membranes and modules containing these membranes.

Table 8-5: Parameters of the membrane modules

Parameters	Values
Number of modules	*177*
Diameter if the module (m)	*1*
Number of membranes per module	*142824*
Surface area of the membranes (m^2)	$5.7\cdot10^4$
Voidage in the module	*0.98*
Volumetric flow rate (m^3/s)	*0.257*
Na_2SO_3 flow rate (kg/s)	*3.2*
Pressure drop (kPa)	*10.04*

The absorbent leaving the membrane, which is rich in SO_2 is lead to the regenerator to regenerate Na_2SO_3.

8.4 Regenerator Na_2SO_3

The absorbent rich in SO_2 solution from the membrane is the feed stream for the Na_2SO_3 regenerator. In the regenerator heat is added to reverse the main reaction in the membrane. This reaction is the conversion of bisulphate to SO_2(g), water and Na_2SO_3(aq). The following reaction is taking place in the regenerator:

$$2NaHSO_3 + heat \rightarrow Na_2SO_3 \downarrow + H_2O + SO_2 \uparrow \qquad (8\text{-}6)$$

The Na_2SO_3 regenerator is depicted in X in Appendix 11.

The simulation is done using Aspen Plus version 11.1 with the RadFrac module. The model chosen is ELECNRTL. To calculate the tower dimensions the same equations are used to calculate the height and diameter of the distillation column and gas absorbers [14]. For the modelling of the Na_2SO_3 regenerator equation 8-3 to 8-5 are applied.

The space at the ends of the column is included for vapor disengagement and the liquid sump is *15%*. The regenerator has 4 trays and the efficiency is estimated to be *0.5*, which is conservative design estimate for atmospheric columns. Assuming the regenerator has 4 trays gives a height of *18.4ft* or *5.6m*.

The tower cross-sectional area is calculated using the equation 8-4. This gives a cross-sectional area of *33.2ft²*. The tower diameter can now simply be calculated by equation 8-5. This gives D_T = *6.5ft*, which is equal to *1.98m*. The diameter is taken as *2m*.

Dimensions of the regenerator are summarized in Table 8-6.

Table 8-6: Dimensions of the the regenerator

Dimensions	Values
Height (m)	*5.6*
Diameter (m)	*2.0*
Cross-sectional area (m^2)	*3.14*

8.5 SO_2 conversion section

In this paragraph the SO_2 conversion section is designed. The reaction given in equation 3-1 is carried out in this section. A gas stream containing the SO_2, CO_2 and an excess of bromine enters the reactor section with a sulphuric acid solution and is converted to HBr gas and sulphuric acid. The reactor is a trickle bed reactor filled with 5mm Raschig rings to increase the transfer area and operated in co-current to prevent flooding.

From Van Velzen and Langenkamp [9] it is known that for total conversion of SO_2 the relative sulphuric acid concentration in the reactor must be below *0.65*. A more concentrated sulphuric acid product however is preferred and therefore the conversion section is split up in two reactors in series. One reactor with a sulphuric acid concentration well below 0.65 (reactor 1) and one reactor with a more concentrated sulphuric acid (reactor 2). The SO_2 rich gas enters reactor 2 and then goes to reactor 1. In reactor 2 around 50% of the conversion takes place and in reactor 1 the rest of the SO_2 is converted. The make up water is introduced in reactor 1 and the sulphuric acid product is removed from reactor 2. A schematic representation of the conversion section is shown in Appendix K.

8.5.1 Reactor Sizing

For designing the two reactors equations 3-3 to 3-7 and a number of assumptions were used. The assumptions and initial design parameters are listed below.

The relative sulphuric acid concentration in reactor 2 is a design parameter and is set to *0.75*. This concentration is chosen because it still is relative concentrated and conversions steeply decline with increasing concentrations. An excess of *10%* of bromine to sulphur dioxide is used to be able to handle fast dynamic variations in the SO_2 content. Since from *1mol* SO_2 gas and *1mol* Br_2 gas *2mol* of HBr gas is produced it is assumed that the gas stream through the reactors is constant. The HBr will not be dissolved in the sulphuric acid concentration since a sulphuric acid solution saturated with HBr is present in the reactor, as shown in chapter 7.A first estimate for the overall number of gas transfer units (N_{og}) for reactor 2 was taken from Van Velzen and Langenkamp [9] and was set on 0.8.

For obtaining the best estimate for the gas film transfer coefficient ($k_g a$) the gas velocity in the reactor has to be as close to the velocity used in the experiments done by Van Velzen and Langenkamp. According to Scot Fogler [29] industrially operated trickle bed reactors have diameters up to *3m*. To minimise the pressure drop this maximum diameter would be preferred. With a diameter of *3m* the calculated height of the bed would be around *2.5m*. After having consulted a student recently graduated on trickle bed reactors it is found that H/D ratios below 1 are not favourable because of in- and outlet effects and poor plug flow behaviour. To avoid these effects but still have a small pressure drop a H/D ratio around 2 was chosen, thus resulting in a diameter of *2.11m* (cross sectional area was halved; *D=3m, A=7.06m; A=2.11m, A=3.5m*)

With the gas flow rate from the mass balance in chapter 7 and the diameter the gas velocity can easily be calculated; $u_g=F/A=28.2cm/s.$ Estimation of the transfer coefficient is done with equation 8-10 taken from lecture sheets on the course Catalysis and Reactor Engineering.

$$k_g \propto \frac{u_g^{\,0.64}}{d_p^{\,0.36}} \qquad (8\text{-}7)$$

From Van Velzen and Langenkamp [9] $k_g a = 50 kmol\ m^{-3}\ h^{-1}$ at *4cm/s* therefore at *28.2cm/s*, $k_g a = 175 kmol\ m^{-3}\ h^{-1}$. With the gas film transfer coefficient known and the sulphuric acid concentration set to *0.75* the overall transfer coefficient can be calculated from equation 3-6 and 3-7; $K_g a = 5.87 kmol\ m^{-3}\ h^{-1}$.

With the initial estimate made for the number of gas transfer units the length of the packed bed inside the reactor can be determined from equation 3-14, $z=5.04m$

From equation 3-13 the SO_2 concentration leaving reactor 2 can be calculated, $Y=21.2\%$.

When assuming that virtually all SO_2 is converted the amount of make up water entering reactor 1 can be calculated. In total *62.2kmol/h* enters the conversion section this means that *124.4kmol/h* of water is needed for the conversion. The amount of water leaving reactor 2 is calculated from the relative concentration and equation 3-12. The sulphuric acid stream leaving reactor 2 has sulphuric acid flow rate of *62.2kmol/h* (all SO_2 is converted to sulphuric acid) and a relative concentration of *0.75*.

Thus flow rate of water leaving reactor 2 is *112.9kmol/h*. In total the amount of water entering reactor 1 therefore is the sum of *112.9kmol/h* and *124.4kmol/h* and has to be *237.3kmol/h*. The gas stream leaving reactor 2 contains *21.2%* SO_2 which is *30.2kmol/h* and is converted in reactor 1. The resulting sulphuric acid concentration leaving reactor 1 can then be calculated again with equation 3-12 and C=0.48.

With this relative sulphuric acid concentration the overall transfer coefficient, number of gas transfer units and the exit SO_2 concentration for reactor 1 are calculated with equation 3-15, 3-14 and 3-13, resulting in an concentration out Y_{out}=*0.0005%* and an overall conversion of >>*99.99%*. Detailed calculations are presented in Appendix K.

8.5.2 Packing

The two reactors are packed with *5mm* Raschig rings with a voidage of *56%* and a density of *900kg/m³*. As is calculated above the bed is *5.87m* in height and *2.11m* in diameter. Therefore in each column around *18.5ton* of packing material is needed.

8.5.3 Pressure Drop

The pressure drop over the two reactors is calculated with the equation taken from Scot Fogler p 158 [29].

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 z}{P_0}\right)^{1/2} \qquad (8\text{-}8)$$

The factor β_0 can be calculated with equation 8-3.

$$\beta_0 = \frac{G(1-\phi)}{\rho D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right] \qquad (8\text{-}9)$$

The overall viscosity in equation 8-3 is estimated as the average viscosity of SO_2, CO_2, HBr and Br_2 at atmospheric pressure and 25°C. Due to a lack of information on the viscosity of Br_2 the viscosity of Cl_2 is used to estimate this viscosity. The viscosities used and the average viscosity are given in Table K-1 in Appendix K.

The density in equation 8-3 is estimated as the average density over the two reactors and calculated with the mass flows entering and leaving the reactors and the ideal gas law. This average density is determined to be *4.02kg/m³*. The superficial mass velocity is calculated by multiplying the average density and the superficial velocity.

The pressure drop over the two reactors is calculated at *803Pa*. This very small pressure drop can be explained by the low superficial velocity in the reactors and the relative small H/D ratio of the packed beds.

8.5.4 Internal Recycle

To maintain sufficient wetting of the raschig rings in the column a sulphuric acid recycle is used. To give an estimate of the size of this recycle the liquid velocity in the column in this process has to be of the same size as the liquid velocity in the column shown in Van Velzen and Langenkamp [8]. The mass flow of the recycle in Van Velzen and Langenkamp is *20kg/h* and the diameter of the column is *3.5cm*.

$$u_l = \frac{{}^{20 kg/h}\!\big/\!{}_{1700 kg/m^3}}{1/4 \cdot \pi \cdot (0.035 m)^2} \cdot \frac{1}{3600} h/s = 0.0034 m/s \qquad \text{(8-10)}$$

With the liquid velocity known the recycle flow in the process can be estimate.

$$M = 0.0034 m/s \cdot 3600 s/h \cdot 1/4 \cdot \pi \cdot (2.11)^2 \cdot 1700 kg/m3 = 72828 kg/h$$

8.5.5 Pump Duty

The pressure drop over the recycle pump can easily be calculated assuming that the liquid is taken from the bottom and has to be pumped back to the top which is around *8m* higher. The resulting pressure drop over the column is given below.

$$\Delta P(bar) = \frac{\rho \cdot g \cdot \Delta h}{1 \cdot 10^5} = \frac{1700 \cdot 10 \cdot 8}{1 \cdot 10^5} = 1.36 bar \qquad \text{(8-11)}$$

8.5.6 Reactor Dimensions

The height and diameter of the packed bed inside the reactors have been calculated above. Besides the packed bed the reactor needs some space above the packed bed for feed distributors and in the bottom a liquid sump. The height for the feed distribution is estimated at *1.5m*. The liquid sump should high enough to contain a liquid supply for 15 minutes. From the product flow rate and the density the hold-up and therefore the height of the sump can be calculated. The resulting column dimensions are shown in Table 8-7, since both columns are identical only one table is given.

Table 8-7: Reactor Dimensions

Reactor 1&2 Dimensions [m]	
Diameter	*2.11*
Height packed bed	*5.87*
Height top end	*1.5*
Height liquid sump	*1*
Level liquid sump	*0.4*
Total height	*8.37*

8.6 H_2SO_4 Concentration Section

8.6.1 Column Specifications

The liquid product stream leaving reactor 2 is a sulphuric acid stream with a concentration of *69.5%*. Commercial valuable sulphuric acid has a concentration of *96wt%* therefore the reactor 2 outlet stream has to be concentrated. Besides concentrating the sulphuric acid the product has to be free of hydrogen bromide and bromine as well. These components are separated from the product in the concentration step as well.

In Van Velzen and Langenkamp [8] a brief summary is given on the sulphuric acid concentration section. To their opinion a simple 2 theoretical tray stripper is sufficient to produce a bromine free sulphuric acid at 95wt% with only traces of HBr present. The bottom of the column was held at *292^oC* and the distillate was around *117^oC*. For the design of the sulphuric acid concentration unit this unit was modelled in Aspen Plus with RadFrac model. As described in chapter 4 the thermodynamic model to be used for a mixture of H_2SO_4, HBr and water is the ELECNRTL model. Because of the electrolytes present the Elec. Wizard in Aspen Plus is used to specify the equilibrium reactions between the water and the electrolytes.

The design results in a 6 theoretical tray distillation column that is fed above stage 3. A total condenser is used and a kettle reboiler. The main characteristics of the column and are given in Table 8-8. Appendix L shows the stream summary of the concentrator.

Table 8-8: Column specifications

H_2SO_4 Concentration Column	
Stages	*6*
Feed (above stage)	*3*
Reflux ratio	*1*
Condenser duty [MW]	*-2.585*
Reboiler duty [MW]	*4.039*
Top stage temperature [^oC]	*107.9*
Bottom stage temperature [^oC]	*305*

The extended result reports on both the column and the streams as obtained in Aspen Plus can be found in Appendix XX.

The simulated sulphuric acid concentration unit is different from the unit used in the article by Van Velzen and Langenkamp [8]. More trays and a reflux in the top are needed to prevent the sulphuric acid reaching the distillate. Furthermore the bottom specification could not be met in one column (*95wt%* where *96wt%* is needed). A possible reason for these deviations is the thermodynamic models used in Aspen Plus. As shown in chapter 4 the ELECNRTL model has enormous problem describing a water/HBr mixture. Therefore if detailed design is to be done on the sulphuric acid concentration unit, a much closer look has to be taken on the thermodynamic models. For the conceptual design the values obtained in Aspen Plus are used.

8.6.2 Column Dimensions

For the determination of the column dimensions the rules of thumb presented in Douglas [14] p. 451-456 are used. The equations applied are given in Appendix L. These values are calculated from the results obtained in the Aspen Plus simulation and with the ideal gas law. The values are taken from the bottom stage where the volumetric flow rate is largest. The resulting column dimensions are given in Table 8-9.

Table 8-9: H_2SO_4 Concentration Unit C02 dimensions

H_2SO_4 Concentration Unit C02 dimensions	
Theoretical stages (incl. cond/reb)	*6*
Theoretical trays (excl. cond/reb)	*4*
Actual trays	*8*
Tray distance [m]	*0.6*
Top end height [m]	*1.5*
Height liquid sump [m]	*0.9*
Total height [m]	*7.2*

8.7 Membrane to remove CO_2

A mixture of CO_2, HBr and Br_2 leaving the top of reactor 1 (RO1) is separated. CO_2 is separated from HBr and Br_2 since they are regenerated. To perform this separation it is suggested to use the same membranes used for the removal of SO_2 from the flue gas. CO_2 is usually removed using alkanolamine solutions. The drawback of the aqueous alkanolamine solution is that it requires much energy. Another option is absorption in carbonate solutions (e.g. K_2CO_3) with small amounts of amine. It is known that small amounts of amine addition to a carbonate solution enhance the rate of CO_2 absorption, improves the regeneration efficiency and prevents corrosion. In this case only a small amount of CO_2 has to be recovered so it is not necessary to use the carbonate solution, instead 1M MEA solution is used. A schematic representation of the membrane module is shown in Figure 3-3. In Table J-2 the advantages and disadvantages of alkanolamine solutions are presented.

8.7.1 Design specifications

This membrane set up has to remove *$1.14 molCO_2/s$*. Dimensions of the membrane are the same as the one treated previously to remove SO_2 and are given in Table 8-10. The flow conditions of the absorbent at the lumen side of the membrane are given in Table 8-11.

Table 8-10: Membrane dimensions

Membrane dimensions		
Outer diameter	do (cm)	*0,18*
Inner diameter	di (cm)	*0,1*
Length of membrane	L (cm)	*200*

Table 8-11: Flow conditions of the absorbent

Flow conditions		
Liquid flow rate	u_L (cm/s)	*0,4*
Gas flow rate	u_G (cm/s)	*11,5*
Flux of CO_2 through membrane	J_{co2} (mol/cm2.s)	*2,0E-09*
Flux of SO_2 through membrane	J_{so2} (mol/cm2.s)	*3,0E-08*
Temperature	T (K)	*298*

To remove this small amount of CO_2 less surface area is required, hence there are less membranes and the number of the modules is reduced compared to the previous membrane. This is caused by the absorption capacity of MEA, which is higher than that of the salts. The parameters of the membrane modules are given in Table 8-12.

The CO_2-rich solution is directed to a regenerator where the CO_2 is stripped from the MEA. The CO_2 from the stripper is combined with the CO_2 from the large MEA absorption section.

Table 8-12: Parameters of the membrane modules

Parameters	Values
Number of modules	*13*
Diameter if the module (m)	*1*
Number of membranes per module	*1554*
Surface area of the membranes (m^2)	*228*
Voidage in the module	*0.93*
Volumetric flow rate (m^3/s)	*0.0073*
MEA flow rate (kg/s)	*0.44*
Pressure drop (kPa)	*10.45*

8.7.2 MEA regenerator

The CO_2-rich absorbent flow from the membrane is directed to the MEA regenerator/stripper to regenerate MEA that can be recycled to the membrane. The top stream is CO_2-rich gas phase. And is combined with the main CO_2 stream from the CO_2 absorber stripper of the main flue gas after it has been cleaned from SO_2. Due to the present of MEA and CO_2 the model used in Aspen is once again ELECNRTL. The reactions taking place are:

$$\text{CO2} + 2\,\text{H2O} \leftrightarrow \text{H3O+} + \text{HCO3-} \qquad (8\text{-}12)$$
$$\text{HCO3-} + \text{H2O} \leftrightarrow \text{H3O+} + \text{CO3--} \qquad (8\text{-}13)$$
$$\text{MEA+} + \text{H2O} \leftrightarrow \text{MEA} + \text{H3O+} \qquad (8\text{-}14)$$
$$\text{MEACOO-} + \text{H2O} \leftrightarrow \text{MEA} + \text{HCO3-} \qquad (8\text{-}15)$$

The stripper is modelled in Aspen plus with RadFrac. The parameter of the stripper are given in Table 8-13

Table 8-13: parameters of the MEA stripper

Parameter	Value
Number of stages	*4*
Reflux ratio	*1*
Distillate rate (kmol/h)	*50*

To calculate the tower dimensions the equations used to calculate the height and diameter of the distillation column and gas absorbers [14] are used. This is a good estimation because what happens in the regenerator is to a large degree comparable to what is taking place in a distillation column. It is assumed that the regenerator has four trays. The dimensions of the regenerator are summarised in Table 8-14.

Table 8-14: Dimensions of the regenerator

Dimension	Value
Height (m)	*5.6*
Diameter (m)	*2.2*

8.8 Bromine Stripper/Hydrogen Bromide Absorber C03

For the design of the bromine stripper or hydrogen bromide absorber, unit C03 resembles the figures presented by Van Velzen and Langenkamp [9]. The data available only allow a rough estimate of the dimensions and the duty required for this unit. To maintain a practically bromine free product the bottom temperature is to be held around 130^oC. The top temperature is around 55^oC.

With equation 3-4 and 3-5 an estimate of the column size are given. Both the HBr inlet and exit concentration are known. From Van Velzen and Langenkamp [9] the exit concentration is *0.8%*. From the mass balance it flows that the inlet gas flow rate is *124.4kmol/h* HBr and *13.8kmol/h* Br_2. The outlet flow rate is *62.2kmol/h* Br_2, *29.2kmol/h* water and *0.7kmol/h* HBr. Therefore the inlet concentration is *90%.* With these figures the required overall number of gas transfer units can be calculated with equation 3-13, resulting in $N_{og}=4,72$.

From the overall number of gas transfer units the volume of the column is determined with equation 3-14. The overall absorption coefficient is given by Van Velzen and Langenkamp as well and is around $80 kmol/m^3h$. The pressure in the column is 1 bar and the gas flow rate is given as the average gas flow rate, which is *115.2kmol/h*. The volume is then $V=6.8m^3$.

8.9 Bromine Electrolysis Unit

The bromine electrolysis unit is designed on the basis of figures shown in Van Velzen and Langenkamp [11]. In this article numerous electrolytic cells are investigated on their performance. The feed enters in the centre of the cell from where it flows outward through the electrodes, which are slightly inclined towards the centre. The bromine rich product leaves the cell at the outside and the hydrogen leaves the cell at the centre. In this way the outlet hydrogen flow is contacted with the bromine free feed, so a practically bromine free hydrogen product is obtained. Some important cell parameters are given in Table 8-15.

Table 8-15: HBr electrolysis cell parameters

Electrode material	*graphite*
Electrode distance [mm]	*5*
Cell voltage [V]	*0.89*
Current density [mA]	*250*
Current efficiency [%]	*94*

In the electrolysis cell *124.4kmol/h* of HBr is converted to *62.2kmol/h* Br_2 and *62.2kmol/h* H_2 is produced.

8.9.1 Sizing

During the process *124.4kmol/h* of hydrogen bromide is formed, which has to be regenerated again in the hydrolysis section. For the regeneration of *124.4kmol/h* hydrogen bromide *124.4kmol/h* electrons have to be transferred. From the current density and the current efficiency the surface area needed to transfer these electrons can be calculated.

$$124.4 kmole^- / h = 34.6 mole^- / s = 2.1 \cdot 10^{25} e^- / s$$

$$0.25 A / cm^2 \cdot 6.24 \cdot 10^{18} e^- / A \cdot 0.94 = 1.47 \cdot 10^{18} e^- / cm^2 s$$

$$surface\_area = \frac{2.1 \cdot 10^{25} e^- / s}{1.47 \cdot 10^{18} e^- / cm^2 s} = 1.42 \cdot 10^7 cm^2 = 1420 m^2$$

8.9.2 Required Duty

The required duty for the cell can be calculated from the current density and the required surface area. With *1420m²* surface are and a current density of *250mA/cm²* the current needed is *3.55*10⁶ A*. At a voltage of *0.89V* a duty of *3.2MW* is needed.

8.10 CO_2 Removal Section

After the first chemical treatment of the flue gas using a membrane, the largest part of CO_2 is still in the flue gas and has to be removed by a conventional MEA absorber. Along with this absorber there is always a stripper to regenerate MEA and the associated pumps and possibly heat exchangers. The primary process simulation is developed using Aspen Technology Inc.'s Aspen Plus, version 11.1 with RadFrac module for modeling the absorber and the stripper. First a RateFrac is tried but it appears that TU Delft has no license for RateFrac module. All of the calculations are based on steady-state conditions for the whole system. The model represents vapor-liquid equilibrium and solution with the ELECNRTL model with data based on MEA data in Aspen.

8.10.1 Absorber

The reactions taking place in the absorber are:

$$H_2O + MEA^+ \leftrightarrow H_3O^+ + MEA \tag{8-16}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{8-17}$$

$$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-} \tag{8-18}$$

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{8-19}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \tag{8-20}$$

$$H_2O + CO_2 + MEA \rightarrow MEACO_2^- + H_3O^+ \tag{8-21}$$

$$MEACOO^- + H_3O^+ \rightarrow H_2O + CO_2 + MEA \tag{8-22}$$

The absorber is the vessel where the MEA-based sorbent contacts the flue gas and absorbs CO_2. It is a vertical packed column with a water wash section at the top to remove vaporised amine from the overhead stream. The height of the packing is approximately *15m* [30]. The cross-sectional area is *9.8m* [30]. Absorber diameters reported in the literature range from *9.7* to *12.8m*. A packed column is chosen, because compared with tray columns they allow for reduced pressure drop, increased gas throughput, an improved gas contacting efficiency and less foaming.

During literature search a comprehensive study about MEA absorber-stripper system is found [30]. The flue gas inlet stream has the same order of magnitude and the composition shows great similarity. Beside the mentioned reasons we have chosen the same dimensions for our absorber because these values seems to be standards for MEA absorbers.

8.10.2 Stripper

The reactions taking place in the stripper are:

$$H_2O + MEA^+ \leftrightarrow H_3O^+ + MEA \tag{8-23}$$

$$2H_2O \leftrightarrow H_3O^+ + HO^- \tag{8-24}$$

$$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-} \tag{8-25}$$

$$2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^- \tag{8-26}$$

$$H_2O + MEACOO^- \leftrightarrow MEA + HCO_3^- \tag{8-27}$$

The first three equations are common to both the absorber and the stripper. All the equations in the stripper are equilibrium reactions, which corresponds to instantaneous reactions in the stripper. The stripper is a packed column. Its main function is to remove CO_2 from the rich solution by stream stripping. The absorption reactions are reversed in the regenerator with heat supplied by stripping generated in the reboiler. The rich solution flows down through the regenerator. Steam rising up through the column strips the CO_2 from the amine solution. Also for the regenerator the standard values are taken from [30] for the same reasons mentioned under the absorber. The height of the column is *10.7m* and the diameter is *5.5m*.

8.10.3 Reboiler

A kettle type reboiler is used to provide the necessary heat needed in the regenerator. Solution flows by gravity from the regenerator to the reboiler. The liquid level is maintained by a weir to ensure that the reboiler bundle is submerged. Steam is used for reboiler heat. The vapour that is produced by the heat exchanger is piped back to the regenerator to provide stripping vapour. The reboiler is by far the most energy consuming part of the plant. To capture *6.3%* CO_2 the reboiler duty is *90MW*. It is possible to capture up to *90%* of the CO_2 using this setup. The only drawback is the amount of energy needed for the regeneration of MEA.

The CO_2 leaving at the top of the regenerator has a pressure of 1bar and is not pressurised as this is beyond the scope of the project. This can be compressed in later stages to the desired pressure at which CO_2 can be sold as a valuable product. In the future the amount of CO_2 removed should meet the values restricted by the law. In that case it will become more attractive to pressurise and sell CO_2 as valuable product. Because of the large amounts of CO_2 it is more obvious it will be pumped in oil or gas wells to withdraw the last barrels of oil out of the well. Furthermore, CO_2 replaces the withdrawn oil or gas and the well is maintained instead of leading to geological displacement.

In Table 8-16 is given a summary of the most important data of the absorber-stripper system.

Table 8-16: Main dimensions and duties of the absorbers-stripper system

Dimensions and duties	Absorber	Stripper
Height (m)	*15*	*10.7*
Diameter (m)	*9.8*	*5.5*
Reboiler heat duty (MW)	*90*	

9 Wastes and sustainability

In this chapter an evaluation is presented of the direct wastes that are produced in this process. Waste stream sizes are given and an overview of waste composition, their effect, disposal methods and a discussion of the possible risks involved in handling these products is given in Appendix XX.

9.1 Direct Wastes

In this process, a waste stream is split up to produce useful products and a less environmental harmful waste gas stream. While processing, a number of wastes are generated; these are chronologically listed in Table 9-1 and their removal is briefly described. Appendix X shows an extensive table of the waste streams and their disposal possibilities.

Table 9-1: Waste streams and their solutions

Waste	Streams (ton/year)	Removal method	Further processing
Fly ash	$1.20 \cdot 10^3$	Electrostatic precipitation	Stored and sold
HF and HCl	$5.68 \cdot 10^4$	Absorption in water	To wastewater treatment plant
MEA salts	$1.12 \cdot 10^3$	Solid-liquid separator	To a specialised wastewater treatment plant
Treated flue gas	$1.59 \cdot 10^8$	Cleaned by process	Released to air

In the first unit the fly ash is separated from the flue gas by means of electrostatic precipitation. This fly ash has to be stored at first, before it can be further processed.

The next unit is an HCl/ HF removal section. The removal is achieved in an absorber column, where these acids are absorbed in water. A wastewater treatment plant can remove the separated HF and HCl in solution up to legal requirements, after which the treated wastewater can be disposed of into the surface water.

In the solvent recovery of the SO_2 separating membrane unit very small amounts of insoluble salts could be formed. However, when the membrane works properly only CO_2 and SO_2 are present in the retentate and this does not lead to salt formation. Therefore, normally no insoluble salts are formed in this unit.

In the CO_2 removal membrane unit, small amounts of insoluble MEA salts could be formed with impurities when are present. Since in normal operation only CO_2 passes through this membrane, no salts will be formed.

In the main CO_2 separation section, in the regeneration of MEA, some insoluble MEA salts can be formed with impurities in flue gas, oxygen, sulphur or nitrogen dioxide and traces of HF or HCl. These salts are separated from the regenerated MEA by a Solid Liquid separator.

The insoluble salts that are formed in this process can be removed with S/L separators and are sent to specialised waste treatment companies. These might dispose of these salts by means of landfill.
The treated flue gas is also a waste stream, which can be emitted to the environment via a stack since it is within legal regulations.

The chemicals that are required in this process (bromine and MEA) are bought in large quantities at a time, so that one-month supply is present on site. Since large amounts are used, large containers are required which the suppliers can reuse (after cleaning if required). Therefore, no additional wastes in the form of used containers are formed.

Since no heterogeneous catalysts are required in this process, no catalytic wastes are formed.

9.2 Process Choice Versus Waste Production

By use of the ESP, the fly ash is separated from the gas stream and obtained in such purity that it can be sold for further use.

The removal of HF and HCl leads a significant waste stream in this process. However, when the aqueous absorber effluent is treated in a wastewater treatment plant, a relatively unharmful stream that can be discharged into surface water is obtained. The need for addition of alkali to neutralize these streams in the process, which might lea to insoluble salt formation, is therefore circumvented.

Due to the use of membranes rather than common absorber columns, the SO_2 present in the flue gas stream can be more efficiently separated from the other components. This leads to negligible concentrations of impurities in the SO_2 conversion process, and therefore the need for purge streams that might contain hazardous process chemicals is removed. The CO_2 that is present in this process can be easily removed and together with the CO_2 that is separated from the remaining flue gas stream in the MEA scrubber, be compressed and sold as a technical grade gas.

In the MEA scrubber the largest waste stream is formed, which consists of deteriorated MEA and several insoluble MEA salts that can be formed with oxygen, sulphur dioxide and nitrogen dioxide contained in the flue gas. Nevertheless, this option for CO_2 removal was chosen since membranes could not be used due to the large size of the gas stream, and scrubbing with amines was not yet considered an available technology.

9.3 Sustainability of the Process

Sustainability is one of the major topics in science and engineering the last decades. According to the authors sustainability is the ability to provide the needs of today's population without damaging the environment and the earth for the future generations. It originally only applied to natural resources, but has expanded its definition to other fields, such as functionality, economics, social, cultural and land utilisation.

This project deals with flue gas coming from a coal-fired power plant and coals are considered one of the future possibilities for energy. Cleaning the waste stream (flue gas) is therefore an important issue for the utilisation of coals.

The process designed in this report uses toxic chemicals, but because of the recycle streams it does not require much raw materials. This means that the production of wastes is relatively small. Almost all chemicals remain in the process, which means that nothing is used. By the means of the authors' definition, our process is therefore sustainable, because everything is recycled.

Concluding, it can be said that the process at hand is a relatively clean and green process, despite the use of potentially dangerous and toxic chemicals. Since these are continuously regenerated and recycled, the total amount of wastes produced remains relatively low. The use of membranes for the separation of SO2 from flue gas prevent the entering of large amounts of impurities from the gas stream to enter the process that can have a detrimental effect on the used solvents. This prevents not only the formation of wastes but also reduces the operating costs since no large chemical make-up streams are necessary.

10 Process Safety

Process safety depends on different terms. Important is the distinction between hazard and risk. Hazard means a physical or chemical characteristic that potentially harms people, environment or property. A hazard includes a hazardous material, an operating environment and the unexpected events as stated in Lemkowitz [31]. Risk includes the possibility or likelihood, the occurrence of the undesired effects and the results of these effects [31].

This chapter deals with the hazard of the operations of the process. Therefore a hazard and operability study is carried out in paragraph 10.1. Another way to analyse the safety of a process is by means of the Dow Fire and Explosion Index (FEI). This is explained and carried out in paragraph 10.2. A HAZOP focuses more on the equipment and control system used, while the FEI is more concerned with the characteristics of the chemicals used. Since it turned out that the chemicals used in the process are not very flammable or explosive, a Dow Chemical Exposure Index is carried out. This focuses on the exposure limits for the personnel and the surroundings. This is therefore another interesting way of determining the potential danger of the process. Paragraph 10.3.2 deals with the Dow Chemical Exposure index.

The procedure of the safety analysis can be seen in Appendix O.

10.1 Hazard and Operability study (HAZOP)

A HAZOP has three goals: to identify and evaluate hazards of the designed process, to identify operating or quality problems and to identify practical problems regarding maintenance operations. It is a qualitative method for hazard analysis that examines the proposed design by generating questions about it in a systematic manner, according to S.M. Lemkowitz in [31]. On the basis of guidewords, deviations in certain parameters of the process (flow, temperature and pressure) are evaluated. These deviations will have possible causes and consequences that require actions. The HAZOP analysis includes these different factors.

The HAZOP analysis for the reaction section is shown in Appendix O. Because the reaction section is considered the most sensitive section of the design process, the HAZOP focuses on this part.

There are many possibilities that the reactors fail, but this is the case in every process. The HAZOP therefore is not the only safety analysis that must be carried. From the table in Appendix O is clear that dikes and control systems (as explained in chapter 6) are necessary for safer operation of the plant. To include the nature of the chemicals used in this process, further investigation is necessary. The following paragraph focuses therefore on the fire and explosion characteristics of the chemicals.

10.2 Fire and Explosion Index (FEI)

10.2.1 Potential dangerous species

In order to determine the problems with the proposed design, it is important to know which species is a potential threat to the surroundings or human's health. In Table 10-1 the most dangerous substance are summarised with their characteristics. Equation O-1 in Appendix O, taken from [35], is used to calculate the LD_{50} for the dissolved HBr (*47%*) in water.

Table 10-1: Important characteristics for potential harmful species

	Phase at standard conditions	Flammability (N_f)	Reactivity (N_r)	Health (N_h)	MAC-value (mg/m^3)	LD_{50} (mg/kg) for rat
SO_2	*G*	*0*	*0*	*3*	*5*	*3120*
CO_2	*G*	*-*	*-*	*-*	*9000*	*-*
Br_2	*L*	*0*	*0*	*3*	*0.7*	*2600*
HBr	*L*	*0*	*0*	*3*	*6.7*	*11840*[1]
H_2SO_4 (98%)	*L*	*0*	*2*	*3*	*1*	*2140*
H_2SO_4 (60%)	*L*	*0*	*2*	*3*	*1*	*2140*
MEA	*L*	*2*	*0*	*3*	*2.5*	*1720*
$CaCO_3$	*S*	*0*	*0*	*0*	10^2	*6450*
$CaSO_4$	*S*	*0*	*0*	*0*	10^1	*3000*

From Table 10-1, it can be concluded that bromine, hydrogen bromide, sulphuric acid and MEA are the most dangerous substances. This is mainly due to the low MAC-values and the flammability factors. Appendix XXX shows the NFPA-code and the Chemiekaarten for the used chemicals.

10.2.2 FEI factors

The FEI consists of three major factors: the material factor (MF), the general process hazards (GPH) and special process hazards factors (SPH). The GPH and the SPH are indicators for the process, but the GPH relates to the process type or the potential and the SPH relates to the amounts of material used in the process, as stated by Lemkowitz in [31]. The FEI is then an indication for the degree of hazard concerning the process.

Since the material factor is zero for bromine, it is not taken into account in the FEI. The material factor for H_2SO_4 is based on the reactivity and the material factor of MEA is based on the flammability. Combining these two factors leads to a material factor MF=24, taken from figure 5.1 in [31]. This is therefore the material factor used for the FEI.

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[1] For the 47% of HBr in water

[1] The MAC-values for $CaCO_3$ and $CaSO_4$ are based on the maximum allowable concentration that is allowed to be inhaled without respiratory hinder.

To give more value to the FEI for the new process, it is compared to the FEI of the current existing process. The table in Appendix M therefore shows both FEI's. The decomposition temperature of the limestone equals T_d = 1192 K (wikipedia), which means that it has a material factor MF=40, taken from [31]. This is used in Appendix M.

From this table, the fire and explosion index is estimated at FEI=122.40. This means that the degree of hazard for the process is considered to be intermediate (index range 97-128), taken from Lemkowitz in [31]. Compared to the current process with calcinations, the FEI has improved significantly. The major problem with the current process is the high adiabatic decomposition temperature (>1098) of the limestone that causes the MF to be so high.

10.3 Chemical Exposure Index (CEI)

Since bromine has a material factor of zero, it is impossible to carry out an FEI. However, as seen in Table 10-1, bromine is very toxic. This characteristic is not treated in the FEI of Dow, but by another index, the Chemical Exposure Index (CEI) also of Dow [33]. To calculate the CEI, the approach followed is given in Appendix O.

The first step is to determine the possible dangerous chemical species. From Table 10-1 it is concluded that bromine is the most toxic species in this process. Therefore, a closer look is taken at the toxicity of bromine.

10.3.1 Toxicity of Bromine

The maximum allowable concentration (MAC) for bromine is $0.7 mg/m^3$ from Table 10-1. This implies that the health rating according to the Dutch Pressure Vessel Code in [31] by Lemkowitz is N_h=5, with MAC-value$<1 mg/m^3$. This is the highest possible ranking. The chemicals of group 5 cause serious injury or death with short exposure. This is therefore a serious problem in this process. No bromine should be able to leave the process at any stage.

The potential danger of bromine is also explained in Appendix L. There, figure L-1 shows the concentration-time exposure plot for bromine. The exposure time of bromine to cause harm is short. Figure L-2 shows that there is no no adverse effect level (NAEL) for bromine exposure. This also makes bromine a dangerous substance.

10.3.2 Chemical Exposure Index

For the second step the CEI uses Emergency Response Planning Guidelines (ERPG's) to estimate the potential harm of a substance as stated in [31] by Bibo et al. There are three different types of ERPG's. For bromine, taken from [31], for sulphuric acid, taken from [33], and for MEA, taken from [34], they are showed in Table 10-2.

Table 10-2: Chemical Exposure Index for bromine

	Br_2 (mg/m^3)	H_2SO_4 (98%) (mg/m^3)	MEA (mg/m^3)	HBr (mg/m^3)	Explanation
ERPG-1	*1*	*2*	*15*	*7*[3]	Maximum airborne concentration below which it is believed that nearly all individuals could be exposed for one hour without experiencing other than mild transient adverse health effects.
ERPG-2	*7*	*10*	*75*	*17*	Maximum airborne concentration below which it is believed that nearly all individuals could be exposed up to one hour without developing irreversible or serious health effects and symptoms.
ERPG-3	*33*	*30*	*75*	*85*[4]	Maximum airborne concentration below which it is believed that nearly all individuals could be exposed up to one hour without developing life-threatening health effects.

With these values it is possible to calculate the CEI, however first the scenario with the largest AQf has to be determined. In general there are six different scenarios for the undesired release of toxic substances [33]:

1. Process pipes failures
2. Hoses rupture
3. Pressure relief valves relief directly to the atmosphere
4. Vessels rupture
5. Tanks overflow and spill
6. Others

The vessels containing toxic substances (e.g. V03 for bromine) are not so large, so they are not considered to rupture or overflow here. The largest release of toxic material will be caused by failure of the outlet valve of the tanks.

The toxic chemicals are bromine, hydrogen bromide, sulphuric acid and MEA and they are all liquids under the conditions of the process. The basis for this calculation is therefore the following equation 10-2 for liquid release, taken from [33]. In Appendix M.5 the calculation method for the CEI is given.

$$G_l = C_d A\rho\left(\frac{2(P-P_a)}{\rho} + 2gh\right)^{\frac{1}{2}} \qquad (10\text{-}1)$$

$$P - P_a = P_g$$

Table 10-3 shows the results for the hazard distances for the ERPG's and the CEI.

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[3] Not available so estimated with the odor threshold value of 2 ppm

[4] Not available so calculated as ERPG-3 = 5 x ERPG-2

Table 10-3: Results of the chemical exposure index

	Chemical Exposure Index	Hazard distance (m) for ERPG-1	Hazard distance (m) for ERPG-2	Hazard distance (m) for ERPG-3
Br_2	*1561 → 1000*	*41292 → 10000*	*15607 → 10000*	*7188*
H_2SO_4	*4*	*82*	*37*	*21*
MEA	*117*	*2617*	*1171*	*1171*
HBr (47%)	*418*	*9337*	*4176*	*1320*

The CEI and the hazard distances for bromine are larger than the maximum so they are determined at 1000 and 10000 respectively. The sulphuric acid has a low vapour pressure and this influences the airborne quantity evaporated from the pool surface. The hazard distances for sulphuric acid are therefore significantly lower than for the other substances.

10.4 Conclusions and recommendations regarding safety

10.4.1 Bromine

The Chemiekaarten recommend using ventilation below the columns that contain bromine. Bromine is a liquid at room temperature, but it has higher density (relative density at *20°C=2.0*) than water (and than air (5.5x) in gas phase). Besides this, bromine has no NAEL. Therefore the employees working with the bromine section must take very much care about their personal safety. The pipelines need to be regularly checked to see whether they are still completely closed. The same holds for the buffer vessels and the reactors. Most of the bromine stays actually in the process. Some bromine will have to be purged, but this will not be much. An excess of water is used to ensure that the heat will not increases too much and no bromine will be left to further react with another substance. The CEI for bromine equals *1000*, which is the highest possible ranking. It is therefore very important that the bromine does not leave the tanks and the plant! Dikes around the reactors and vessels will prevent the formation of large liquid pools in case something fails.

10.4.2 Sulphuric Acid

Sulphuric acid has a reactivity ranking of *2*, which means that it is significantly reactive without heating. Caution is therefore necessary when working with this product. Ventilation is important, so the reactor should be placed outside. H_2SO_4 is harmful for the environment, so a drainage system to a basin would be a good solution to prevent damage from possible leakages. Since the final product of the process is concentrated sulphuric acid, it should be very well stored and preferably transported immediately. Sulphuric acid has a CEI of *4*, which is very low. This is mainly due to the low vapour pressure. Liquid sulphuric acid is still not healthy and it must be treated with care.

10.4.3 MEA

MEA has a flammability ranking of *2*, which means that it has a flash point between *40^oC* and *100^oC*. Flames or any other kind of fire must therefore be excluded from the site near the MEA section. The CEI of MEA is *117*. This means that care is necessary for working with MEA. The difficulty with MEA is that the ERPG-2 is equal to the ERPG-3. There is no difference between developing irreversible or serious health effects and life-threatening effects.

10.4.4 Hydrogen bromide

Hydrogen bromide is in between the other chemicals. It has a CEI of *418*. Because it is dissolved in water, the HBr is not that toxic as expected. It should still be treated with care in the process and just as like the other sections, dikes are a necessity. It dissolves completely in water, so it is assumed that no HBr gas will leave the water once it is accidentally released from a reactor or tank.

10.4.5 Overall conclusion

In general, this process utilises many toxic chemicals. It should therefore be situated far from housing areas and environmental areas. The materials for the reactors must be careful chosen.

The HAZOP analysis does not show unexpected difficult situations. This is mainly due to the fact that the operating conditions of the reactors and vessels are mild. The Fire and Explosion index shows an improvement compared to the current process with limestone, because the material factor for the new process is much lower. The degree of hazard according to the FEI is considered to me intermediate, which is an acceptable ranking for the process.

However, the toxicity of most of the different chemicals utilised is very high, especially for bromine. This results in high Chemical Exposure Indices and hazard distances. It is therefore very important that emergency measures are clear to all employees and that dikes and emergency basins are available.

Overall, this process is dangerous, not because of the operating conditions or explosiveness sensibility, but because of the potential harm the chemicals can cause when accidentally released.

11 Economy

After the process and equipment design is finished, the economic evaluation is carried out. Is the process economically feasible or should the process be discarded, because the benefits are exceeded by the costs? Since the designed process is basically a waste treatment plant and this is necessary, otherwise there would not be given out a permit to run this plant, perhaps it is not even necessary to be stand-alone profitable. Is the process comparable to other flue gas desulphurisation plants around the globe or are the costs much higher than other plants.

11.1 Cost of equipment

First the cost of the process equipment needs to be calculated. The complete calculation of all equipment costs can be found in Appendix N. For the estimation of the purchased equipment different sources are used and this could lead to different estimations of same pieces of equipment. It is expected however that the discrepancies of the sources will not deviate too much from each other.

The heat exchangers cost around *€1.13 million*, the columns *€2.6million*, the reactors *€280.000*, the separators *€20.1million*, the vessels *€100.000* and the pumps *€390.000*.

The total equipment cost is *€24.7million*. By far the largest part is the cost of the separators and the biggest part of that are the costs of the membrane. This is an inevitable parameter because it is difficult to split of sulphur dioxide from the flue gas stream at such a high efficiency (*99.5 %*).

With the cost for purchased equipment (PEC) known the total investment cost (TIC) is calculated. First, the direct capital cost (DCC) is calculated from the purchased equipment cost. The direct capital cost consists of all physical objects of the plant. So not only purchased equipment, but also piping, instrumentation, storages etc. From [2] for liquid processes a typical value to multiply the equipment cost with is 3.4. Equation 11-1 shows the relation of the DCC to the PEC.

$$DCC = 3.4 * PEC \qquad (11\text{-}1)$$

From the direct capital cost the fixed capital cost is calculated. From [2] follows that the direct capital cost should be multiplied by 1.45 to get to the fixed capital cost (equation 11-2):

$$FCC = 1.45 * DCC \qquad (11\text{-}2)$$

The difference between the fixed capital cost and the direct capital cost is the indirect capital cost. The indirect capital cost consists of non-physical parts of the plant erection, such as design and engineering costs, contractor's fee and contingency. So the fixed capital cost will be *€121.9million* and the indirect capital cost *€37.8million*, as shown in equation 11-3:

$$ICC = FCC - DCC \tag{11-3}$$

Table 11-1 shows a summary of the calculated costs so far.

Table 11-1: Purchased equipment cost

Purchased equipment cost	*€ 24,731,439.92*
Direct capital cost	*€ 84,086,895.72*
Indirect capital cost	*€ 37,839,103.07*
Fixed capital cost	*€ 121,925,998.80*

According to [2] the fixed capital cost makes up *80%* of the total investment cost. So the total investment cost for this process will be *€152.4million*. The other *20%* consist for *14%* out of licence cost and for *6%* of working capital.

$$FCC = 0.8 * TIC \tag{11-4}$$

Table 11-2: Total investment cost

Cost	percentage of TIC	
Total investment cost	*100.00%*	*€ 152,407,498.49*
Fixed Capital cost	*80.00%*	*€ 121,925,998.80*
Licence costs	*14.00%*	*€ 21,337,049.79*
Working capital	*6.00%*	*€ 9,144,449.91*

11.2 Operational cost

To determine the total operational cost it is split up in fixed and variable costs. Maintenance is taken as *10%* of the fixed capital cost. Appendix N.2 shows the operational costs for the process. The plant is operated by 4 shifts of 5 operators. An operator earns approximately *€30.000* per year so this makes *€600.000* annually. Laboratory cost and supervision both are about *20%* of the operating labour cost. Plant overheads are *50%* of the operating labour cost. Capital charges are about *15%* of the fixed capital cost and rates and local taxes will be *6%* of the fixed capital. Insurance and licence fees and royalty payments both are about *1%* of the fixed capital cost.

The variable operating cost consists mainly of raw materials and utilities, but also some miscellaneous materials.

In Appendix N-2 the cost for the raw materials are calculated. The price of MEA is *$1360/ton*, it is *30wt%* in water solution and water costs *$0.50/ton*. Hence the cost per ton is *$408.35*. The information has been taken from [1]. Bromine is *$992/ton* [36], but is not really of importance, since normally the bromine make-up will be 0. The same holds for the sodium sulphite make-up stream, which has been estimated to be *$100/ton*.

The prices for utilities have been taken from [2]. The prices are in pound sterling in 1998 and have to be converted to euros in 2005. Appendix N-2 shows the costs of the utilities necessary for the operation of the plant. Table 11-3 shows the costs per year for the raw materials and the utilities.

Table 11-3: Costs for raw materials and utilities per year

Raw Materials	€344.314,63/year
Utilities	€8.837.984,47/year

The cost of miscellaneous materials is taken as *10%* of maintenance, so *1%* of fixed capital cost. Shipping and packaging are expected to be costing anything.

Adding up the variable and fixed operating cost gives the direct production cost. Sometimes some additional process costs will have to be accounted for. These consist of sales expense, general overheads and R&D. In this case these costs are expected to be about *20%* of the direct production cost. This leads to an annual production cost of *€56.2million.*

11.3 Net cash flow

Now the annual net cash flow is calculated. The gross income consists of two things: income from the sulphuric acid sales and the evasion of fines because of the carbon dioxide capture. The sulphuric acid will be sold at *€70/ton* and this leads to an annual income of *€3.5million*. In the future (2012) for each ton of carbon dioxide that is emitted *€100* fine has to be paid. The process will capture approximately *180000tons*; so *€18million* of fines will be evaded.

Table 11-4: Calculation of net cash flow

			cost
Total annual production cost			*€ 56,280,118.49*
Gross income	price/ton (euro)	ton/year	price
Fine evasion (CO2)	*€ 100.00*	*181776.5*	*€ 18,177,648.74*
Sulphuric acid	*€ 70.00*	*50844.96*	*€ 3,559,147.20*
total			*€ 34,543,322.54*

However it can be concluded that this process is economically not feasible. The annual net cash flow is negative so at first it is possible to say that the process is economically not feasible. Being profitable is not a boundary condition for this process. If nothing would be done on sulphur dioxide capture the plant would certainly not be given a permit and as the process is a waste treatment plant it does not necessarily have to be profitable.

The annual production cost is very high, because of the high equipment cost. This is mainly due to the very expensive membranes. The membranes' main purpose is sulphur dioxide removal and that part of the process is the least profitable. The process could be much more profitable if a cheaper alternative would be chosen. The biggest problem is that it is difficult to reach the specification of *99.5%* sulphur dioxide removal. Conventional scrubbers cannot reach this specification. Therefore has been chosen for the costly option of membrane separation.

The production costs are related to the purchased equipment cost and the plant cannot be profitable since the equipment is relatively expensive. This makes the annual production cost higher than the annual income.

According to [38] a flue gas desulphurisation plant of an *840MW* power plant costs approximately *€650million*. In this article in Bulgaria a flue gas desulphurisation plant is built in addition to an existing power plant that emits large amounts of sulphur dioxide. This is done because the plant emits much more sulphur dioxide than allowed by the European Union and it is necessary that it is done before Bulgaria can join the European Union. It is therefore comparable to the designed process, which only beholds flue gas desulphurisation (and some additional carbon dioxide capture).

The total investment cost of the designed process is approximately *€150million*, so this is substantially lower than a comparable plant. So from a comparison with a real-life flue gas desulphurisation plant can be concluded that the designed process is economically feasible.

12 Creativity and Group Process Tools

In this chapter an outline of the project setup will be given. The goal of this project setup is to give an idea of when and how creativity was implemented into the project. The different creativity tools will be explained and it will be pointed out when these different tools were used. During the project many decisions and choices were made. In this chapter an overview will be given of how and when the most important decisions were made.

12.1 General Project Setup

The project setup is shown in a diagram given in Figure 0-1 of Appendix 12-X. This setup follows a rather general build up which is used for smaller sub problems as well.

First the task to be solved is defined, in the overall conceptual design this is the separation and conversion of at least *99.3%* of the SO_2 and the separation of *6%* of the CO_2. After defining a clear task, an orientation phase is started in which the team familiarises itself with the subject and gathers general information on the subject. With the general knowledge of the subject present after the orientation phase a directed literature review is performed. The search items looked for are shown in Figure 0-1 of Appendix 12-X as well.

The results from the literature review are compared with each other and from the most promising process bases a preliminary basis of design is made. These results are given in Figure 0-1 of Appendix 12-X under the heading alternatives.

These preliminary bases of design enable the team to make a better selection between the processes available. During the construction of a preliminary basis of design multiple new problems may arise and new literature search may be necessary. Therefore feedback from the preliminary BOD block to the selection and the literature review block is shown in Figure 0-1 in Appendix 12-X. The factual conceptual design can be started after the selection for the best process option from the preliminary bases of design. The conceptual design is off course followed by the reporting of the results. The reporting is shown only at the bottom of the diagram but is off course in reality already present over the duration of the project.

The project setup described above is rather general, therefore to give more insight in the decisions made and the creativity tools used, the project is divided in three main phases. These phases are split up by the three main meetings, the project kick-off meeting, preliminary basis of design review meeting and the final presentation. This setup is schematically given in Figure 0-2 Appendix 12-X. All three phases will be discussed separately in the next three paragraphs.

12.2 Phase 1

The first phase of the project runs from the start of the project to the kick off meeting which is from 3 Oct 2005 to 18 Oct 2005, around 2 weeks. In this phase an orientating investigation in stimulating creativity during the project done. Furthermore a clear assignment definition was made, an orientation into the problem and already part of the literature research were done as shown in Figure 0-1 of Appendix 12-X.

12.2.1 Creativity

At the start of the project it is investigated how to stimulate the creativity of the group and the group members during the project. All group members read two articles on creativity and stimulating creativity and summarised the useful techniques in a three page article that were discussed with the creativity coach. The most important findings from this creativity are treated below.

Group Brainstorm Sessions
Group brainstorm sessions will enhance the creativity of the group. It is hereby important that the so-called process blocking (people cannot express their ideas when other people are talking) and free riding (people don't feel their ideas being appreciated) are prevented. This can be done by good organisation of brainstorm sessions and writing ideas down instead of just discussing. Another important point of attention is that the group takes enough time to let the ideas settle which enhances the individual creativity. One scheduled brainstorm session was held during the first phase and some smaller sessions were held more spontaneously.

Critical Analysis Sessions
To enhance creativity and communication a so-called critical analysis session tool can be used, meaning the group takes the time during the project to critically analyse the results and progress made until that point.

Non-Technical Analysis Sessions
The non-technical analysis sessions are meant to stimulate communication between the group members. It is important in these sessions to let go the technical aspect of the project and to discuss aspects such as planning and communication.

Creativity Coach Meetings
The creativity coach meetings are very important for the creativity and the group progress. It is very useful to have a third person who can function as a soundboard. Furthermore the creativity coach can indicate when the group gets too focused or the other way around. One meeting was held at 12 Oct 2005.

12.2.2 Important Decisions

Two important decisions are made in phase 1 of the project. First after orientation into the problem it became clear that for the conversion of CO_2 no promising options are available at the moment and that leaving this outside the scope of the project would give a more reasonable problem for the amount of time available. Therefore the group made in consultation with the supervising team the decision that the assigned task is to make a conceptual design for the separation and conversion of at least *99.3%* of the SO_2 and the separation of *6%* of the CO_2.

The second important decision made in the first phase is that a preliminary basis of design will be made for the most promising process options to be able to make a better choice for the best process option. The result was that in the second phase of the project two team members were responsible for the preliminary BOD of the bio-treatment process, one team member for the preliminary BOD of the Mark-13A based process, one team member for the SO_2 separation and one for the CO_2 separation.

12.3 Phase 2

The second phase in the project is defined as the period between the kick-off meeting and the preliminary basis of design review meeting. This phase takes around 2.5 weeks from 18 Oct 2005 to 4 Nov 2005. The literature is continued in this phase and finished. Furthermore the preliminary BOD's are made and a selection.

12.3.1 Creativity

During the second phase of the project one creativity coach meeting was held at 1 Nov 2005. One scheduled brainstorm session was held accompanied by multiple spontaneous sessions. In this phase also one critical analysis session was held which resulted into the combined treatment of the THIOPAQ process and the biotreatment process by S. Ebrahimi. These processes turned out to be quite similar. Numerous non-technical sessions were held. The non-technical issues were mainly discussed at the and in the so-called end of day meetings where the main focus was on planning and other varying problems.

12.3.2 Important Decisions

The three most important decisions made in the second phase of the project are discussed in this paragraph. After the main part of the literature study was finished the different process options were compared as is described in chapter 2. From the comparisons the group has decided that SO_2 separation could be best performed by means of a membrane and that the only feasible option for the separation of CO_2 is the MEA scrubber. Within the team some discussion occurred about the choice between the bio-treatment based process and the Mark-13A process for the conversion of the SO_2 therefore is was decided that for these two processes a preliminary basis of design would be made.

12.4 Phase 3

The third phase of the project lasts from the preliminary BOD meeting to the final presentation. This is the period from 4 Nov 2005 to 12 Jan 2006. In this phase the process is selected and the conceptual design is made.

12.4.1 Creativity

During the third phase no scheduled brainstorm sessions were held. The creativity in this phase of the project mostly came from the informal discussions during work. The week after the preliminary BOD review meeting multiple critical analysis sessions were held and resulted eventually in the selection of the Mark-13A based process instead of the bio-treatment process. The non-technical analysis sessions had place in the similar way as in the second phase of the project. Once or twice a week the progress made and the time planning were discussed in the so-called daily end of day meetings.
One creativity coach meeting was held on 7 December 2005.

12.4.2 Important Decisions

Two major decisions were made during the third phase. The first decision made was the initial selection for the bio-treatment process on the basis of the preliminary BOD's. This decision was made after the discussion with the supervisory team during the preliminary BOD review meeting and based on the team's own view of the best alternative.

The second decision made in the third phase of the project and the most important decision made in the project is to change from the bio-treatment process to the Mark-13A based process. This decision was made after intensive team efforts during the multiple critical analysis sessions held in the week after the preliminary BOD review meeting. It was decided to take one step back in the project and use the preliminary BOD of the Mark-13A based process present to further develop into a conceptual design instead of developing a new bio-treatment process, which would be time consuming.

13 Conclusions and Recommendations

List of Symbols

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Pros and cons of examined process options

13.1 SO_2 conversion/removal

13.1.1 Mark 13A

The Mark-13A based process uses bromine to convert sulphur dioxide into sulphuric acid. During this reaction water is consumed and hydrogen bromide is formed. This reaction is shown in equation A1-1.

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr \qquad \text{(A1-1)}$$

The hydrogen bromide is then electrolysed to form bromine and hydrogen according to the reaction shown in equation A1-2.

$$2HBr \rightarrow Br_2 + H_2 \qquad \text{(A1-2)}$$

The bromine is recycled to the reactor where the sulphur dioxide is converted. The produced sulphuric acid is concentrated to technical grade (96 wt% pure) and can be sold. The produced hydrogen can either be sold or can be used to generate energy needed for the process. The advantages of the process are the good performance of the sulphur dioxide conversion and the production of two useful and sellable products. The biggest disadvantage of this process is the use of bromine, which is a very reactive and volatile component. Bromine can form very toxic substances with organic compounds. Another disadvantage of this process is the high-energy use, due to the electrolysis.

13.1.2 THIOPAQ

The THIOPAQ process has a number of advantages, a major advantage is that it is a proven technology; currently there are worldwide a number of units in operation. Besides this, the high performance is what makes this process so interesting for SO_2 removal. Without the use of large amounts of dangerous chemicals, a very large SO_2 removal of flue gas can be achieved (down to *4ppmv* or even less). In the simplest form, the THIOPAQ process uses a scrubber, two bioreactors and a solid/liquid separation step to produce up to *50ton/day* of elemental sulphur. Moreover, the process is highly flexible in operation with regard to stream and composition fluctuations and the presence of contaminations in the gas that is to be treated.

According to [19], a disadvantage of the process is the large recycle stream required. Due to relatively low scrubber efficiency, large amounts of solvent are required that are continuously recycled. Another inconvenience of this process is that in order to conceptually design a process, taking a complete process option off the shelf would not make much sense. Regarding the advantages it was decided to use the THIOPAQ process as an important option for the process to be chosen, however it must be mentioned that the lack of creativity should be compensated for. This paragraph is based on information as was found in [24], [25] and [26].

13.1.3 Bio-treatment

S. Ebrahimi describes a new approach to flue gas desulphurisation in [20]. This consists of four sequential reactors with biochemical and chemical reactions. The first reactor is the absorption of SO_2 in a solution of $NaHCO_3$, which subsequently is fed to a biochemical reactor with bacteria. These bacteria convert the dissolved SO_2 into H_2S gas at a pH of 6,5-7,5. This gas continues to the third reactor where a chemical reduction by Fe^{3+} to elemental sulphur occurs. The Fe^{2+} is oxidised by bacteria in the fourth reactor and a liquid-solid separator purifies the elemental sulphur slurry. The main advantage of this process is that it is a combination of chemical and biochemical reactions. It combines mild operating conditions with the absence of toxic wastes. The H_2S is collected as a gas and this reduces the mass stream significantly. A disadvantage is that there are four different reactors and one slurry separator necessary, which cause the plant size to be large.

13.1.4 SCOT/(Super)-Claus [14]

The (Super)-Claus process is a widely used process in industry for treating refinery off gas. This off gas contains relatively high amounts of H_2S and this is usually converted into sulphur through a couple of Claus units. Because H_2S is not the only sulphur containing compound in the refinery off gas with just a Claus plant it is not possible to remove almost 100 % of the sulphur from the flue gas. In order to be able to remove these compounds (SO_2, COS, CS_2) from the flue gas, Shell developed the SCOT process (Shell Claus Off gas Treatment). In the SCOT process the sulphur containing compounds react with hydrogen to form H_2S and this is sent back into the Claus plant. The main advantage of these processes is that they are long proven and a lot of knowledge concerning kinetics etc. is available.

A big disadvantage for SO_2 removal is that at least a SCOT plant has to be built to convert SO_2 into H_2S and also a Claus plant will have to be built to convert the H_2S into elemental sulphur. Usually these plants (SCOT) are designed for low SO_2 streams; in this case the off gas contains no H_2S but a lot of SO_2. Therefore, a very large SCOT plant is required (larger than conventional SCOT plants) and also a large Claus plants. The investment costs will be very large and operational costs are also expected to be substantially larger since SCOT and Claus plants operate at much higher temperatures than the other options.

13.1.5 CrystaSulf

The Crystasulf process is a non-aqueous process in which H_2S is removed from gas streams and converted into elemental sulphur. In this process, H_2S reacts with SO_2 following the Claus reaction, reaction 0.

$$2\cdot H_2S + SO_2 \rightarrow \frac{3}{8}S_8 + 2\cdot H_2O \qquad \text{(A1-3)}$$

The process seems very promising, especially for the removal of H_2S from small to medium size streams. The disadvantages of this process regarding its use for the removal of SO_2 from flue gas are its small scale and the requirement of H_2S. When this process option would be chosen, a separate SO_2 to H_2S conversion unit (SCOT or biochemical) should be designed and placed after the absorber. This would lead to large process complexity and the advantage of a simple sulphur-producing unit would be lost. For these reasons, it was decided not to take the Crystasulf process as a viable process option for this design project. The information used for this paragraph can be found in [28].

13.1.6 Limestone scrubbing [21]

Limestone scrubbing is a widely used technology for sulphur dioxide removal from flue gas. Flue gas is contacted with limestone and water in an absorber and desulphurized through a chemical reaction between SO_2, calcium carbonate and water. Two slightly different kind of limestone scrubbing techniques are available: a dry limestone scrubber and a wet limestone scrubber. Often first a pre-scrubber is added to the system to remove hydrogen chloride and hydrogen fluoride from the flue gas stream. A wet limestone scrubber produces slurry consisting of calcium sulphate/sulphite and fly ash. In the USA this slurry is simply dumped and for that large areas are needed for this sludge disposal. In Europe usually these areas are not widely available and therefore more dry limestone scrubbing is applied. A dry limestone scrubber produces gypsum, which can be used for example in construction. The gypsum also contains certain amounts of fly ash containing heavy metals. Due to stricter future regulations, the gypsum will not meet the quality requirements and the construction companies also require gypsum of higher grade. Therefore, this gypsum will have to be landfilled. A second disadvantage is that the current scrubbers are at maximum capacity, whereas it is necessary to remove a larger amount of sulphur dioxide from the flue gas stream.

A big advantage is the fact that in a limestone scrubber also fly ash and acid gases, such as hydrogen chloride and hydrogen fluoride are removed from the flue gas. This is a relatively cheap way of disposing these acid gases, fly ash and SO_2. Another big advantage is that limestone scrubbing is the most widely used technology for current flue gas desulphurisation and therefore a lot of knowledge is available.

13.1.7 Membrane separation

Conventional capture technologies based on physical and chemical processes such as adsorption, absorption, cryogenics and membranes affect the (energy) efficiency and economics of the plant negatively [3]. Membrane contactors are efficient and flexible on removing greenhouse gases from flue gases, while operating over a wide range of concentration levels and volumetric flow rates. It is a hybrid process combining two conventional techniques. Separation of a pollutant through the membrane is completely integrated with the absorption operation in order to make optimal use of the benefits of both technologies. The membrane offers a flexible, modular and energy efficient device with a high specific surface area. The absorption process offers a high selectivity and a high driving force for transport even at low concentrations. The solvent used affects absorption selectivity and capacity.

In this project the membranes can be applied first to separate SO_2 from the flue gases and later to separate as much CO_2 as possible but within the boundaries laid on by the economics. Removing CO_2 completely requires too much membrane modules, which makes membrane application practically not feasible. Since in both cases the same hydrophobic hollow fibres are used, selectivity is based on the physical and chemical properties of the solvent and the gas velocity. First, to remove SO_2 a solution of 0.1M Na_2SO_3 can be used at 298K. A fixed gas velocity of 11.5cm/s and a liquid velocity as low as possible should be applied. All these parameters enhance the selectivity towards SO_2 in presence of CO_2. Second, to remove CO_2, a solution of K_2CO_3 can be used. However, the flux obtained is rather low. Addition of small amounts of amines in the range of 10wt%, to an aqueous carbonate solution enhances CO_2 absorption [2]. It also improves regeneration efficiency as well and largely avoids corrosion. MEA addition is the best choice as it is the cheapest and

improves the absorption to a larger extent than all other amines such as DEA (diethanolamine) or MDEA (methyl diethanolamine).
Besides membrane-based gas adsorption, this technique can be easily adapted to the specific demands of an individual plant and can be applied to most systems currently treated by conventional gas absorption technology. The membrane modules exist of hollow fibres fixed in modules. These hollow fibres are fragile; they are not very resistant to mechanical forces that are inevitably present. To make them usable the modules should have a moderate diameter to make it possible to repair and replace broken hollow fibres. To process flue gases on the required scale a lot of modules are needed, which significantly raises the investment costs.

13.1.8 Ammonia absorption

When a sulphur dioxide containing flue gas stream is contacted with ammonia, ammonium sulphate will precipitate; this can easily be separated from the ammonia. An advantage is that the ammonium sulphate that is formed can be sold as fertilizer and therefore is a valuable product. A drawback is that carbon dioxide will also be absorbed and therefore ammonia scrubbing of CO_2 is required and no choice can be made concerning the way carbon dioxide can be removed from the flue gas stream. This is a drawback, because from the literature search appears that MEA scrubbing is a more promising option than ammonia scrubbing. Another drawback is that if there is any NO_x in the flue gas stream ammonium nitrate will be formed and that is an explosive precursor, which is mildly hazardous.

13.1.9 Spheres [25]

Fluidised bed combustion (FBC) is a process to clean coal combustion. It is a favourable process to clean coal combustion, because there is the possibility for regenerative desulphurisation. In regenerative desulphurisation a sorbent is used to capture sulphur oxides *in situ* in the combustor at 859°C. Converted sorbent is separated from ash and transported to a second reactor (regenerator), where reducing conditions are applied to regenerate it. The regenerated sorbent is again fed to the combustor, while the sulphur-rich regenerator off-gas, containing, ± 10v% of SO_2 is used to produce an economically attractive product, e.g. sulphur of sulphuric acid. This minimizes both SO_x emissions, and soil contamination by spent sorbent. It appears that only certain mixed oxides are, at 850°C, capable of both capturing SO_x under oxidising conditions, and releasing it under reducing conditions. Calcium aluminates ($CaO.yAl_2O_3$) are most promising of oxides. Thy easily react into $CaSO_4$ in the combustor. During regeneration at 850°C, this $CaSO_4$ reacts to calcium aluminate rather than to CaS. This is the reason for the good regeneration selectivity. This sorbent is produced using the sol gel method. The gel particles are dried, and calcined at 850°C to yield strong porous γ-Al_2O_3 beads containing CaO.

Natural sorbents like limestone ($CaCO_3$) or dolomite ($CaCO_3.MgCO_3$) are fed to the combustor where the calcium oxide in these materials reacts with the sulphur oxides to form gypsum-like products. The sol-gel sorbent performs 6 times better than the other types of sorbent. But this cannot compete economically with the non-regenerative desulphurisation using limestone.

13.1.10 Activated carbon for SO_2 removal

Activated carbon can be used in a couple of ways to remove SO_2 from flue gas. It can for instance be used in a moving bed, where SO_2 is adsorbed in the presence of oxygen and water vapour on the activated coke, which leads to the formation of H_2SO_4. The regeneration of the activated carbon requires large amounts of water, and strongly adsorbed H_2SO_4 is not easily removed, which is a disadvantage.

Activated carbon can also be used in the form of fibres. These fibres show high SO_2 adsorption capacity and rates at temperatures of *100–180°C*, in the presence of oxygen and water vapour. An advantage is that carbon fibres show very high surface areas as commonly observed for activated carbons, but lack the separation difficulties as are observed for granular/ powder activated carbons. Also, it was shown that activated carbons are not very selective to SO_2 adsorption when more chemicals are present in the gas that is to be treated. The production costs of these fibres are very high, which is an important disadvantage. Moreover, the low stability of the performance, resistance to particulate matter and a lack of applications at large scales do not favour (fibrous) activated carbons for use in flue gas desulphurisation. For this paragraph information as found in [27] was used.

13.2 CO2 conversion/removal

13.2.1 Mineralization 0

For carbon capture two different options are available. The first option is the reaction of CO_2 with calcium carbonate or limestone and water to form calcium and bicarbonate ions. These ions can be deposited in the ocean short-circuiting the carbon cycle. The other option is the reaction with magnesium silicate forming the two stable salts silicon dioxide (quartz) and magnesium carbonate. A big advantage of mineralization is the formation of safe and stable salts, which can easily be deposited. A big drawback however is that the fraction that needs to be mined of magnesium silicate is even larger than the volume of the coal whose CO_2 it mineralizes. Another drawback is that mineralization is quite energy consuming.

13.2.2 Micro-organisms [16] and [17]

Autotrophic microbes can be used for converting carbon dioxide into biomass. The microbes can be grown in a photo-bioreactor and the grown biomass could be used as a food source for cattle. A big advantage for these processes is that they only require light to grow and are very low on energy consumption. A major disadvantage is that all investigated microbes do not grow sufficiently fast enough, so that enormous reactors are needed for a respectable removal of carbon dioxide from a flue gas stream. For a certain “well-growing” microorganism a 1-meter high reactor with an area of 386 km^2 has been calculated [17].

13.2.3 Methanol synthesis

Methanol can be synthesised through the reaction of carbon dioxide and hydrogen:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \text{(A2-1)}$$

Hydrogen is produced usually in syngas production:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \text{(A2-2)}$$

With the water gas shift reaction, the carbon monoxide can be converted into hydrogen and carbon dioxide:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{(A2-3)}$$

The following overall reaction is obtained:

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \text{(A2-4)}$$

So from each mole of methane, the feedstock for 1 mole of methanol is produced but also 1 additional mole of hydrogen. Therefore if carbon dioxide from flue gas is to be converted into methanol, for each mole of carbon dioxide 3 moles of methane will have to be converted. This is all at 100% conversion, which is not realistic; therefore even more methane will have to be burned in real-life. For this reason, methanol is not a very attractive option for carbon dioxide conversion.

13.2.4 Epoxides [18]

Carbon dioxide can react with epoxides such as propylene oxide or ethylene oxide to form cyclic carbonates. These cyclic carbonates are building blocks for polycarbonates and other polymeric materials. An advantage of such reactions is that they occur at very mild conditions (25 ^oC). A very big disadvantage is that there is approximately no knowledge available on kinetics and the catalyst and feedstock that are being used are relatively expensive.

13.2.5 Use of plant growth in greenhouses [23]

In the Netherlands a system has been developed to use carbon dioxide in a regenerative matter. In the Westland a lot of greenhouses are concentrated on a relatively small area. The plants in these greenhouses grow faster and deliver products of higher quality if carbon dioxide is added to these plants. To produce more carbon dioxide, it was common use to combust extra gas for carbon dioxide production. Only 20 kilometres further Shell used to emit high-grade carbon dioxide into the earth’s atmosphere. To reduce the total carbon dioxide emissions, an old pipeline that was already present in the Westland was used to feed high-grade carbon dioxide from Shell directly to the greenhouse to induce plant growth.

If relatively pure carbon dioxide could be produced it can be used for plant growth and it is a highly regenerative option. A big problem however is that any greenhouses should be very close to the power plant, since pipelines of that size are very expensive. Otherwise this will inevitably lead to enormous investment costs.

13.2.6 MEA scrubbing

The major advantage of MEA scrubbing is that it is a proven technology and a lot of knowledge regarding MEA scrubbing is available. The knowledge on this subject stretches from equilibrium constants to heat needed for regeneration of the MEA. Moderate process temperature and pressure is used. A major disadvantage is that the regeneration of loaded MEA (which has absorbed carbon dioxide) is very energy consuming. Another disadvantage is that MEA is very sensitive to impurities such as sulphur dioxide and HCl or HF. These components cause the degradation of MEA and will react irreversibly into insoluble salts, which have to be removed from the system. A result is that a MEA make-up stream is required, which leads to high costs since MEA is relatively expensive compared to other absorbents such as ammonia.

13.2.7 Ammonia scrubbing

Ammonia is much cheaper than conventional absorbents such as MEA and the energy consumption for the regeneration of ammonia is significantly lower than that of the MEA regeneration. Furthermore, this process operates at moderate temperatures and pressures. Together this leads to low process costs. The sulphur dioxide present in the flue gas will be converted to ammonium sulphate, which is a valuable product and can be sold as such. The biggest disadvantage of ammonia scrubbing is that virtually no information is available on the reaction kinetics, which makes it very hard for designing and sizing the absorber and regenerator. Another large drawback is that ammonia is rather volatile and thus it is possible that ammonia evaporates during regeneration and ends up in the carbon dioxide stream. This is highly unwanted and therefore expensive quality control will be needed, which will be a substantial part of the operational cost and investment cost.

13.2.8 Membrane separation

The membrane technology for CO_2 separation is comparable with that for SO_2 separation. See for chapter 13.1.7 for further information.

13.2.9 Cryogenic separation

Cryogenic separation of carbon dioxide from a flue gas stream is basically a distillation of the flue gas. An advantage of this process is that very pure carbon dioxide is produced, but this process has far more drawbacks. First of all the boiling point of carbon dioxide at atmospheric pressure is 194 K. To operate a distillation column at that temperature is very energy consuming. The fact that the flue gas stream is so enormous does not benefit this option too. Working at such low temperatures also leads to a substantial increase of safety measures and this is also directly cost-related and will lead too much higher operating costs.

13.2.10 DECAB amino acid absorption

DECAB is a new separation technology to remove CO_2 from flue gases. Its separation ability is based on an aqueous amino acid solution that precipitates after it has absorbed CO_2. This result in a higher driving force, meanwhile the slurry is highly loaded with CO_2. Due to this, investment costs are reduced, less equipment is needed and it also reduces the operation costs, less energy is needed to heat up the streams and to regenerate the solvent in comparison to the conventional amine based absorption technology. According to a study performed by TNO, the costs for capturing CO_2 cut in half when DECAB is used as an alternative of MEA technology. Furthermore, energy consumption can be reduced by 45% due to the higher absorption capacity and heat integration during regeneration. DECAB is not yet fully developed and cannot be applied. It will be in near future, because of the profits of this process.

13.2.11 Desiccant absorption [19]

A molecular sieve is a specially designed sieve that separates molecules based on their molecular weight or molecular size. The arguments in favor of this type of separation technology are that they are cost effective (once developed on a commercial level), produce minimal waste and can be adapted to a variety of carbon sequestration schemes. This type of sieve has an open structure that allows fluid to flow freely through the material. This material has been especially successful in the adsorption of polar and some flat non-polar molecules, such as CO_2. Up to 90–95% of the adsorbed gas can be desorbed upon application of a low voltage across the adsorbent.

13.2.12 Molecular sieve/basket [19]

Using zeolites as desiccant, carbon dioxide can be regenerated under depressurization. As the absorbent is heated, the carbon dioxide can be adsorbed at near normal pressure. Further regenerative capacity and power reductions can be achieved with a moderate temperature swing. A temperature regeneration range of *50–100ºC* was found to be effective. A problem with this process was found to be the reaction of the desiccant with SO_2 present in the flue gas. Carbon dioxide recovery was also attempted in the dehumidifier tower of the test pilot plant using alumina as the desiccant. The desorbed gas is then fed back into the inlet of the pilot plant for an improvement in terms of system configuration. This resulted in an overall reduction in power consumption of 3%. In the overall test results, the target removal efficiencies of 90–99% purity of CO_2 removed were achieved. Very little information is available of this option, so this is a very big drawback.

14Process Selection Diagrams

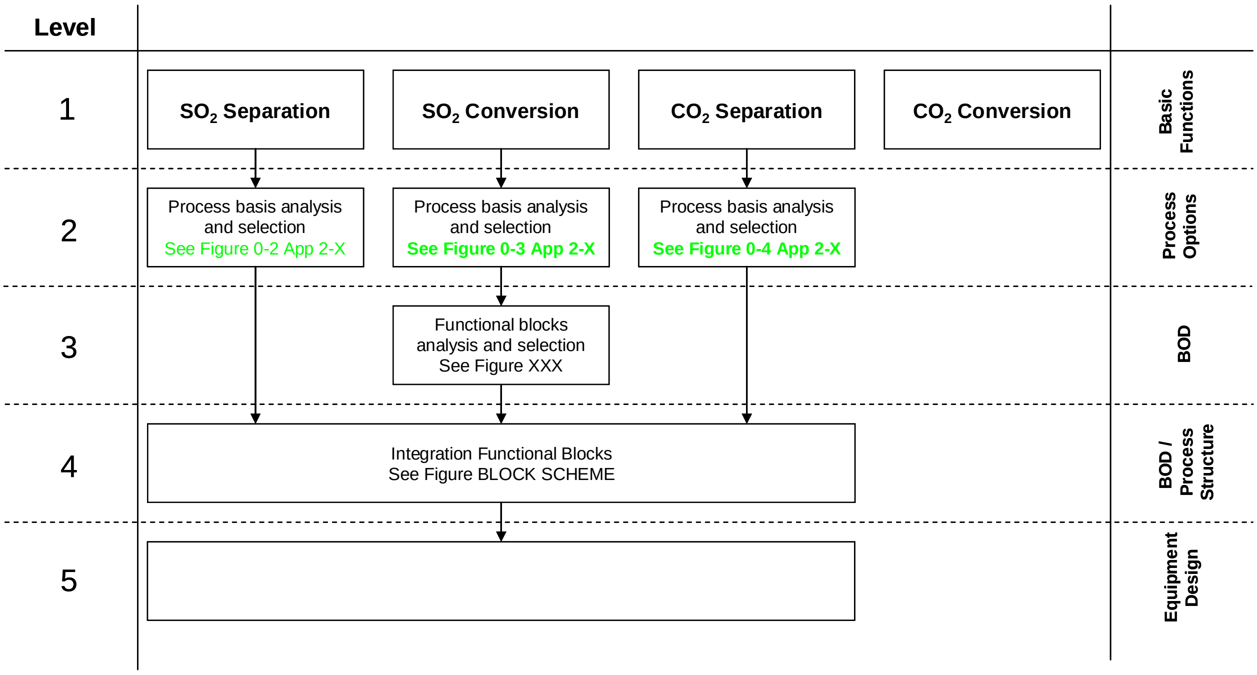


Figure 14-1: Process selection diagram

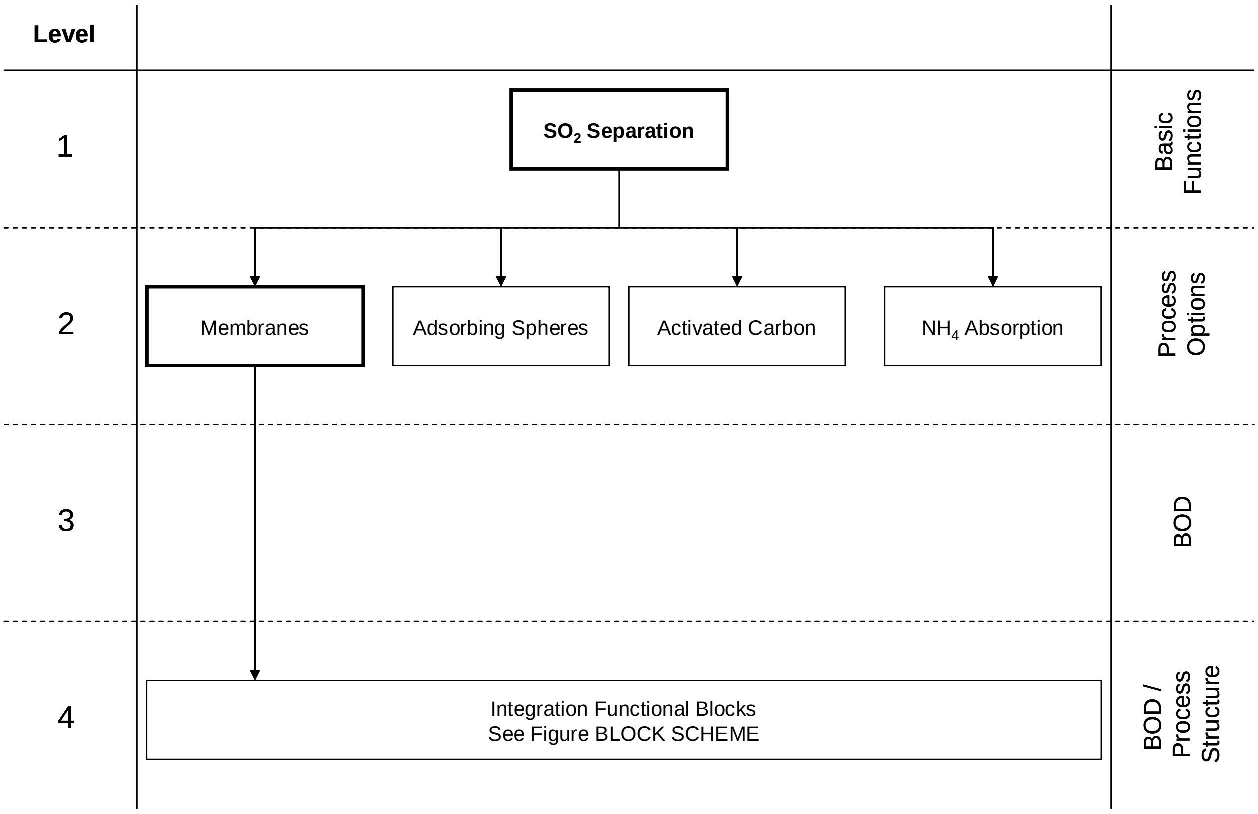


Figure 14-2: Process selection diagram SO_2 separation

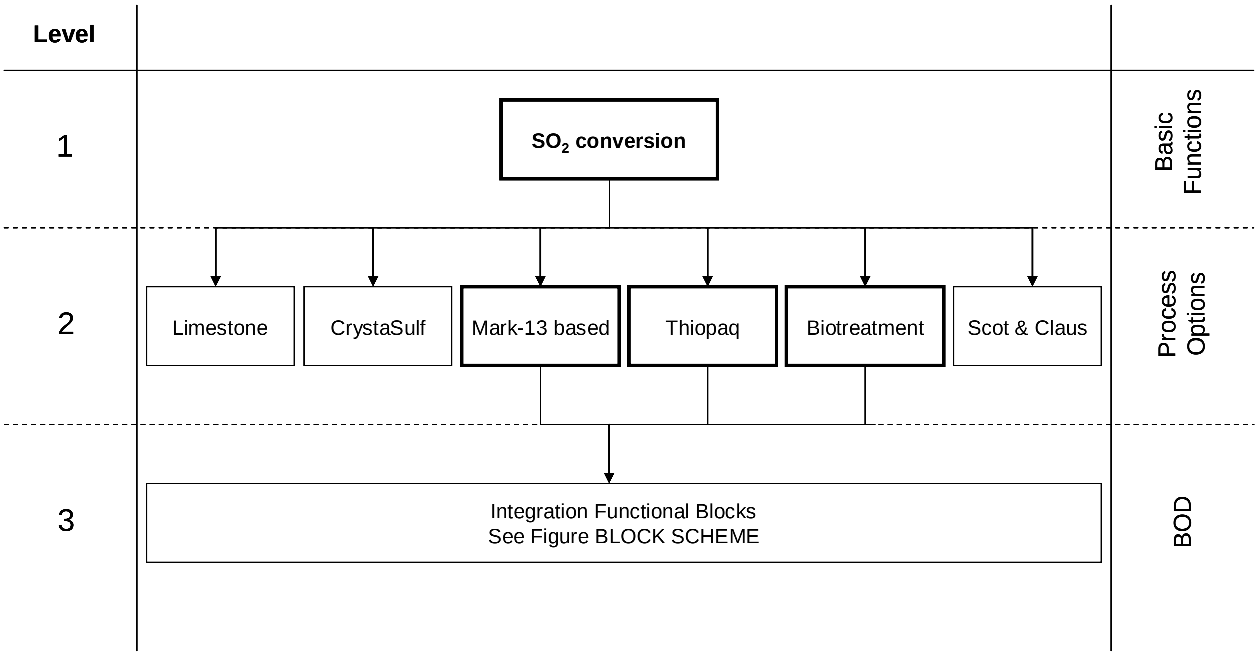


Figure 14-3: Process selection diagram SO_2 conversion

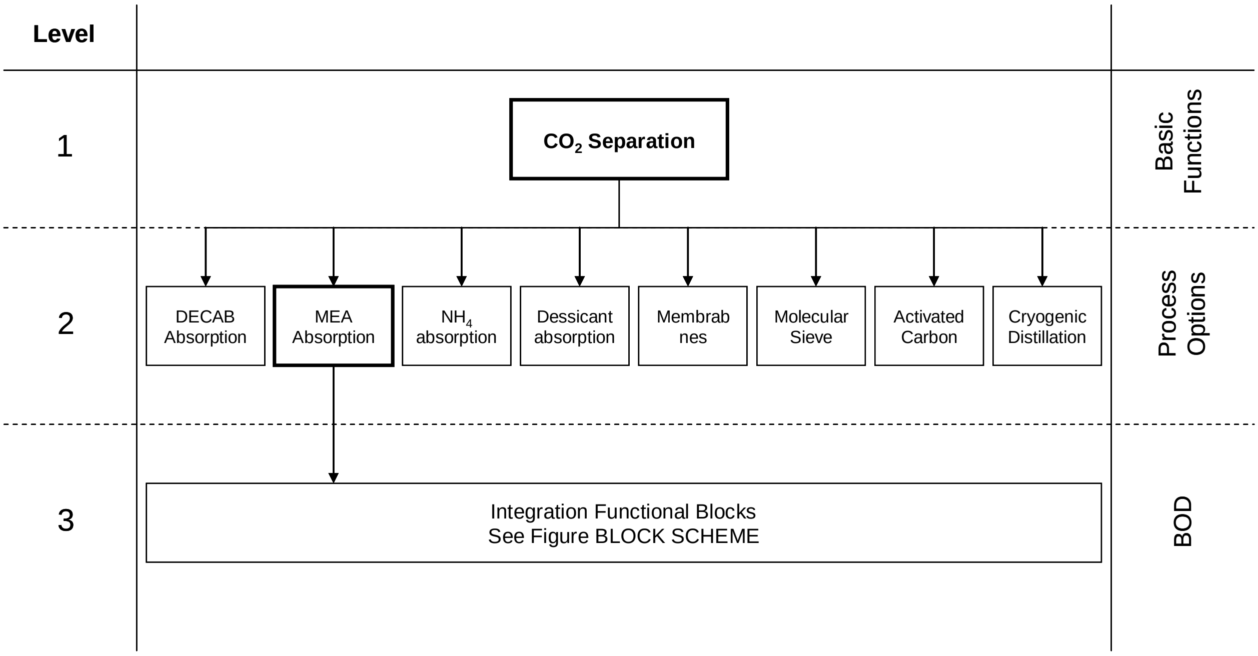


Figure 14-4: Process selection diagram SO_2 separation

15Preliminary Bases of Design

15.1 Mark-13A based process

15.1.1 Process analysis

The basis for this flue gas desulphurisation process is the ISPRA Mark-13A process which was extensively investigated by Van Velzen and Langenkamp [1],[9],[10],[11]. This regenerative process is based on a hybrid cycle that converts sulphur dioxide to sulphuric acid and hydrogen. The following two reactions from the basis for this process:

$$SO_2 + Br_2 / I_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr / HI \qquad \text{(C1-1)}$$

$$2HBr / HI \rightarrow Br_2 / I_2 + H_2 \qquad \text{(C1-2)}$$

The conversion section of the ISPRA Mark-13A process takes a highly concentrated sulphur dioxide gas stream. Since the flue gas stream itself is dilute in sulphur dioxide, a flue gas pre-treatment is needed. The pre-treated gas stream is fed to two Bunsen reactors in series. In these reactors the sulphur dioxide reacts with bromine or iodine and water to sulphuric acid and hydrogen bromide or hydrogen iodine at around *320K – 370K*. The second step of the process is the regeneration of the hydrogen bromide / hydrogen iodine. With an electrolysis reaction, hydrogen and bromine / iodine are formed. The bromine / iodine is then fed back to the first step in the process. The overall process yields two useful products, sulphuric acid and hydrogen, as can be seen from the two reaction equations. The process will remove *99.7mole%* of the sulphur dioxide present in the feed. No other components will be converted. Concentrated sulphuric acid with a quality of *96%* will be produced. Per mole of sulphur dioxide one mole of hydrogen will be produced. No wastewater is produced since all the chemicals in the process are regenerated and recycled to the reactor.

From the description above, the process can be decomposed in three different functions: the flue gas pre treatment, the conversion section and a section were the products and raw chemicals are separated and either recycled or finished to a sellable product. These different functions are shown schematically in Figure 3-1.

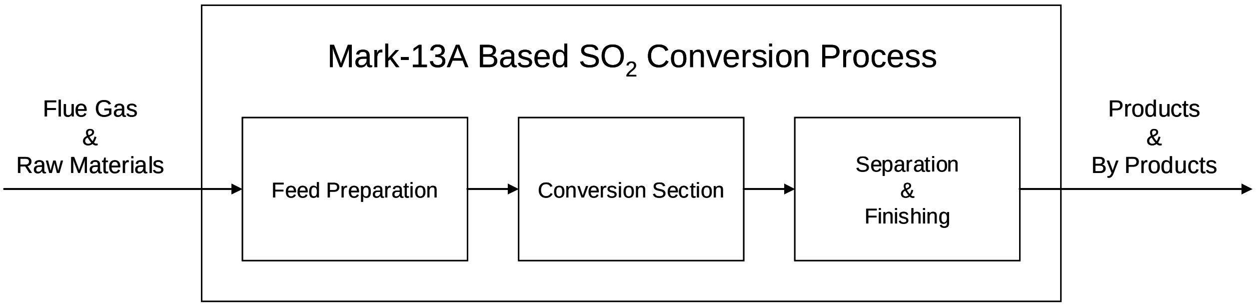


Figure 15-1: Mark-13A based process decomposition

15.1.2 Process alternatives

The three different functions within the process can be performed with different methods. To come to a solid choice regarding the method to use, the alternative process configurations diagram shown in Figure 3-2 was used. In this diagram all process options are shown and the selection for each method is described per level in the following paragraph.

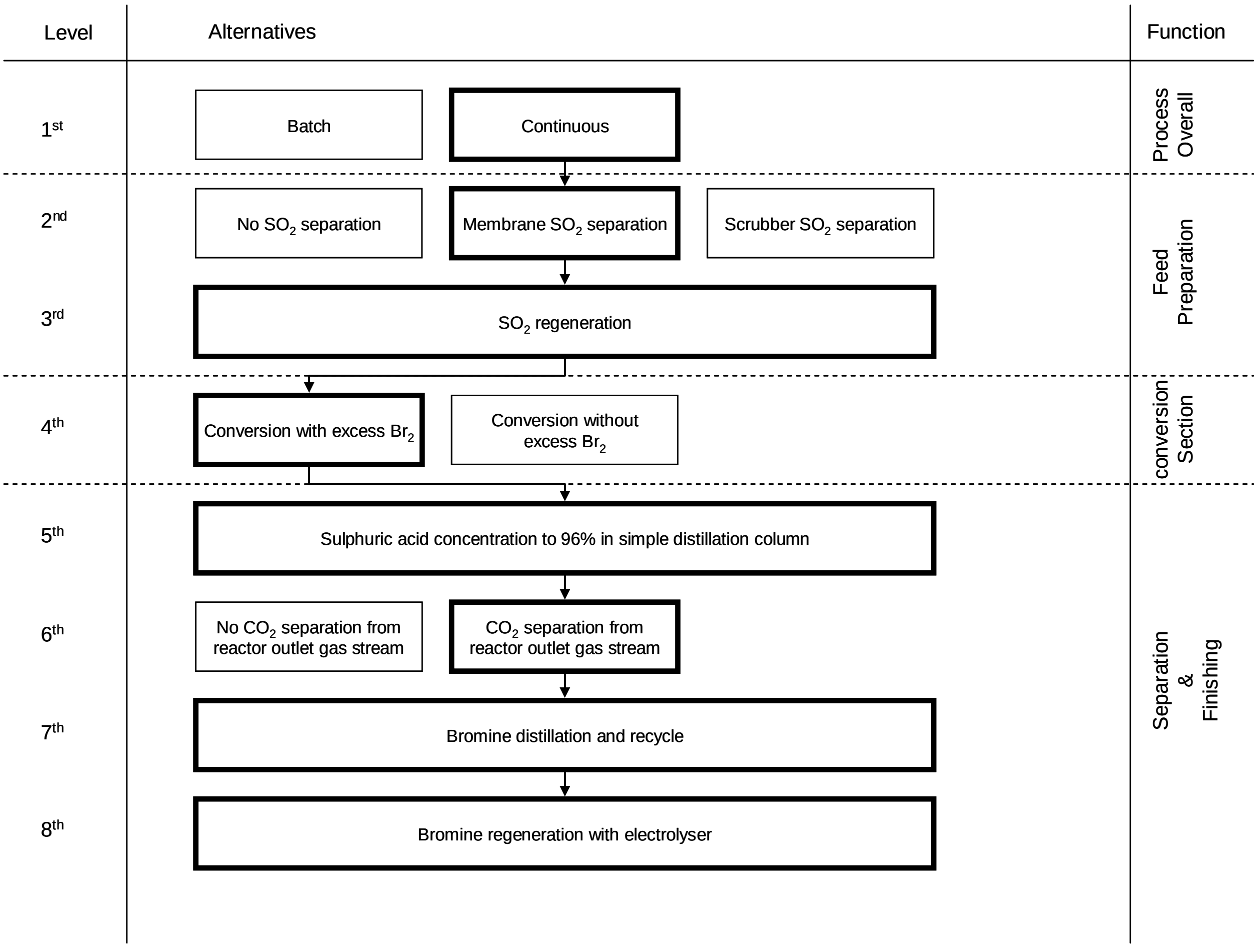


Figure 15-2: Alternative process configurations for the Mark-13A based process

Level 1

The first decision to make when designing a process is to choose between batch and continuous operation. A number of rules of thumb for this decision are given in Douglas [[14]]. The most important decision parameter for the desulphurisation of flue gas is the capacity; Douglas uses a capacity larger than *10Mlb/yr* or around *5Mkg/yr*, as a criterion for continuous operation. Since the amount of sulphur dioxide to be processed is around *32Mkg/yr* continuous operation is the more convenient mode of operation.

Level 2

The first step in the desulphurisation process is the feed preparation. Three different options were identified, separation of the sulphur dioxide from the flue gas stream with either a membrane or a scrubber and no separation of the sulphur dioxide. The last option is not suitable since the conversion section was originally developed for a highly concentrated sulphur dioxide stream and no separation would result in pumping huge amounts of useless gas through the process.

For this process the membrane SO_2 separation has been selected over the scrubber. The criterion for this selection is the higher selection shown by the membranes towards SO_2 as described by Nii et. al. [2].

Level 3
When separating SO_2 from the flue gas, it gets dissolved in a solvent, since the conversion section takes in a highly concentrate SO_2 gas stream, the loaded solvent has to be regenerated. The only method known to regenerate the SO_2 from the solvent is heating (by use of steam).

Level 4
The highly concentrated SO_2 stream from the feed preparation section is converted to sulphuric acid. This reaction can be performed with or without an excess bromine inlet in the reactor. The advantage of not having an excess bromine inlet is that a bromine free reactor outlet is obtained. The biggest disadvantage of not having excess bromine is that when fluctuations in the SO_2 gas stream occur part of the SO_2 will not be converted and therefore the specifications will not be met. Since part of the assignment is to be able to handle fluctuations in the SO_2 loading a conversion section with an excess of bromine is chosen.

Level 5
The concentration of sulphuric acid is performed with a simple distillation column. This method is taken directly from the original Mark-13A process [1]. No alternatives were considered due of the simplicity, effectiveness and possibilities of heat integration with the flue gas stream.

Level 6
The outlet gas stream from the conversion section contains some CO_2, which will not be converted in the process. To prevent this CO_2 from building up in the system, it has to be removed from the system. This CO_2 will be removed with a membrane and can be combined with the CO_2 coming from the CO_2 separation section.

Level 7
The un-reacted bromine from the conversion section will be recycled back. For the separation of this bromine a simple distillation column is used. This distillation column is used in the original Mark-13A process [1] as well. Again no alternatives were considered due to the simplicity and effectiveness of this method.

Level 8
The bromine regeneration is performed with an electrolyser as in the original Mark-13A process. Together with the conversion section, the HBr electrolysis forms the backbone of both the desulphurisation process described in this paragraph and the original Mark-13A process.

On the basis of the choices made in this chapter a preliminary basis of design can be made for the desulphurisation process.

15.1.3 Process definition

Process concept chosen
The choice is made to use a variation of the Mark-13A process to remove the SO_2 from the flue gas.

Block scheme

The block scheme from the process for the sulphur dioxide removal based on the Ispra Mark-13A process is given in Figure 15-3.

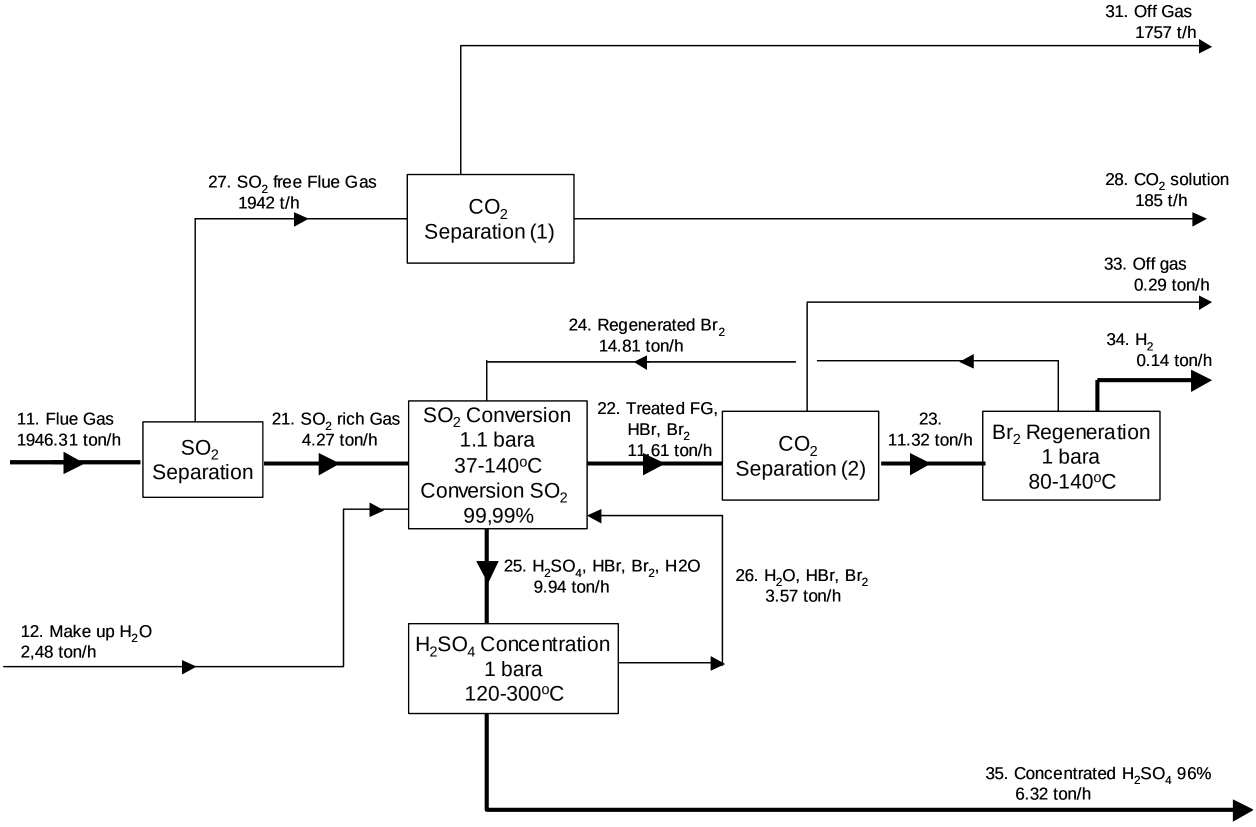


Figure 15-3: Block scheme Mark-13A based sulphur dioxide removal process

The sulphur dioxide rich gas enters the process in the sulphur dioxide conversion block. Here the sulphur dioxide reacts with the bromine and the hydrogen bromide and sulphuric acid are formed. The gas leaving the conversion block is first cleaned from the small amount of carbon dioxide and subsequently goes to the regeneration section were the hydrogen bromide is converted to hydrogen and bromine.

The sulphuric acid formed in the conversion block is concentrated to 96% purity. The hydrogen bromide and un-reacted bromine leaving the concentration section are fed to the regeneration section.

Thermodynamic properties & reaction kinetics

Sulphur dioxide separation

Before the sulphur dioxide from the flue gas can be converted it has to be separated from the flue gas stream. This separation is done with a hydrophobic Microporous Teflon Hollow Fibre (HF) membrane that has a high selectivity towards sulphur dioxide due to the specific solvent used as shown by Nii et al. [6]. A schematic overview of the used set-up is given in Figure 3-3.

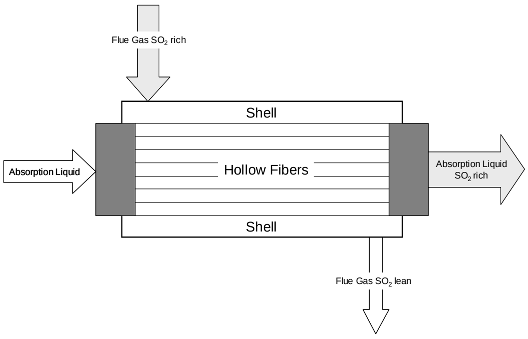


Figure 15-4: Schematic membrane unit overview

This solvent is a sodium sulphite solution of *0.1M*. Besides sulphur dioxide it will also separate some carbon dioxide from the flue gas stream. In this system the following reactions in the liquid film are considered:

$$SO_2 + SO_3^{2-} + H_2O \leftrightarrow 2HSO_3^- \qquad \text{(C1-3)}$$

$$CO_2 + SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + HCO_3^- \qquad \text{(C1-4)}$$

$$SO_2 + HCO_3^- \leftrightarrow 2HSO_3^- + CO_2 \qquad \text{(C1-5)}$$

The dimensionless equilibrium constants K_1, K_2 and K_3 for the reactions C1-3, C1-4 and C1-5 are $2.76x10^{5}$, *7.12* and $3.08x10^{4}$ respectively, at infinite dilution and *298K*. Reaction 2-3 proceeds much faster than the others: its reaction rate constant k is of the order of $10^{5}\ m^{3}\ mol^{-1}\ s^{-1}$; that of reaction 2-4 is $2.39x10^{-2}\ m^{3}\ mol^{-1}\ s^{-1}$.

In the simultaneous membrane absorption of SO_2 and CO_2, the SO_2 dissolved in the liquid reacts instantaneously with SO_3^{2-}, and is depleted in the liquid boundary film. Figure 15-5 shows the absorption rates of SO_2 and CO_2 against the liquid velocity u_L. The CO_2 flux decreases considerably with decreasing u_L, whereas the SO_2 flux is hardly influenced by u_L as long as SO_3^{2-} ion in the liquid boundary is not depleted. Thus, for flue gases containing a much lower SO_2 than CO_2 partial pressure, we can expect that the selective removal of SO_2 with respect to CO_2 is possible in hydrophobic hollow-fibre membranes under the conditions that the liquid flow rate is low; in other words when the SO_3^{2-} concentration near the gas-liquid interface is low. This can be seen in Figure 15-14.

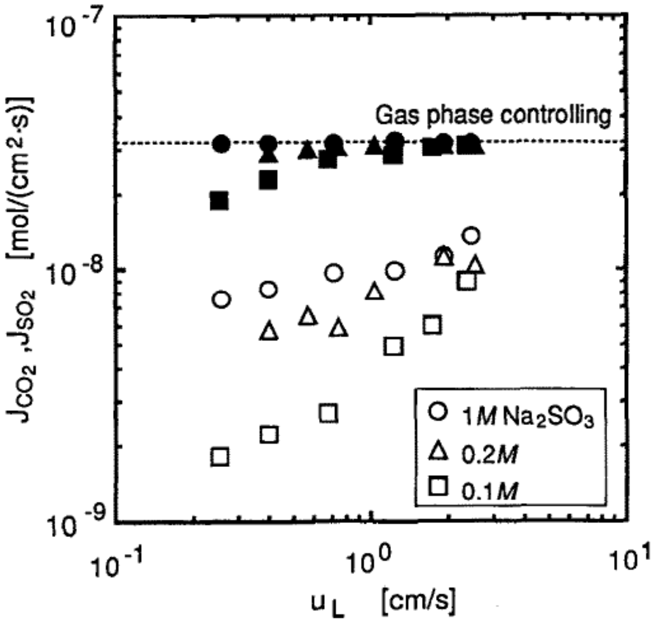


Figure 15-5: Dependence of the CO_2 and SO_2 flux on the liquid flow rate for simultaneous membrane absorption in Na_2SO_3 solutions. Feed gas: 9% CO_2, 0.5% SO_2, and 90.5% N_2. u_G = 11.5cm/s; T = 298K.

After absorbing the sulphur dioxide and carbon dioxide in the solvent, the mixture has to be regenerated. This means that upon heating with steam, the reactions given in equations C-3 to C-5 occur in opposite direction. The resulting gas stream contains mainly sulphur dioxide and around *6%* carbon dioxide. This gas stream is then further processed. To achieve the separation specifications 16 membrane modules with a diameter of *20m* and a height of *2m* are needed. The inner diameter of the hollow fibres is *0.1cm.* The superficial gas velocity at the shell site of the membrane modules is *11.5cm/s*, while the solvent velocity in the fibres is *0.8cm/s*. For the general design equations for the membranes see Appendix H3.

Sulphur dioxide conversion section

The sulphur dioxide is removed in two Bunsen reactors. These reactors are packed columns containing a liquid collector with overflow and a recycle pump. The recycle is present for sufficient wetting of the columns. Both reactors operate in co-current flow since this gives better mass transfer coefficients. Another reason for choosing co-current operation is that when large amounts of HBr are dissolved in the reactor slight temperature changes will then lead to significant gas release that would cause frequent flooding in counter-current operation.

The sulphuric acid concentration has a large influence on the sulphur dioxide conversion in this process, therefore the following definition for the relative sulphuric acid concentration (*C*) is of great importance for the design of the process. For this special case the numbers between the square brackets are the mass flow rates of the species.

$$C = \frac{[H_2SO_4]}{[H_2SO_4]+[H_2O]} \qquad \text{(C1-6)}$$

Another important design parameter in this process is the number of overall gas transfer units (N_{og}). The relation for this number is given in equation C1-7.

$$N_{og} = \int_{0}^{1} \frac{dY}{Y - Y_{eq}} \qquad \text{(C1-7)}$$

The Y in equation C1-7 is the sorbent mol fraction in the gas phase; in this case that is the mole fraction of sulphur dioxide. In this process the composition of the liquid phase in the column does not change significantly from the inlet of the reactor to the exit of the reactor. Therefore equation C-7 can be simplified to equation C1-8.

$$N_{og} = \ln \frac{(Y - Y_{eq})_{in}}{(Y - Y_{eq})_{out}} \qquad \text{(C1-8)}$$

An alternative expression for the number of overall gas transfer units is found from the mass balance and is given in equation C1-9.

$$N_{og} = \frac{K_g azAP}{G} \qquad \text{(C1-9)}$$

Combining the overall gas phase transfer coefficient (K_g) with the interfacial area (a) yields the overall absorption coefficient ($K_g a$). This overall absorption coefficient is divided in a diffusion part and a reaction part; the relation between these parameters is given in equation C1-10.

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{1}{R} \qquad \text{(C1-10)}$$

The reaction rate in the reactor is given in equation C1-11.

$$R = K_1 (0.82 - C)^2 \qquad \text{(C1-11)}$$

The value for K_1 was experimentally determined and found to be $1.24x10^3 kmol\ m^{-3}\ h^{-1}$; C and the constant are dimensionless.All the equations used above come from research done by D. van Velzen et al., [4].

Sulphuric acid concentration

The sulphuric acid is concentrated to a quality of 96% (technical grade) in a simple distillation column. The column feed is a concentrated sulphuric acid solution saturated with hydrogen bromide and un-reacted bromine. The bottom temperature will be maintained at a temperature of around 295^oC to guaranty the product composition. The product will only contain technical grade sulphuric acid and traces of hydrogen bromide. The top temperature will be around 120^oC. The distillate then contains the remaining water, bromine and hydrogen bromide. The thermodynamic model used to design this concentration unit is found in Aspen. The Txy diagram that was obtained with the UNIQUAC model as can be seen in Figure 15-6;this gives the most optimal mixture behaviour when compared to the other available models.

Part of the heat available in the flue gas can be used to concentrate the sulphuric acid.

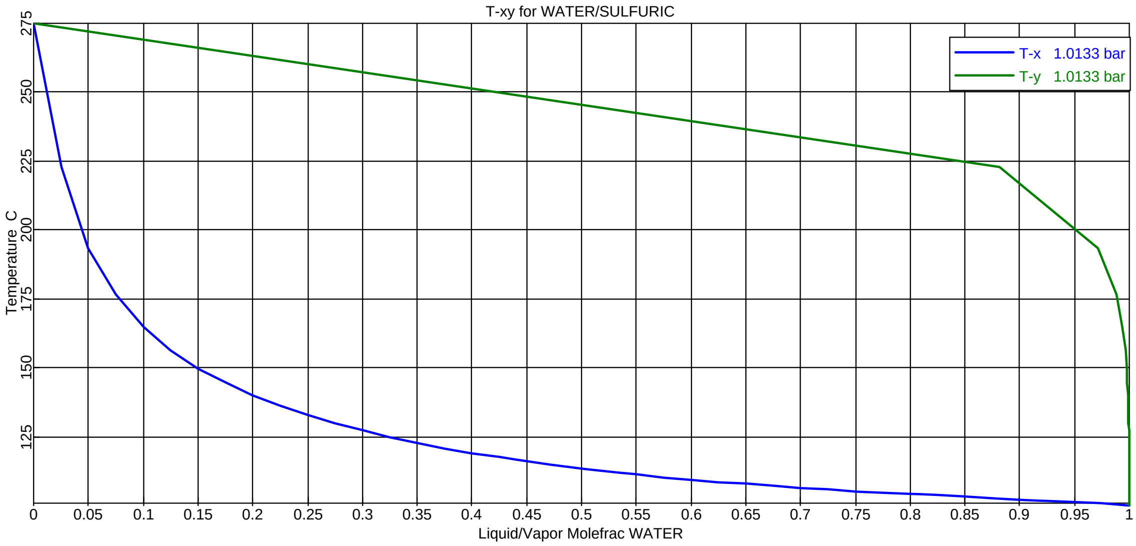


Figure 15-6: Txy diagram of a binary water / sulphuric acid mixture

Bromine regeneration

The bromine regeneration section consists of two operations, first the separation of the unreacted bromine from the stream out of the sulphur removal section and the stream out of the sulphuric acid concentration section, secondly the electrolysis of hydrogen bromide to hydrogen and bromine. The bromine is fed back to the reactors and the hydrogen can be sold or used to generate part of the energy needed for the electrolysis.

The separation from bromine is performed by a simple distillation column. The bottom temperature of this column will be operated around *130°C* to guaranty a practically bromine free bottom product. This product is send to the hydrogen bromide electrolysis, which consists of a mono-polar electrolyser with an electrolyte distance of *5mm*.

The thermodynamic model to be used to design this concentration unit is found in Aspen. The Txy diagram that gives the optimal mixture behaviour in ASPEN+ was obtained with the UNIQUAC model as can be seen in Figure 15-7.

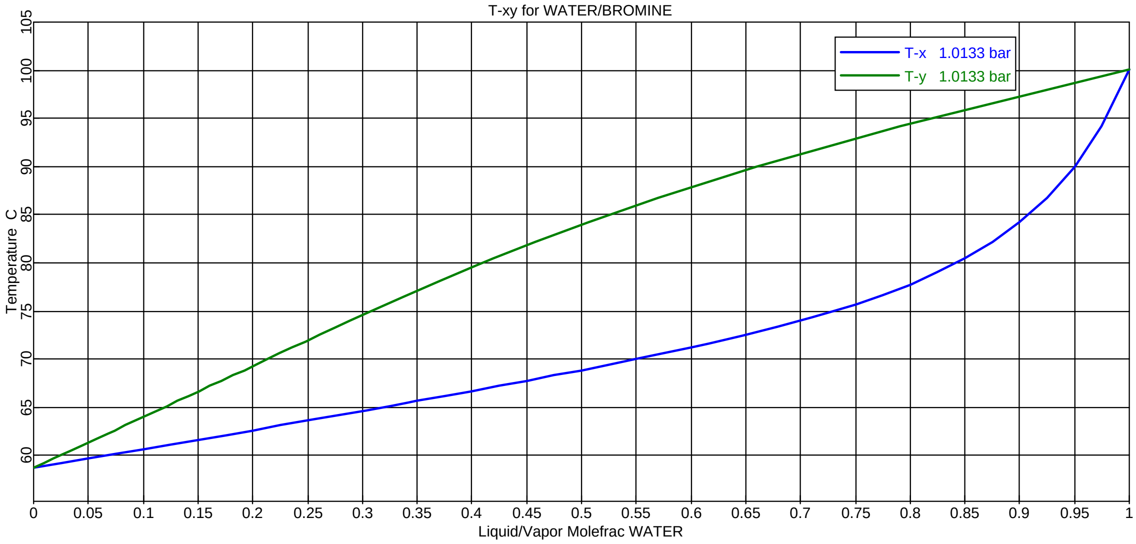


Figure 15-7: Txy diagram for a binary water / bromine mixture

Carbon dioxide separation

The un-reacted sulphur dioxide and the carbon dioxide present in the stream leaving the sulphur dioxide removal section are separated with a membrane selective for sulphur dioxide and carbon monoxide. The membrane used is the same as in the sulphur dioxide separation section only with a different solvent composition for higher selectivity towards carbon dioxide. Until so far it is assumed that the membrane can achieve a performance of *95%* separation of carbon dioxide from the gas stream and a similar separation performance for sulphur dioxide. The influence of the composition of the solvent on the selectivity is shown in Figure 15-8. In this process monoethanolamine (MEA) is used because of the high selectivity, moderate costs, low volatility and high solubility in water.

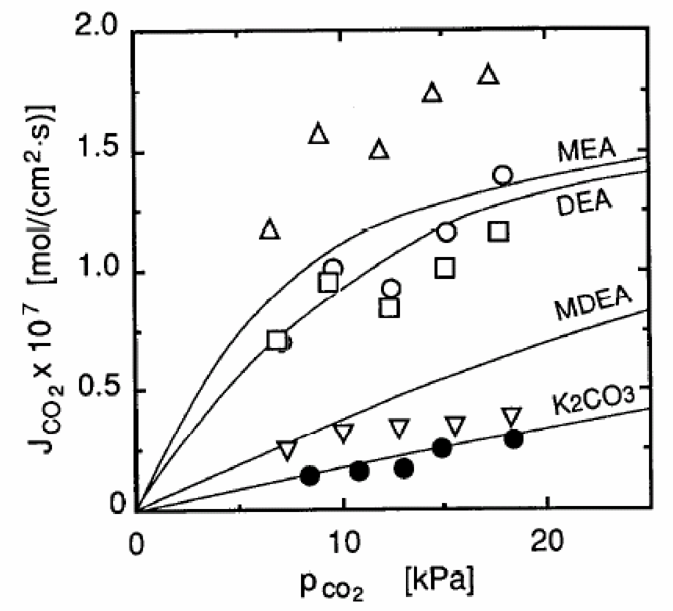


Figure 15-8: Effect of alkanolamines to K_2CO_3 solution (2M) on CO_2 absorption flux: u_G = 10cm/s, u_L = 1.1cm/s, T = 294K; Δ MEA; o DEA; □ AMP; ● without amine

Again the general design equations for the membranes are given in Appendix H3.

List of pure component species
In the mass balance a list of pure component species can be found. For further details, see Table 15-1.

Process stream summary & mass balance
In Table 15-1 the mass balance of the process is given.

Table 15-1: Mass Balance over Mark-13A based sulphur dioxide removal process

Mass Balance / [ton/h]												
	11	**12**	**21**	**22**	**23**	**24**	**25**	**26**	**31**	**32**	**33**	**34**
SO_2	*4.00*		*4.00*	*0.03*						*0.03*		
CO_2	*372.67*		*0.27*	*0.27*	*0.01*				*372.40*	*0.26*	*0.01*	
H_2O	*81.55*	*2.48*				*2.35*	*2.60*	*2.35*	*81.55*			*0.25*
N_2	*1382.49*								*1382.49*			
O_2	*105.05*								*105.05*			
HCl	*0.50*								*0.50*			
HF	*0.05*								*0.05*			
HBr				*8.80*	*8.80*		*1.22*	*1.22*				*Trace*
Br_2				*2.51*	*2.51*	*12.46*	*0.05*					
H_2SO_4							*6.07*					*6.07*
H_2											*0.12*	
Total	*1946.31*	*2.48*	*4.27*	*11.61*	*11.32*	*14.81*	*9.94*	*3.57*	*1942.04*	*0.29*	*0.14*	*6.32*

15.1.4 Basic assumptions

Plant capacity
The feedstock of this plant is flue gas, coming from a coal fired power station. This flue gas is produced at a rate of $2 \cdot 10^6 m^3/h$, and contains $2 g/m^3$ SO_2. This implies that per hour *4ton* of SO_2 is produced. From this SO_2, *99.3mol%* has to be removed, which means roughly *3.97ton* per hour.

The plant is assumed to be on-stream for 8000 hours per year, and the capacity is then *31760ton ~ 32Kton/a*.

Location
The location of the plant will be near a 600MW coal fired power plant; the country is not of direct importance. In Figure 3-6 a schematic representation of the battery limit of the process is shown.

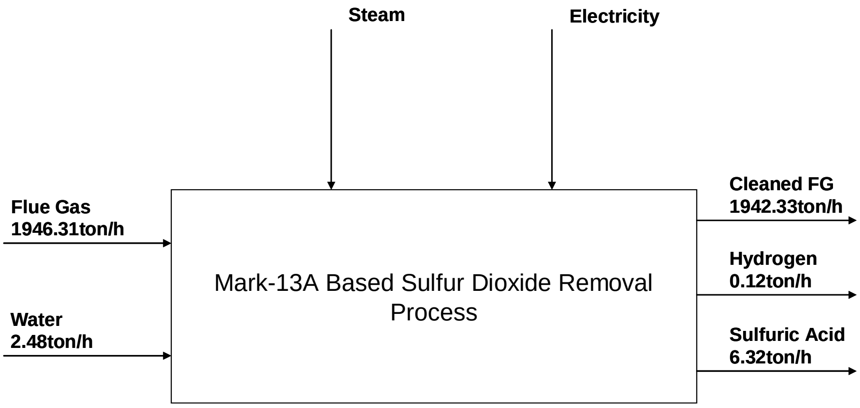


Figure 15-9: Schematic representation of the battery limit of the process

Battery limit
The most important equipment within the battery limit is the separation membranes, the two sulphur dioxide conversion reactors, the sulphuric acid concentrator, bromine distillation column and the electrolyser. The most important equipment outside the battery limit is

steam generation for regenerating the membrane solvent and the electricity plant for the electrolyser.

All in- and outgoing streams
The feedstock of the process consists of flue gas that is cleaned from fly ash. Two products are formed, technical grade sulphuric acid (96%) and hydrogen. Besides the treated flue gas, three small waste streams are produced, which consist of insoluble salts. Besides product and waste streams three other important base chemicals are present within the battery limit, bromine, sodium sulphite and mono ethanolamine. These chemicals are regenerated within the battery limits and only small amounts of the compounds have to be added during operation. Due to the high reactivity and high toxicity of bromine the process should be equipped with a good emergency plan for both on and off site.

15.1.5 Economic margin

The prices of raw base chemicals used in this chapter are taken from the website http://ed.icheme.org/costchem.html. The prices on this website are estimates of prices for educational use only. There is no guaranty that the chemicals can be purchased for the prices especially not since this website was last updated in February 2002.

The price of one ton of technical grade sulphuric acid is around *€70,-.* The price of *100m*^{3} hydrogen is *€30,-*. The price of process water is around *€0.10* per ton.

The revenue of sulphuric acid on a yearly basis is therefore around *€3.5M*. The revenue for hydrogen is around *€2.7M*. The raw material cost for the process only consists of the make up water and several make-up streams. The total process water cost would be approximately *€23000.-*.

The margin in the process depends on whether the produced hydrogen is sold or used as an energy source for the electrolysis. Because of the relative low purity hydrogen produced we have chosen to us the hydrogen as energy source for the electrolysis. The margin of this process is therefore around *€3.5M*.

In chapter 2 of Douglas [8] a number of rules of thumb are given for the determination of the start up costs, working capital and salvage value. These rules are given in the equations below.

$$Working\_Capital = 0.15 \cdot Total\_Investment \tag{C1-12}$$

$$Salvage\_Value = 0.03 \cdot Total\_Investment \tag{C1-13}$$

$$Start\_Up\_Costs = 0.10 \cdot Total\_Investment \tag{C1-14}$$

The basis of the method is that the present value of the money invested in the plant is equal to the present value of the money earned in the upcoming years. This basis is represented in equation C1-15.

$$PV\_Cash\_Flow + WC + SV = PV\_Total\_Investment + WC + SUC \tag{C1-15}$$

With these rules and by rearranging the method described on page 59 in Douglas [8], the total investment possible for this process can be calculated. Assuming a life span of 10 years for the plant, a building time of 4 years and a Discount Cash Flow Rate Of Return (DCFROR) of *10%*, the total investment possible is around *€14.7M*. The calculation sheet used for these calculations is given in Appendix 4.

15.2 Biochemical process

15.2.1 Process analysis

The biochemical process can be seen as a combination of the THIOPAQ and the Biotreatment process, combined with a membrane separation unit as an alternative to an absorber for SO_2 removal from the flue gas. This process can be divided in three parts, as illustrated in Figure 15-10: the separation section, the conversion section and the separation/ recirculation section.

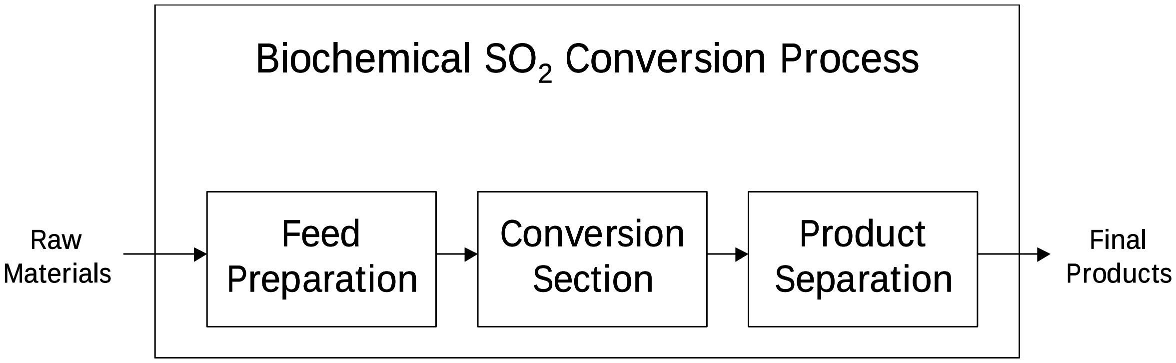


Figure 15-10: Process decomposition scheme

The feed preparation section consists of the SO_2 removal and treatment of the ingoing air. No choices have to be made with regard to the feed of H_2 and CO_2 to the anaerobic reactor, so these are not included in the diagram.

The conversion section contains the outgoing airflow, the anaerobic and the aerobic reactor. Some choices with regard to the operating conditions and micro cultures have to be made, which is further explained in Figure 15-11 and the subsequent description.

Bleed, recycles and product treatment are included in the product separation section.

15.2.2 Process alternatives

The choices that have to be made in order to come to an optimal process configuration and the path followed to come to the optimal process configuration are schematically given in Figure 15-11.

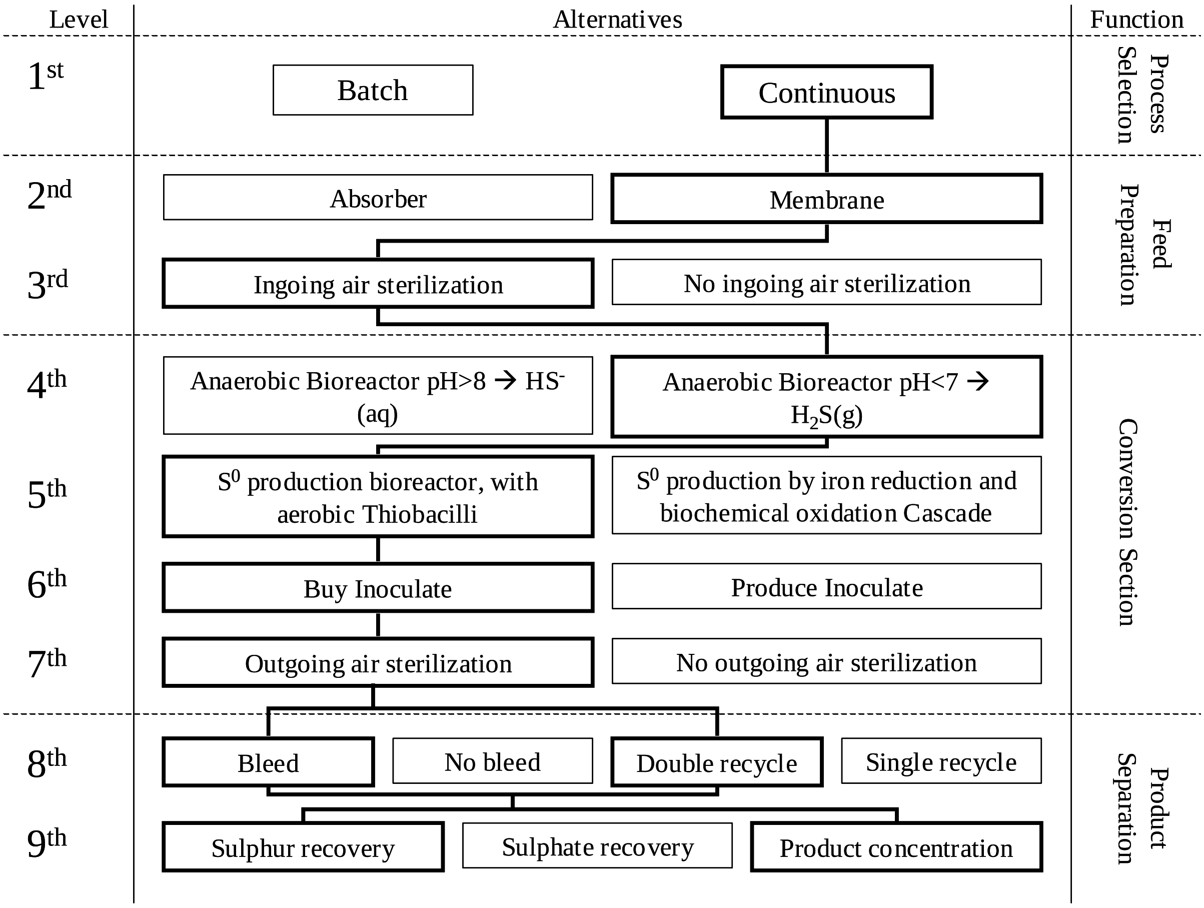


Figure 15-11: Alternative process configurations and path of choices made for the biochemical process

Level 1

The first choice to be made is the choice between batch and continuous operation. Since the flue gas stream is so large, only continuous operation is a realistic option. This choice therefore was relatively straightforward.

Level 2

SO_2 removal from flue gas can be performed through absorption in an absorber/scrubber or by means of a membrane unit. In literature, [19], it is found that the large liquid recycle stream is a weakness of the THIOPAQ design. Since an absorber requires a lot of absorbent to remove the SO_2 on specification from the flue gas, use of a membrane unit is chosen. In general a higher solvent efficiency can be achieved in a membrane unit when compared to an absorber. This choice therefore will lead to a smaller solvent stream through the system and thus bypass the problem of the large liquid recycle stream.

Level 3

When air is fed in a bioreactor, there is a risk of contaminating the micro culture with microorganisms coming from outside the system boundaries. This might influence the system in such a way that the desired process is put to death. For this reason, sterilization of the ingoing air might be required. In this process it is decided to ban the risk of reaction broth contamination and therefore sterilize the air that is fed to the aerobic reactor.

Level 4

To separate the sulphur product as good as possible from the anaerobic reaction broth and to prevent large streams recycling through the whole system, it is decided to operate the anaerobic reactor at a relatively low pH ($6 < pH < 7$). At this pH, the HS^- formed is converted to H_2S gas, which easily escapes from the reaction mixture. The regenerated solvent can then be recycled, and only H_2S will be brought into the aerobic reactor.

Level 5
The conversion of H_2S into elemental sulphur can be performed via two different biochemical routes: by direct conversion with Thiobacilli or by reduction using iron ions in solution and subsequent re-oxidation of the reduced iron by Leptospirillum ferrooxidans bacteria in a second reactor. It is chosen to use the direct conversion to sulphur in order to preserve a low process complexity.

Level 6
Inoculate (THIOPAQ bio-cultures) can be grown in the reactor to the desired specifications, but can also be bought straight from Paques. The advantage of this is that the culture is directly able to perform as required. Rather than generating the specific knowledge of how to handle the bio cultures in house, it is better to use the experience that already exists with this by Paques. Therefore it is decided to buy the required inoculate.

Level 7
The choice to sterilize the outgoing air actually is a choice made by the government, who decided that any off gas from bioprocesses should be sterilized in order to exclude any possibility of bacterial matter to escape to the environment. Therefore sterilization of the outgoing gas flow is chosen.

Level 8
When the decision was made that the anaerobic reactor is to operate at low pH, the choice for a double recycle was implicitly made. When H_2S escapes from this reactor as a gas, the alkali is reformed and can directly be recycled. When impurities are transferred from the feed to the reaction liquid, these have to be removed from the system by a bleed. The second recycle is necessary to move the alkali from the solid/ liquid separator back to the aerobic reactor. A bleed in this section of the process is not required, since the loss of fluids in the sulphur product replaces this. Due to these bleeds, alkali make-up streams are required.

Level 9
It is decided that the sulphate that is formed as a by-product in the oxidation of H_2S to S^0 will not be recovered or converted to S^0 (which is possible when required). Naturally, the produced S^0 is recovered and further treated to lower the liquid content of this slurry.

15.2.3 Process definition

This process is a combination of a SO_2 removal step from flue gas, and a series of microbiological reactions to convert this SO_2 to hydrophobic elemental sulphur. The SO_2 removal takes place in either a scrubber/ absorber or a novel membrane unit. The microbiological conversion steps occur in an anaerobic reactor and an aerobic reactor, both of which are in some ways similar to the THIOPAQ [2] or the Biotreatment [1] processes. The current SO_2 removal processes use calcium compounds (lime/limestone scrubbing) to produce gypsum that can be used in the construction industry. However, the quality demands in the construction industry become much stricter with respect to gypsum contaminations. Furthermore, the lime scrubbers reach their maximum capacity and selectivity [1] and therefore cannot satisfy future SO_2 emission legislation.

This process is based on the following overall reaction:

$$SO_2 + 3H_2 + \frac{1}{2}O_2 \rightarrow S^0 + 3H_2O \qquad \text{(C2-1)}$$

There are some choices that can be made with regard to the aerobic sulphur formation; the sulphur compound, which comes from the anaerobic reactor can enter in two different forms; when the pH in this reactor is relatively low, gaseous H_2S is formed, which then has to be bubbled in the aerobic reactor. When the anaerobic pH is higher, the sulphur remains in solution as HS^-. The microorganisms present can convert the sulphur compound with oxygen and carbon dioxide to elemental sulphur.

It is also possible to blow the H_2S into an iron solution, where the iron ions in solution form the elemental sulphur. The iron solution then has to be regenerated with microorganisms. This option "costs" one extra regeneration reactor. The Ebrahimi process uses this option.

15.2.3.1 Process concept chosen

The concept as chosen consists of the following units:

Fly ash removal
To be able to use the membrane unit for SO_2 separation, all particulate matter should be removed in order to prevent clogging problems.

Membrane SO_2 separation unit
Reaction (1-2) takes place in this unit, in which SO_2 is separated from the rest of the flue gas. A number of membrane units in parallel are used. The gas flows around the membranes, which are flown through with $NaHCO_3$.

Anaerobic reactor
Reaction (1-3) takes place in the anaerobic reactor. H_2 is the electron donor required for this reaction. In this unit, the $NaHSO_3$ is regenerated to $NaHCO_3$, which is recycled to the membrane unit. This microbiological regeneration is a large advantage when compared with the traditional high energy consuming solvent regeneration. This unit can operate at low or at high pH. When a low pH is used, the sulphur escapes in the form of gaseous H_2S, and the NaHCO3 is regenerated. At high pH, the sulphur remains in solution as HS^-.

Aerobic reactor
In this reactor the sulphur, which comes from the anaerobic reactor can enter in two different forms, as described before. The microorganisms present convert the sulphur compound with oxygen and carbon dioxide into elemental sulphur following reaction (1-4).

Solid/liquid separator
In this unit, the sulphur formed is separated from the process fluid that has to be reused.

With this process more SO_2 can be removed from the flue gas than is strictly necessary according to the assignment. In this design however, the process will be defined as such that the maximum required SO_2 removal would be realized. This implies that the outgoing flue gas is be designed to contain only *0,7%* of the SO_2 content of the ingoing stream.

This process alternative is chosen for a couple of reasons:

- Minimal chemical consumption.
- Due to the membrane, low fluid recycles exist in the plant, which is a significant advantage when compared to the THIOPAQ process.
- H_2S removal below 4*ppmv* can be guaranteed if necessary.
- *100%* conversion of sulfide in the bioreactor with a selectivity of *95-98%* to S^o.
- Low process complexity. In [2] it was mentioned that this would also lead to a low complexity of the process control loops.
- The process has proven robust and resistant against dust and heavy metals in the flue gas.
- The process is very safe, since not much streams after the scrubber contain SO_2 or H_2S gas.
- High conversions of SO_2 are observed, with a very low (if any) dependence on fluctuations of the sulfur content in the feed.

Moreover, this is a continuous process, in which hydrophobic elemental sulphur is produced. No catalyst is utilized, only a mix of various microorganisms is required for the sulphur production. Up to a maximum of *50ton* of sulphur produced per day, the process is competitive with more traditional processes.

The production of elemental sulphur from SO_2 in this process option mainly occurs according to reactions (3-2) to (3-11).

$$SO_2 + Na^+ + HCO_3^- \rightarrow Na^+ + HSO_3^- + CO_2 \qquad \text{(C2-2)}$$

$$Na^+ + HSO_3^- + 3H_2 \rightarrow Na^+ + HS^- + 3H_2O \qquad \text{(C2-3)}$$

$$HS^- \xrightarrow{pH<7} H_2S \qquad \text{(C2-4)}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad \text{(C2-5)}$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad \text{(C2-6)}$$

$$H_2S(g) + OH^- \rightarrow HS^- + H_2O \qquad \text{(C2-7)}$$

$$H_2S(g) + CO_3^{2-} \rightarrow HS^- + HCO_3^- \qquad \text{(C2-8)}$$

$$HS^- + \frac{1}{2}O_2 \rightarrow \frac{1}{8}S_8 + OH^- \qquad \text{(C2-9)}$$

$$HS^- + 2O_2 + OH^- \rightarrow SO_4^{2-} + H_2O \qquad \text{(C2-10)}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \qquad \text{(C2-11)}$$

In Table 15-2 an overview of the reactions that occur in each unit can be found.

15.2.3.2 Block scheme

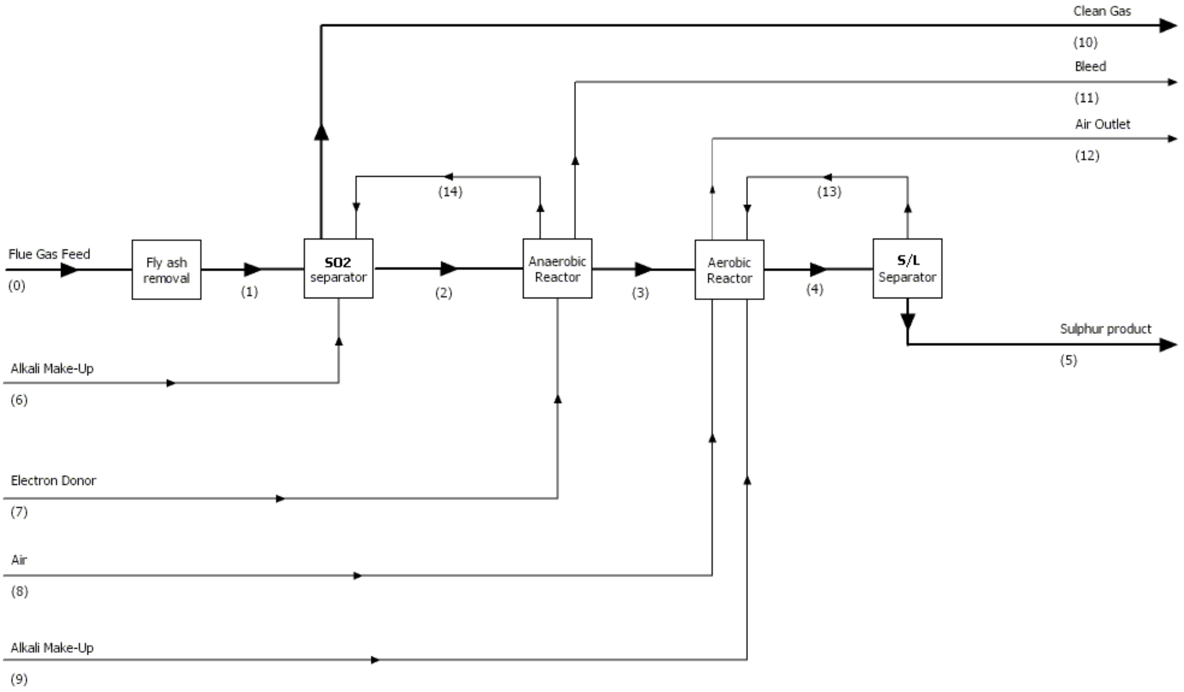


Figure 15-12: Block scheme of the biochemical SO_2 removal process

Preliminary specifications of the streams can be found in Table 15-3; it must be mentioned that this mass balance is calculated using some of assumptions that were made due to a lack of quantitative stream data.

Below follows an extensive list of the assumptions made per process unit.

Unit 1: Fly ash removal
It is assumed that all fly ash is removed from the flue gas stream in this unit.

Unit 2: SO_2 separation membrane unit
The assumption made to model the membrane unit is that all solvent is used for the removal of *99,3%* SO_2 from the flue-gas stream. This means that no excess of $NaHCO_3$ is present.

Unit 3: Anaerobic reactor
All formed $NaHSO_3$ (aq) is assumed to be converted to NaHS (aq), from which the HS^- as H_2S escapes the reactor via stream 3 to the aerobic reactor.

Unit 4: Aerobic reactor
$NaHCO_3$ absorbs all H_2S, and this is *100%* converted to elemental sulphur, while the $NaHCO_3$ is reformed. No sulphate is formed. Air is blown into the reactor to provide the oxygen required in this conversion. In the mass balance all oxygen from the air is taken up by the microorganisms, and used for the reaction. The rest of the gasses present in the air leave the reactor via stream 12.

Unit 5: S/L separator
In this separator all formed sulphur is removed from the recirculating alkali solution. The sulphur product formed, contains *40%* of liquid, which is taken as being plain water (in real life a mixture of water and $NaHCO_3$, which is compensated for by the second alkali make-up, stream 9).

Also a number of assumptions with regard to the feed quality and the overall process behavior are made:

- HCl and HF are assumed to exit the system with the clean gas, and not be absorbed in the scrubber.
- H_2O is not modeled as a separate component. Although in the anaerobic reaction some water is produced, the assumption is made that in the addition of make-up caustic this water content is taken into account, thus to maintain the required pH and concentration of reactants in the system.
- It is assumed that it is not necessary to treat stream 14 in order to remove all microorganisms that possibly come from the anaerobic reactor. These can be removed from this stream by various methods, if required to ensure proper operation of the membrane unit.

Table 15-2: Reaction overview per process unit

Unit	Reactions	Conditions	Description
SO_2 separator	(3-2)	P = *1,1bar* T = *303K*	Membrane unit in which SO_2 is absorbed through the membrane in $NaHCO_3$.
Anaerobic reactor	(3-3) (3-4) (3-5) (3-6)	P = *1,1bar* T = *303K*	Anaerobic reactor; reactions (3-5) and (3-6) are responsible for the regeneration of $NaHCO_3$. Reaction (3-3) is responsible for HS^- formation which, according to (3-4) escapes this reactor as H_2S at low pH values.
3 Aerobic reactor: Absorption of H_2S	(3-5) (3-6) (3-7) (3-8)	*P =* 1,1bar T = *303K*	Reactions (3-5) and (3-6) are responsible for the regeneration of $NaHCO_3$. Reactions (3-7) and (3-8) give reaction mechanisms that cause the absorption of H_2S in the bioreactor.
3 Aerobic reactor: conversion of absorbed H_2S to S^0	(3-6) (3-9) (3-10) (3-11)	*P =* 1,1bar T = *303K*	Reactions (3-9) and (3-10) show the S^0 formation and sulphate formation, which is practice occurs only very little. Reactions (3-6) and (3-11) also give some side reactions that occur with regard to $NaHCO_3$.

Thermodynamic properties & reaction kinetics

The chemicals present in this process are HF, HCl, SO_2, S^0, H_2S, $NaHCO_3$, CO_2, H_2, $NaHSO_3$, NaHS, O_2, and possibly some metals or other impurities present in fly ash. The sodium salts are readily soluble in the reaction mixture, so they are/ behave essentially the same as their respective ions in solution. These data are combined for all the process options.

List of pure component properties

The “other” components used in this process are sodium salts of H_2CO_3, H_2SO_3 and H_2S. These salts are present in aqueous solution, so they are ionized. Therefore no different properties than the acid properties of the ions will be observed.

Process stream summary & mass balance

It is important to have an overview of the process streams, since these determine the size of the equipment that is to be used. In real-life, the bioreactors are designed on the basis of the sulfur load contained in the flue-gas. In order to be able to calculate the system without too much problems, a number of assumptions were made, which are mentioned in paragraph C.1.2.

The overall result for the process system without the recycle can be found in Table 15-3. The complete mass balance can be found in APPENDIX 2.

Table 15-3: Total in- and outgoing streams

	INGOING STREAMS					OUTGOING STREAMS			
Massflow [ton/h]	1	6	7	8	9	10	11	12	5
Chemicals		Alkali	H2/CO2	Air	Alkali	Clean gas	BLEED	Air outlet	S prod.
SO2	*4,00E+00*					*2,80E-02*			
CO2	*3,73E+02*		*2,73E+00*	*1,06E+02*		*3,73E+02*		*1,06E+02*	
O2	*5,91E+01*			*5,58E-01*		*5,91E+01*			
HF						*2,01E-05*			
HCL						*0,00E+00*			
H2O						*6,39E-05*	*4,46E-03*		*4,46E-01*
N2	*1,38E+03*			*1,82E+01*		*1,38E+03*		*1,82E+01*	
S0									*1,99E+00*
H2S									
NaHCO3		*1,04E-02*			*TRACE?*		*1,04E-02*		*TRACE?*
H2			*3,72E-01*						
NaHSO3									
NaHS									
Fly ash	*0*								
Total mass	*1,82E+03*	*1,04E-02*	*3,10E+00*	*1,25E+02*	*0,00E+00*	*1,81E+03*	*1,49E-02*	*1,25E+02*	*2,44E+00*

15.2.4 Basic assumptions

Plant capacity

The feedstock of this plant is flue gas, coming from a coal fired power station. This flue gas is produced at a rate of $2\cdot10^6 m^3/h$, and contains $2g/m^3$ SO_2. This implies that per hour *4ton* of SO_2 is produced. From this SO_2, *99.3mol%* has to be removed, which means roughly *3.97ton* per hour.

The plant is assumed to be on-stream for 8000 hours per year, and the capacity is then *31760ton ~ 32Kton/a*.

In this process, the removed SO_2 is converted to elemental sulphur that can be used as a fertilizer. A small amount of this SO_2 is oxidized to sulphate; this is allowed for in order to make sure that the conversion of NaHS is *100%*.

Besides flue gas, this process requires a certain amount of alkali make-up, to compensate for the alkali lost in the products and off gasses. Moreover, this alkali also serves to maintain the pH in the system within system boundaries. Acids present in the flue gas can otherwise influence the pH to undesirable levels.

In the anaerobic reactor, H_2 is required as electron donor, so hydrogen feed will be necessary. The aerobic reaction requires both oxygen and carbon dioxide, which are provided by blowing air into the aerobic reactor.

In addition to elemental sulphur, some other products or wastes are formed. These include the cleaned flue gas and air, a bleed stream which contains at least $NaHCO_3$, but might also contain $NaHSO_3$ and NaHS and when metals are present in the flue gas e.g. in the form of fly ash, metal sulphides can be formed. These can easily be separated from the reaction liquid.

These metal sulphides can then be used in metal recovery plants in which pure metal and sulphur can be reformed.

Table 15-4: Total in- and outgoing streams in *ton/a*

	INGOING STREAMS					OUTGOING STREAMS			
Massflow [ton/a]	1	6	7	8	9	10	11	12	5
Chemicals		Alkali	H2/CO2	Air	Alkali	Clean gas	BLEED	Air outlet	S prod.
SO2	*3,20E+04*					*2,24E+02*			
CO2	*2,98E+06*		*2,18E+04*	*8,51E+05*		*2,98E+06*		*8,51E+05*	
O2	*4,73E+05*			*4,46E+03*		*4,73E+05*			
HF	*0,00E+00*					*0,00E+00*			
HCL	*0,00E+00*					*0,00E+00*			
H2O	*0,00E+00*					*0,00E+00*	*3,57E+01*		*3,57E+03*
N2	*1,11E+07*			*1,46E+05*		*1,11E+07*		*1,46E+05*	
S0									*1,59E+04*
H2S									
NaHCO3		*8,33E+01*			*TRACE?*		*8,33E+01*		*TRACE?*
H2			*2,97E+03*						
NaHSO3									
NaHS									
Fly ash	*0*								
Total mass	*1,45E+07*	*8,33E+01*	*2,48E+04*	*1,00E+06*	*0,00E+00*	*1,45E+07*	*1,19E+02*	*9,96E+05*	*1,95E+04*

The economical plant life for this process is approximated to be 20 years since no severe conditions and chemicals are used.

Location

The plant is located within the range of a *600MW* coal fired power plant, such as near the Amercentrale in Geertruidenberg. It must be checked that the required chemicals such as H_2 and the alkali can easily be provided. Large transport differences can lead to higher production costs.

Battery limit

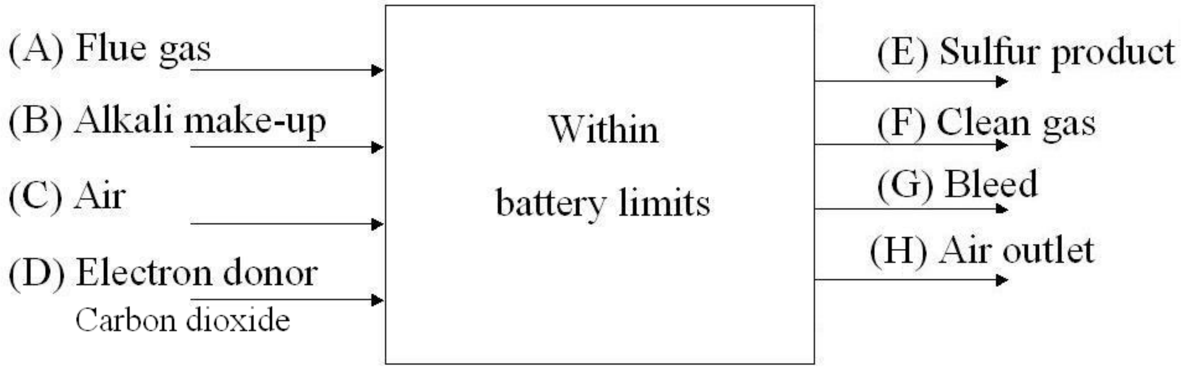


Figure 15-13: Battery limit diagram of the process

This plant basically uses a fly ash removal, a membrane unit, a solid/liquid separation unit and two bioreactors. Besides these basic units, other equipment is also required, such as caustic and make-up water tanks, the bleed water has to be collected for further processing and the produced sulphur has to be precipitated, decanted and transported to a sulphur paste storage.

The air required for the aerobic reaction can be taken in on-site and the cleaned flue gas can be blown into the air on site. However, when a certain amount of CO_2 is to be removed from this cleaned gas, this gas has to be brought to the CO_2 removal unit. The process does not use a catalyst, and when the microbiological cultures are present, these should be self-preserving.

It is assumed that the required alkali make-up (water + caustic), electron donor (H_2) and carbon dioxide can be obtained from outside the Battery limit.

Except for pumping requirements in principle no other utility than cooling water to cool the incoming flue gas steam is required.

All in- and outgoing streams

The process is operated at temperatures or around *303K*, and at the available pressure of *1,10bar* (the process can be used up to pressures of *75bar)*. The incoming flue gas enters at a temperature of *393 - 413K*; this means that the incoming flue gas has to be cooled. This cooling is possible before the absorber, but the absorber can also take up a lot of heat, which partially could be removed by means of a heat exchanger.

The total ingoing and outgoing amounts of chemicals and the magnitude of the total streams are given in Table 15-5.

Table 15-5: Total in- and outgoing stream data

Massflow [ton/a]	A	B	C	D	E	F	G	H
Chemicals								
SO2	2,56E+08					2,24E+02		
CO2	3,47E+10		8,51E+05	2,18E+04		2,98E+06		8,51E+05
O2	1,35E+10		4,46E+03			4,73E+05		
HF	1,03E+07					0,00E+00		
HCL	5,62E+07					0,00E+00		
H2O	1,86E+10				3,57E+03	0,00E+00	3,57E+01	
N2	2,03E+11		1,46E+05			1,11E+07		1,46E+05
S0					1,59E+04			
NaHCO3		8,33E+01			TRACE?		8,33E+01	
H2				2,97E+03				
Total mass	2,70E+11	8,33E+01	1,00E+06	2,48E+04	1,95E+04	1,45E+07	1,19E+02	9,96E+05
Yield (t/t)	1,17E+03	1,10E-03	3,00E+00	1,00	1,10E-03	0	4,85E+01	
Phase	g	l	g	s	l	s	g	
Temperature (K)	393-413	293	293	303	303	303	303	
Pressure (bar)	1,10	1,10	1,10	1,10	1,10	1,10	1,10	
Price (€/ton)	0,00	337,50	0,00	30,00	67,50	0,00	0,00	0,00
Price (€/h)	0,00	3,51	0,00	92,95	164,38	0,00	0,00	0,00

For the cost estimation it is assumed that CO_2 could be obtained free of charge from the CO_2 separation plant.

15.2.5 Economic margin

The economic margin of a process is defined as:

Margin = income from sales – costs for feedstock and waste streams

The sales of this process are coming from the sales of elemental sulphur. Sulphur costs around *67,50€/ton*. In total each year $1{,}95\cdot10^{4}$ *ton* is produced, which amounts to a total income from sales of roughly *1,3M€*. The costs of the chemicals used in the process were calculated as being roughly *120K€*. Therefore a margin of roughly *1,2M€* was calculated.

With this margin, and the known DCFROR the total investment possible can be calculated. With the method mentioned in chapter 5.4 the total investment possible was determined to be around *€5.1M*.

15.3 CO_2 & SO_2 separation membranes

Gas mixtures can be separated using membranes. Membranes act as barriers between the gas phase and the liquid phase preventing flooding that otherwise can happen when these two phases are mixed. Flue gases have flow rates in the range of millions of N $m^3.h^{-1}$. When applying conventional absorbers (packed column) to clean the flue gases we need large amounts of absorbent and large vessels to prevent flooding. The most effective way to provide a large surface area of contact between the two phases and improving the operability at low liquid flow rates is by using hollow-fibre (HF) module with a high density packing. Both, porous and non-porous membranes can be used. Furthermore, the membrane itself can enhance selectivity for a gaseous species from a gas mixture. Aqueous solutions of different chemicals as absorbents can be used. They are; K_2CO_3, $NA3SO_3$, NaOH and different alkanolamines. The absorbent liquids flow on the lumen side of the HF in laminar flow.

15.3.1 Mass transfer characteristics of multiple HF modules

Microporous hydrophobic Teflon HF is tested and proved to be able to do the separation. The inner diameter is 0.1cm while the outer diameter is 0.18cm and the pores have a maximal diameter of 2µm and a porosity of 0.5.

The gas stream containing a solute as permeate is in contact with an absorbent liquid flowing in the lumen side of the fibres, through the membrane pores. Because of the hydrophobic membranes the gas-liquid interface is on the inner surface of the fibres since under laminar flow conditions no liquid escapes through the pores. Thus film theory for the transfer of gaseous solutes across the membrane can be applied. The permeate in the gas stream diffuses through the gas boundary film outside the fibres and the membrane pore and is absorbed at the gas-liquid interface inside the fibres. Subsequently, the solute dissolved in the liquid phase diffuses through the liquid boundary film or reacts with the reactant in the film and liquid bulk. A concentration profile of the solute in the steady state without chemical reaction is shown in Figure 15-14.

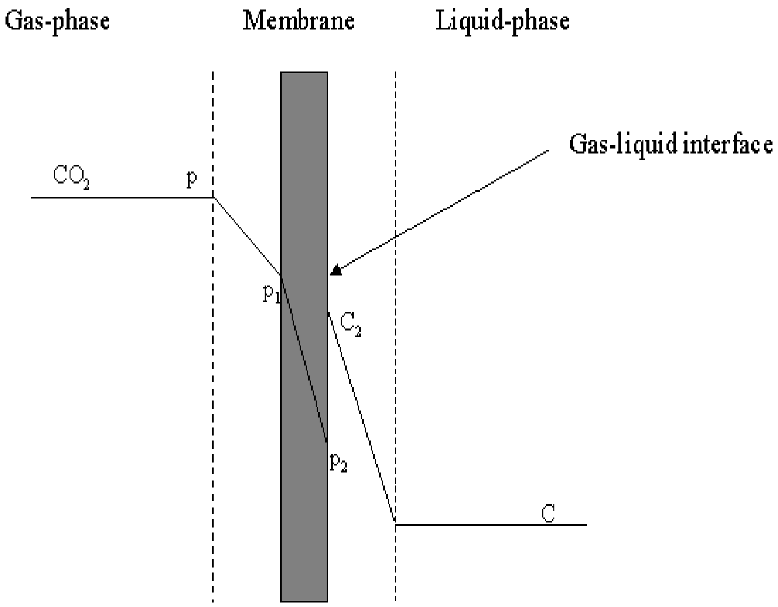


Figure 15-14: Concentration profile of membrane absorption with a hydrophobic porous membrane

The flux for the permeate gas can be expressed as:

$$J = k_G(p - p_1) = k_M \varepsilon (p_1 - p_2) = k_L(C_2 - C) \tag{C3-1}$$

In which k_G and k_L are the mass-transfer coefficients for the gas and liquid boundary films respectively, and k_M is the membrane-transfer coefficient given by:

$$k_M = \frac{D_G}{\delta R T \tau} \tag{C3-2}$$

Where D_G is the diffusion coefficient in the gas phase, δ the membrane thickness and τ is the tortuosity. Henry's law reads p=HC, so the molar flux is represented in terms of the partial pressure as being:

$$J = K_G(p - p^*) \tag{C3-3}$$

K_G is the overall gas-phase mass-transfer coefficient, expressed as the some of the three transfer resistances:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{\delta R T \tau}{D_G \varepsilon} + \frac{H}{k_L} \tag{C3-4}$$

The k_L can be evaluated from:

$$\frac{k_L d_i}{D_A} = 1.62 \cdot \left[\left(\frac{d_i}{L} \right) \cdot R_e \cdot Sc \right]^{0.33} \tag{C3-5}$$

Values of k_G and k_M are determined using SO_2 in aqueous alkaline solution. A gaseous feed of 0.2% SO_2 (in N_2) is brought in contact with 1.2 M NaOH. SO_2 reacts instantaneously with the OH^- ion at the gas-liquid interface inside the HF, thus the overall coefficient K_G becomes

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k_M \varepsilon} \tag{C3-6}$$

Figure 15-15 shows the dependence of k_G on the Reynolds number for three modules with different number of hollow fibres. The specifications are included in Table 15-6
The slope has a value of 1/3 implying that the values of K_G are a function of $u_G^{1/3}$.

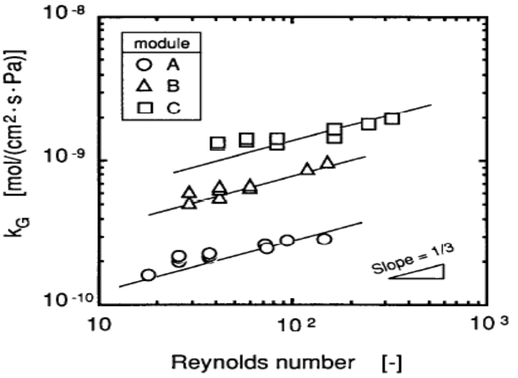


Figure 15-15: Effect of the Reynolds number on the gas-film mass transfer coefficient: pCO_2 = 200 Pa, absorbent NaOH, T = 303 K

Table 15-6: Specifications of membrane modules

Module	Number of HFs	Effective area (cm^2)	Effective HF length (cm)	I.D. of shell tube (cm)
A	14	134.2	30.5	1.7
B	5	35.7	22.7	1.25
C	1	6.7	21.3	0.8

Figure 15-16 shows the Wilson plot of K_G vs. $u_G^{1/3}$.

A Wilson plot is a technique to estimate the film coefficients in several types of heat transfer processes and to obtain general heat transfer correlations. The intercept is $1/k_M$; this is found to be 5.34 x 10^{-10} mol $cm^{-2}s^{-1}Pa^{-1}$. This value is equal to what is predicted from (A3-2 with the membrane tortuosity τ = 2 and D_G= 0.108 cm^2s^{-1}.

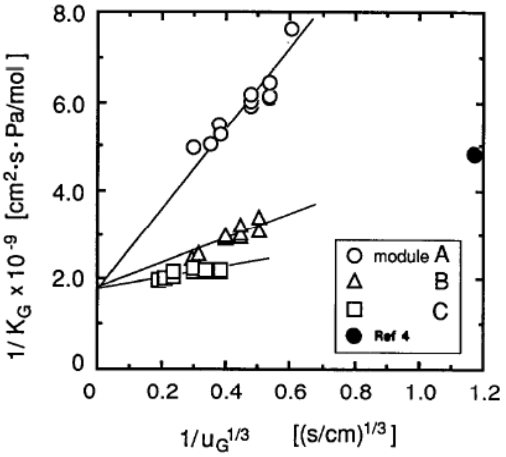


Figure 15-16: Wilson plot for single and multiple HF membrane modules: pCO_2 = 200 Pa, absorbent 1.2 M NaOH, T = 303 K

15.3.2 Membrane absorption using aqueous NaOH solution

Absorption rates of CO_2 in aqueous solution with different NaOH molarities is depicted in Figure 15-17 as a plot of the flux J, versus p_{CO2}, together with calculated values based on the gas absorption accompanied by the second-order reaction between CO_2 and OH^- ion.

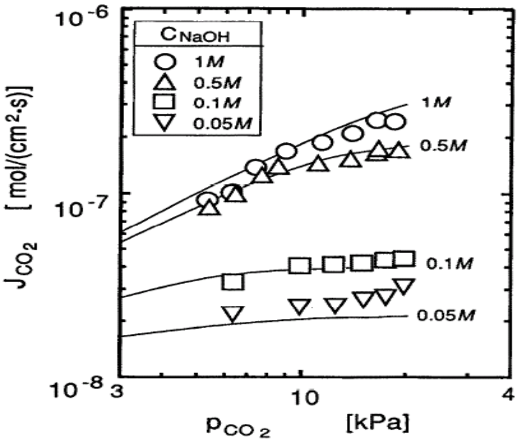


Figure 15-17: Effect of CO_2 partial pressure on absorption flux; solid lines represent calculated values; u_G = 10 cm/s; u_L = 2.0 cm/s; T = 294

CO_2 concentration in the liquid bulk, C, is negligible in the presence of OH^- in the effluent liquid, the absorption rate is given by:

$$J = \beta k_L C_2 \qquad \text{(C3-7)}$$

β is the enhancement factor, which can be evaluated from the equation given in [1]. Thus the CO_2 permeation flux can be calculated using equation (C3-7).

15.3.3 CO_2 removal using alkanolamine solutions

Alkanolamines exhibit a high absorption rate and capacity for CO_2 and accordingly have a good absorbent to remove CO_2 from flue gases. CO_2 absorption by amines is accompanied by a fast reaction leading to the formation of carbamate. For primary and secondary amines, the following reaction occurs:

$$CO_2 + 2RNH_2 \rightleftharpoons RNHCOO^- + RNH^+ \qquad \text{(C3-8)}$$

.

Followed by a slow reaction:

$$RNHCOO^- + H_2O \rightleftharpoons RNH_2 + HCO^-_3 \qquad \text{(C3-9)}$$

The CO_2 absorption rate depends on the aqueous solutions of the amines MEA, DEA, or MDEA. CO_2 absorption by different alkanolamine solutions is plotted versus p_{CO2} in Figure 15-18.

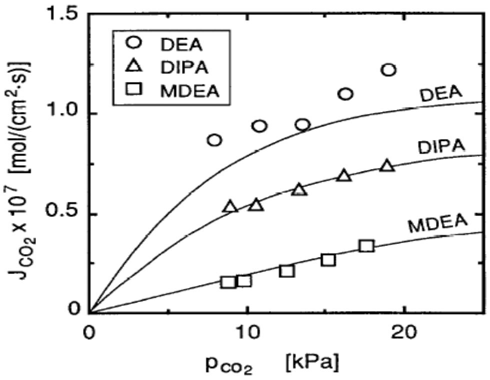


Figure 15-18: CO_2 membrane absorption in 10 wt% alkanolamine aqueous solution: solid lines are based represent calculated values based on a second reaction: u_G = 10cm/s; u_L = 1.1cm/s; T = 294K

The diffusivities CO_2 in the amine solutions are estimated using:

$$N_a = -D\frac{dC_a}{dx} \qquad \text{(C3-10)}$$

As it is seen in Figure 15-18 the absorption rates decreases in the sequence of amine basicity and therefore the reaction rates decrease in the same sequence.

Figure 1-6 shows the absorption of MEA solutions. The CO_2 flux for MEA is much higher than those for other amines because of the high reaction rate and basicity.

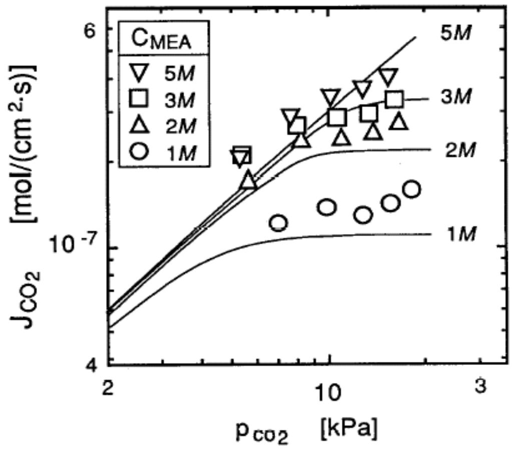


Figure 15-19: CO_2 membrane absorption in MEA aqueous solution: solid lines are calculated values; u_G = 10cm/s; u_L = 1.1 cm/s; T = 293K

15.3.4 Effect of amine addition in K_2CO_3 solution

Amines addition gives rise to an enhancement in CO_2 absorption rate, but they have the drawback of a much higher energy requirement for regeneration of the CO_2-rich solution compared with the carbonate solution. On the other hand, the addition of small amounts of amines to an aqueous carbonate solution not only enhances the rate of CO_2 absorption but also improves the regeneration efficiency and corrosion is largely avoided. For the absorption of CO_2 in a mixed amine carbonate solution, the fast reacting amine combines with CO_2 near the gas-liquid interface and releases it again in the bulk of he liquid; the free amine diffuses back to the interface to react with CO_2. In Figure 1-7, the effect of the addition of alkanolamines on CO_2 absorption by aqueous K_2CO_3 solution is shown.

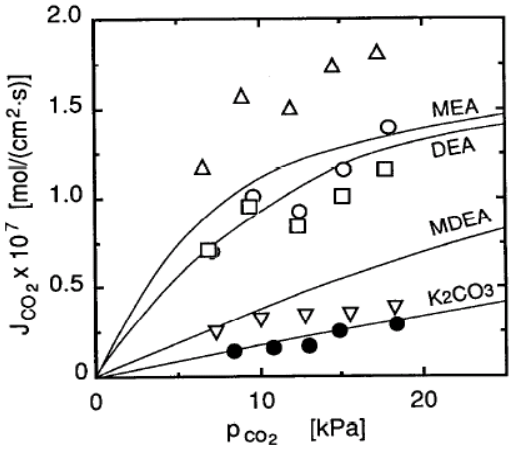


Figure 15-20: Effect of alkanolamines to K_2CO_3 solution (2M) on CO_2 absorption flux: u_G = 10cm/s, u_L = 1.1cm/s, T = 294K

16Thermodynamics

16.1 Thermodynamical Properties

Table 16-1: Heat capacities of gases in the ideal gas state [1,2]

Chemical species	T_{max} (K)	$(Cp/R)_{298}$	A	10^3 B	10^6 C	10^{-5} D
CO_2	2000	4.467	5.457	1.045	-	-1.157
H_2	3000	3.468	3.249	0.422	-	0.083
HCl	2000	3.512	3.156	0.632	-	0.151
N_2	2000	3.502	3.28	0.593	-	0.04
O_2	2000	3.535	3.639	0.506	-	-0.227
SO_2	2000	4.796	5.699	0.801	-	-1.015
H_2O	2000	4.038	3.47	1.45	-	0.121
Br_2	3000	4.337	4.493	0.056	-	-0.154

Table 16-2: Heat capacities of gases [1]

Chemical species	T_{min} (K)	T_{max} (K)	$(Cp/R)_{298}$	A	B	C	D	E
HF	50	1500	3.50	3.50	1.16E-04	-5.38E-07	8.16E-10	-2.64E-13
HBr	200	1500	3.50	3.63	-9.66E-04	2.01E-06	-8.99E-10	9.99E-14
H_2SO_4	100	1500	9.82	1.14	4.06E-02	-4.58E-05	2.56E-08	-5.64E-12
MEA	298	1500	10.3	-6.68E-02	4.45E-02	-3.85E-05	1.90E-08	-3.89E-12

Table 16-3: Heat capacities of liquids [4]

Chemical species		State	$(Cp/R)_{298}$	A	10^3 B	10^6 C	D
Water	H_2O	/	9.069	8.712	1.25	-0.18	
Ammonia	NH_3	/	9.716	22.626	-100.75	192.71	
MEA	C_2H_7NO	/	23.237	2.78	0.1477E3	-0.375E3	0.369E-6
Sulphuric acid	H_2SO_4	/	16.831	3.1277	0.0846E3	-0.167E3	0.1244E-6

Table 16-4: Heat capacities of solids [3]

Chemical species		T_{max} (K)	$(Cp/R)_{298}$	A	10^3 B	10^{-5} D
Sodium bicarbonate	$NaHCO_3$	400	10.539	5.128	18.148	-

Table 16-5: Standard enthalpies of formation at 298.25K [5]

Chemical species	State	ΔH^{o}_{f298} (kJ/mol)
CO_2	(g)	-393,509
H_2	(g)	0
HCl	(g)	-92,307
HF	(g)	-542
N_2	(g)	0
O_2	(g)	0
SO_2	(g)	-296,830
H_2O	(g)	-241,818
H_2O	(l)	-285,830
Br_2	(g)	0
HBr		-36.3
NH_3	(g)	-46,110
H_2SO_4	(g)	-783.850
H_2SO_4	(l)	-846.70
MEA	(l)	-210.19
Na_2SO_3	(l)	-1161.139

Table 16-6: Solubility and density data [6,7]

Gas	Solubility fraction @25°C	Solubility (mol/l) @25°C	Solubility (mol/l) @55°C	Density (kg/m^3) @298K	Acidity (pK_a)
CO_2	$61.48*10^{-5}$	$33.5*10^{-3}$	1.51E-02	1.98 (g)	6.35 and 10.33
H_2	$1.411*10^{-5}$	$0.79*10^{-3}$	7.28E-04	0.09 (g)	
HCl	$3.55*10^{-4}$	19.0	1.23E+01	1.64 (g)@273K	-4
N_2	$1.1774*10^{-5}$	$0.638*10^{-3}$	5.04E-04	1.251 (g)@273K	
O_2	$2.3011*10^{-5}$	$1.26*10^{-3}$	9.12E-04	1.429 (g)@273K	
SO_2	$2.64*10^{-2}$	$1.46*10^{-3}$	5.80E-01	2.93(g)@273K	
HBr		24.4(@293K)		3.307 (g)	
NH_3	$57.08*10^{-2}$	27.8		0.6813 (g)	

Table 16-7: Critical and boiling points of species [8]

Chemical species	T_b (K)	T_c (K)	P_c (bar)	V_c (cm^3/mol)
CO_2	194.8	304.13	73.75	94
H_2	20.28	32.97	12.93	65
HCl	188.15			
HF	293	416	64.8	69
N_2	77.36	126.21	33.9	90
O_2	90.2	154.59	50.43	73
SO_2	263.1	430.8	78.84	122
H_2O	373.15	647.14	220.6	56
Br_2	332	588	103.4	127
HBr	206.75			
NH_3	239.82	405.5	113.5	72
H_2SO_4	610	924	64	177
Air	-	132.2	37.45	84.8

Table 16-8: Heat of evaporation parameters

Chemical species	A	T_c (K)	n
Br_2	*41.279*	*584.15*	*0.38*
HBr	*25.3*	*363.15*	*0.401*
H_2SO_4	*56.115*	*925*	*0.38*
MEA	*74.024*	*638*	*0.304*

Table 16-9: Vapour pressure parameters

	A	B	C	D	E	Vapour pressure (kPa)
Br_2	*23.72*	*-2.28E+03*	*-5.61E+00*	*2.26E-09*	*1.79E-06*	*179.74*
HBr	*34.4939*	*-1.64E+03*	*-1.09E+01*	*7.57E-03*	*-2.55E-12*	*3553.11*
H_2SO_4	*2.0582*	*-4.19E+03*	*3.26E+00*	*-1.12E-03*	*5.54E-07*	*0.00*
MEA	*72.9125*	*-5.86E+03*	*-2.19E+01*	*-7.15E-10*	*5.98E-06*	*19.46*

16.2 Pure Component Properties

Properties	Components					
Name	Ammonia	Ammoniak	Bromine	Carbon dioxide	Carbon monoxide	Hydrogen
Structural formula	NH_3 H_20	NH_3	Br_2	CO_2	CO	H_2
Molecular weight		17	159.808	44	28	2
Phase			l	g	g	g
Boiling point (^{o}C)	38	-33	58.8	-79	-192	-253
Melting point (^{o}C)	-58	-78	-7.2	sublimation	-205	-259
Flash point (^{o}C)						
Igniton temperature (^{o}C)	651	651	inflammable			560
LEL (vol% in air)	15	15	inflammable		17.5	4
UEL (vol% in air)	30.2	30.2	inflammable		74	74
Liquid density (rel. to water)			3.1			
Vapour density (rel. to air)			5.5	1.79	1.145	0.082
MAC (ppm)	20	20	0.1	5000	25	N/A
LDxx			14			
LD50 (mg/kg)				N/A	3760	N/A
Chemical reactivity			Extreme reactive with inflammable components, reducing components, many organic components, many metals and phosphor upon heating with hydrogen, affects rubber and plastics	low		Strong reaction with acetylene dinitrogen oxide, nitrogen oxide and fluor. Is explosive with air and chlorine

Properties	Components					
Name	Hydrogen bromide	Hydrogen chloride	Hydrogen fluoride	Hydrogen sulfide	Methane	Monoethanolamine
Structural formula	HBr	HCl	HF	H_2S	CH_4	C_2H_7ON
Molecular weight	80.9	36.5	20	34.1	16	61
Phase	l	g	g	g	g	l
Boiling point (^oC)	-66.4	-85	20	-59.55	-161.5	172
Melting point (^oC)	-86	-114	-83.3	-85.5	-182.4	10.3
Flash point (^oC)						93
Igniton temperature (^oC)	inflammable			260	537	420
LEL (vol% in air)	inflammable			4	5	5
UEL (vol% in air)	inflammable			44	15	17
Liquid density (rel. to water)	1.5					1.015
Vapour density (rel. to air)	1.7	1.49	0.818	1.393	0.4228	
MAC (ppm)	2	0	0	10		
LDxx						
LD50 (mg/kg)		3120	1276	712	N/A	
Chemical reactivity	Strong acid, corrosive, affects many metals under formation of hydrogen, forms bromine under reactions with oxidizing agents					

Properties	Components							
Name	Nitrogen	Oxygen	Potassium carbonate	Sodium sulfite	Sulfur	Sulfuric acid (98%)	Sulfur dioxide	Water
Structural formula	N2	O2	K2CO3	Na2SO3	S	H2SO4	SO2	H20
Molecular weight	28	32	138.2	126.1	32.1	98.1	64.1	18
Phase	g	g	s	s	s	l	g	g
Boiling point (^oC)	-196	-183			444.6	330	-10	0
Melting point (^oC)	-210	-218	891	600	115.21	3	-76	100
Flash point (^oC)								
Igniton temperature (^oC)			inflammable			inflammable		
LEL (vol% in air)			inflammable			inflammable		
UEL (vol% in air)			inflammable			inflammable		
Liquid density (rel. to water)						1.8		0.995
Vapour density (rel. to air)	1.145	1.308				3.4	2.619	
MAC (ppm)	N/A	N/A				1	2	N/A
LDxx								
LD50 (mg/kg)	N/A	N/A		820			3120	N/A
Chemical reactivity			avoid moisture and acids	avoid: high T and moisture, oxidizers (cause vigorous exothermic reactions), acids (releases SO2)		Upon heating decomposes to sulphur dioxide, strong oxidizing agent, heavy reaction with flammable and reducing components, strong acid, corrosive, affects many metals with formation of hydrogen, does not affect steel and lead.		

16.3 Txy-diagrams

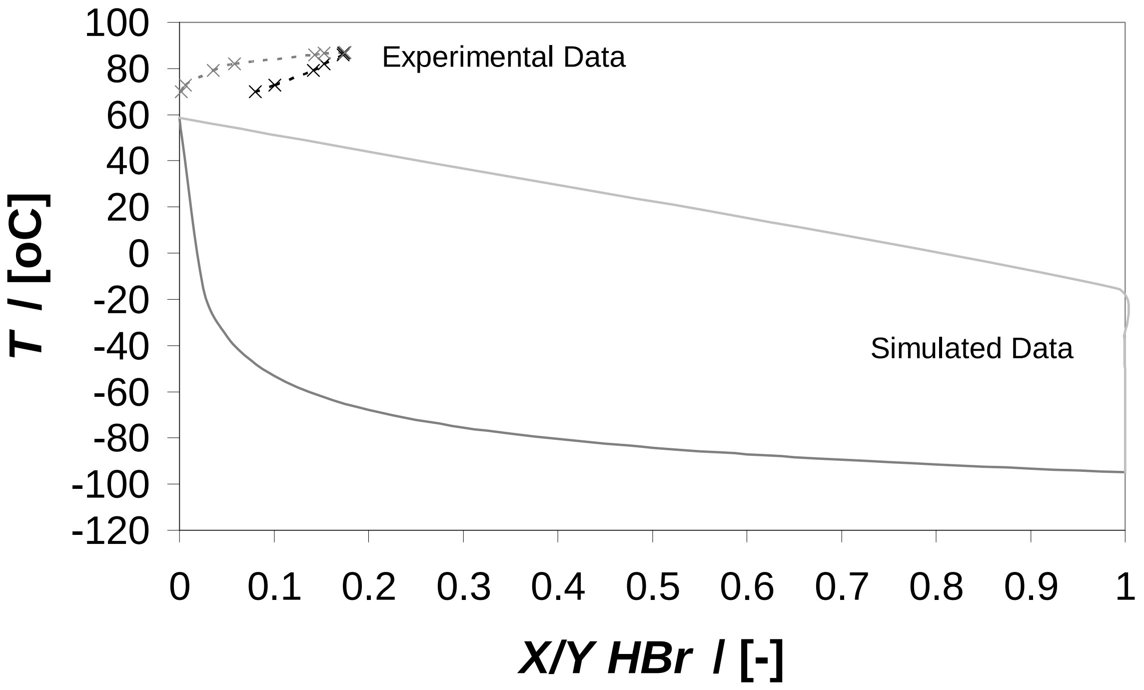


Figure 16-1: Simulated and experimental Txy data for a water/HBr mixture at 0.186bar

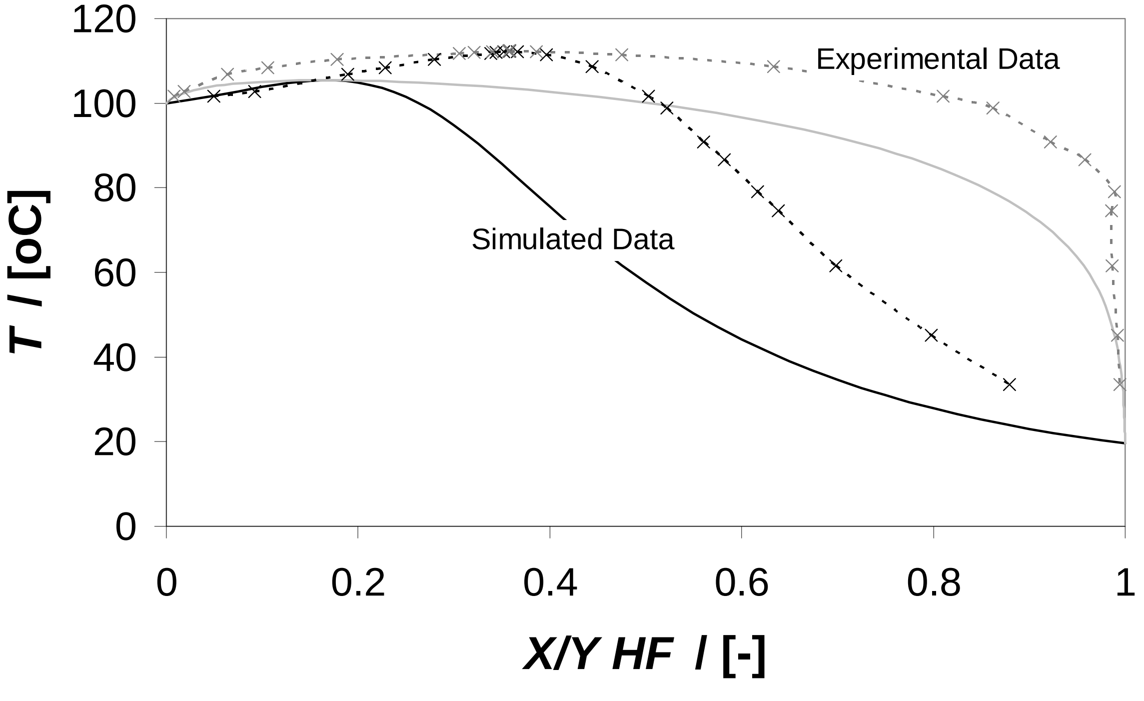


Figure 16-2: Simulated and experimental Txy data for a water/HF mixture at 1 atm

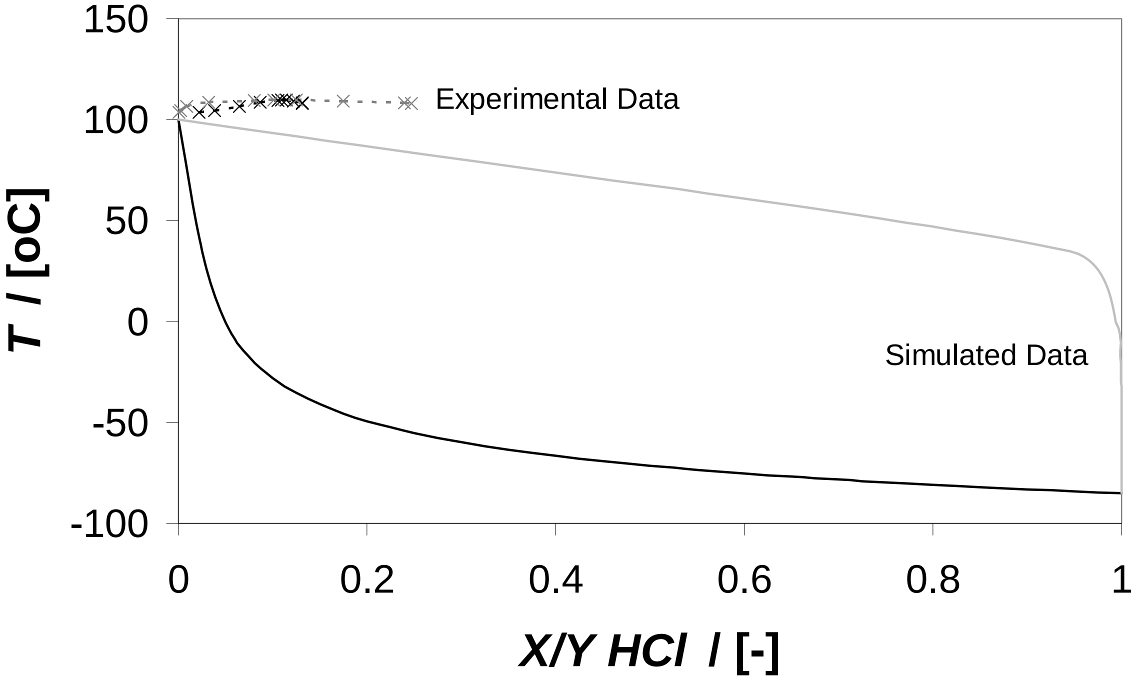


Figure 16-3: Simulated and experimental Txy data for a water/HCl mixture at 1 atm

17Process Flow Scheme walkthrough

Appendix for chapter 5.2

The flue gas feed <101> enters the process via the feed pre-treatment section. This section consists of an electrostatic precipitator (S01) where the fly ash present in the feed is removed. The separated fly ash is removed via <909>; the flue gas <201> then enters an absorber column (C01) in which the present HCl and HF are removed from the gas. A small amount of scrubbing water make-up <105> is added and the loaded water containing both HCl and HF is removed via <908> to the wastewater treatment plant.

Next, the gas stream <202> enters the membrane unit (S02) in which the SO_2 and a small part of the CO_2 present is separated from the rest of the flue gas by permeation through the membrane. The treated flue gas <305> continues to the CO_2 removal section (C04) and (C05).

The loaded solvent <302> coming from the membrane enters the thermal regeneration vessel (V01) in which the SO_2 and CO_2 leave via <304>. The regenerated solvent <303> is recirculated to the membrane unit where if necessary, it is combined with a Na_2SO_3 solvent make-up stream <106> and enters the membrane unit as <301>. Insoluble salts that might be formed in the absorption can be removed from the solvent regeneration vessel as <907>, after filtration in a solid/ liquid filter. In normal operation however, no such salts are formed.

<304> is mixed with gaseous bromine <401>, and this mixture, <402> is brought into the second reactor (R2), together with the reaction mixture <404> coming from reactor 1 (R1). From this reactor, <407> leaves as the stream containing the liquid product stream, containing hydrogen sulphide, unreacted bromine and hydrogen bromide. The other outgoing stream <403> is a vapour stream containing the unreacted vapours. Stream <403> enters (R01) at the top together with <405>, a mixture of water and some hydrogen bromide, coming from the water storage vessel (V03). From the bottom of this reactor, the liquid reactant and product containing mixture <404> is sent to (R02), and the vapour <406> is sent to the membrane unit that removes the rest of the CO_2 (S03).

The liquid product that comes from the second reactor (R02), a mixture of hydrogen sulphate, water and hydrogen bromide <407> is brought up to spec in (C02), which essentially is a simple distillation column. The bottoms product <501>, after cooling down (E05) is concentrated technical grade hydrogen sulphate <906> and brought to product storage. Over the top of column (C02) the rest of the water and hydrogen bromide is removed <502>. Via a total condenser (E03) and a liquid hold-up vessel (V02) this stream is pumped to the water storage vessel (V03) as <503>, where also the water make-up stream <103> enters the process.

The gaseous bottom outflow <406> of reactor 1 (R01), consists of a mixture of CO_2, unused Br_2 and possibly some HBr. The CO_2 is removed from this stream by use of a membrane separation unit (S03), where the CO_2 permeates through the membrane into a MEA solution <603> and the Br_2 and HBr leave via <604> to the bromine regeneration section (C03) and (S04). The loaded solvent <601> is transferred to the MEA regeneration section (V04), where upon heating the CO_2 desorbs and the lean solvent is reformed. This stream, <602> is sent back to (S03) after addition of MEA if necessary <107> and pumped into the membrane unit as <603>. When insoluble MEA salts are formed, these are removed through a solid/ liquid separator as <905>. In normal operation, no insoluble salts are formed, so normally <905> has no flow. The separated CO_2 leaves (V04) via <605> and is combined with the separated CO_2, coming from (C05) as <809>. This combined stream <903> of essentially pure CO_2 is collected and can be transported/ sold.

The mixture of bromine, hydrogen bromide and traces of CO_2 coming from the CO_2 separating membrane unit, stream <604> is together with stream <702> and the reflux <704> entered into the Br_2 recovery column (C03), which essentially is a simple absorption. The bromine together with CO_2 if present leaves over the top as a gaseous flow <703> and after condensation of the Br_2 by (E09), pumped as <408> to the bromine storage vessel (V05), together with the required bromine make-up <104>.

The hydrogen bromide (in a watery mixture) leaves over the bottom as stream <701>. This stream is introduced in the electrolysis unit (S04) where hydrogen bromide is converted in bromine and hydrogen. The formed bromine stays in solution<702>, which is sent back to (C03). The formed hydrogen is removed from the system as <904> and is used for energy production.

Stream <305>, containing flue gas from which SO_2, HCl and HF is removed, is sent to the CO_2 separation section (C04) and (C05), where 6% of the CO_2 present in the flue gas is separated from this stream. MEA make-up <102>, recycled MEA <805> and the flue gas <305> enter the MEA absorption column (C04). The lean flue gas leaves this column over the top, as stream <901>, which is emitted via the plant stack into the environment. The loaded MEA stream, <801> is heated by means of heat exchange with the MEA recycle stream in (E11), and is pumped as <802> to the MEA stripper (C05). In (C05), the MEA stripper, the CO_2 is desorbed from the MEA. This regenerated MEA <803> is pumped back to the MEA absorber as <804> after passing through heat exchanger (E08). The top product, stream <806> is partially condensed in (E12) to remove the MEA or water that is present from the CO_2. This mixture of liquid and vapour <807> is collected in vessel (V07), from which the pure CO_2 <809> is combined with <605> and collected for further handling. The condensed liquid <808> is sent back into the stripping column (C05) as reflux. Insoluble salts that might be formed are separated from this column (C05) and removed from the process as <902>.

18Process Stream Summary

Table 18-1: Mass and heat balances of all streams

IN						OUT				
Plant		Equipment			Equipment	Equipment			Plant	
Mass kg/s	Heat kW	Mass kg/s	Heat kW	Stream Nr.	Identif.	Mass kg/s	Heat kW	Stream Nr.	Mass kg/s	Heat kW
541.21	219448.89	541.21	219448.89	<101>	**S01**	541.17	219448.89	<201>		
						0.04	0.00	<909>	0.04	0.00
		541.21	219448.89		total	541.21	219448.89			
20.00	2012.24	20.00	2012.24	<105>	**P04**					
		541.17	219448.89	<201>	**C01**	559.25	191873.20	<202>		
					P07	1.96	408.77	<908>	1.96	408.77
		561.1694	221461.1		total	561.2111	192282			
		559.25	191873.20	<202>	**SO2**	261.20	338091.67	<302>		
		260.01	341488.17	<301>		558.02	193204.63	<305>		
		819.26	533361.37		total	819.22	531296.30			
		261.1952	338091.7	<302>	**V01**	1.19	363.87	<304>		
					P08	260.01	365328.32	<303>		
					P09	0	0	<907>	0	0
			27600.51		**E02**					
		261.1952	365692.2		total	261.1952	365692.2			
		260.01	365328.32	<303>	**P05**	260.0079	341488.2	<301>		
0.00	0.00	0.00	0.00	<106>						
			-23840.15		**E01**					
		260.01	341488.17		total	260.01	341488.17			
0	0	0	0	<104>	**P03**	3.37	244.05	<401>		
		3.37	244.05	<408>	**P17**					
					V05					
		3.37	244.05	<401>	**V06**	4.56	619.33	<402>		
		1.19	363.87	<304>						
			11.42		**E10**					
		4.56	619.33		total	4.56	619.33			
		4.56	619.33	<402>	**R02**	4.01	540.85	<403>		
		1.89	1160.52	<404>	**P10**	2.44	871.63	<407>		
		6.45	1779.85		total	6.44	1412.48			
		4.01	540.85	<403>	**R01**	1.89	1160.52	<404>		
		1.36	1418.77	<405>		3.48	402.60	<406>		
		5.37	1959.62		total	5.37	1563.11			
		2.44	871.63	<407>	**C02**	1.77	254.91	<501>		
						0.67	801.25	<502>		
			184.53		**E04**					
		2.44	1056.16		total	2.44	1056.16			
		1.76545	254.9077	<501>	**P11**	1.77	134.31	<906>	1.77	134.31
			-120.595		**E05**					
		1.76545	134.3127		total	1.76545	134.3127			
		0.671694	801.2505	<502>	**V02**	0.67	611.99	<503>		
			-189.2575		**E03**					
		0.671694	611.993		total	0.671694	611.993			
		0.671694	611.993	<503>	**V03**	1.36	1418.77	<405>		
0.69	831.02	0.69	831.02	<103>	**P02**					
		1.364194	1443.008		total	1.364194	1418.769			
		3.48	402.60	<406>	**S03**	0.87	789.63	<601>		
		0.82	703.89	<603>	**P12**	3.41	372.65	<604>		
		4.31	1106.48		total	4.28	1162.28			
		0.87	789.63	<601>	**V04**	0.08	32.49	<605>		
						0.82	917.90	<602>		
					P13	0.00	2.70	<905>	0.00	2.70
			163.46		**E06**					
		0.87	953.09		total	0.90	953.09			

Table 18-2: Mass and heat balances of all streams (continued)

		0.82	917.90	<602>		0.823238	703.8869	<603>		
		0.00	2.07	<107>	**P06**					
			-216.08		**E07**					
		0.83	703.89		total	0.82	703.89			
		3.41	372.65	<604>	**C03**	3.55	383.66	<703>		
		75.38	63305.56	<702>	**P14**	75.41	63439.44	<701>		
					P15					
			144.90		**E08**					
		78.78	63823.10		total	78.96	63823.10			
		75.41	63439.44	<701>	**S04**	75.38	63305.56	<702>		
					P16	0.03	161.36	<904>	0.03	161.36
		75.41	63439.44		total	75.41	63466.92			
		3.550596	383.6639	<703>		3.373067	244.0514	<408>		
					V08	0.18	81.48	<704>		
			-58.12838		**E09**					
		3.550596	325.5355		total	3.550596	325.5355			
		0.076265	32.48711	<605>		6.31	2618.95	<903>	6.31	2618.95
		6.24	2587.30	<809>						
		6.311684	2619.787		total	6.311684	2618.946			
		558.02	193204.63	<305>	**C04**	551.78	190683.41	<901>	551.78	190683.41
		0.01	6.53	<102>	**P01**	66.74	59231.43	<801>		
		60.46	57220.51	<805>	**P18**					
		618.49	250431.67		total	618.52	249914.84			
		66.73653	59231.43	<801>	**E11**	66.74	63681.23	<802>		
		60.46	67416.48	<803>		60.46	63094.15	<804>		
		127.2003	126647.9		total	127.2003	126775.4			
		60.46375	63094.15	<804>		60.46375	57220.51	<805>		
			-5873.643		**E14**					
		60.46375	57220.51		total	60.46375	57220.51			
		66.73653	63681.23	<802>	**C05**	60.46375	67416.48	<803>		
		0	0	<808>	**P19**	0.04	11.02	<902>	0.04	11.02
					P20	6.24	2851.88	<806>		
					P21					
			6598.152		**E13**					
		66.73653	70279.38		total	66.73653	70279.38			
		6.235418	2851.885	<806>		6.24	2587.30	<807>		
			-264.5844		**E12**					
		6.235418	2587.3		total	6.235418	2587.3			
		6.235418	2587.3	<807>	**V07**	0	0	<808>		
						6.235418	2587.3	<809>		
561.90	222292.15				total				561.93	194020.52

For calculation of the heat balances has been assumed that the processes are performed at constant pressure and that no work is done on or by the system. In that case it is possible to state that the enthalpy is equal to energy of the streams and this way also duties of coolers and heaters are calculated.

Electrostatic precipitator

From the data provided by the project description the composition of stream <101> has been determined. The first unit consists of an electrostatic precipitator (S01), which removes fly ash from the flue gas. So an easy subtraction of the fly ash mass completed the mass balance. The enthalpy of the stream was calculated with the data from chapter 4.

HF/HCl scrubber

The next unit is the HF/HCl scrubber (C01), which has been simulated using ASPEN. The incoming streams (<201> and <105>) where entered in an absorber and using an Electrolyte NRTL model the compositions of the outgoing streams were calculated. The mass balance for this unit is correct, however there is substantial difference in the heat balance. This is most probably since ASPEN has calculated a temperature for stream <202>, which is most likely too low (324 K). The temperature of the incoming flue gas stream is much higher and the size of the flue gas stream is much larger than the size of the water stream (<105>), so it is most probable that ASPEN made a calculation error. The temperature calculated by ASPEN however will be used for further calculations. Furthermore the pumps P04 and P07 can be seen as a part of this unit and are therefore added to the balance.

Sulphur dioxide membrane units

The membrane units, which remove sulphur dioxide from the flue gas stream (S02), contact the flue gas stream with a sodium sulphite solution. According to calculations Lawien, The size of the sodium sulphite solution needs to be quite large to be able to remove 99.5 % of the sulphur dioxide from the flue gas stream. Inevitably some carbon dioxide is also dissolved by the sodium sulphite and this amount turns out to be 10 wt % of the sulphur dioxide content. There is a slight difference in the mass balance and this is probably due to some minor miscalculations. There is also a small difference in the heat balance and this is due to slight differentiations of the heat capacity values compared with the real values.

Sodium sulphite regenerator

The next units for which one mass and heat balance can be made are the sodium sulphite regenerator (V01) along with two pumps (P08 and P09) and a heat exchanger (E02). The outgoing streams are a sulphur dioxide stream (<304>) that also contains some carbon dioxide and a sodium sulphite stream that will sent back to the membrane units (S02). The mass balance turns out to be correct after it has been calculated. In the regeneration unit the temperature has to be increased to release sulphur dioxide (and some carbon dioxide) from the solution. Heating with low-pressure steam does this. The duty for this heat exchanger has been calculated by the difference in enthalpies of the in- and outgoing streams. Therefore the heat balance is also right.

Sodium sulphite cooler

The hot sodium sulphite stream needs to be cooled down to be able to take up a large amount of sulphur dioxide in the membrane units. This will be done with cooling water in a heat exchanger (E01). Pumping this stream will be done by pump P05. The duty has been calculated by the difference of the ingoing stream and the specification of the outgoing stream. The masses of the in- and outgoing streams are similar and the heat balance is logically also correct.

Bromine collection vessel

In the bromine collection vessel (V05) bromine make up (<104>) is added to the bromine recycle stream (<408>). Since only small amounts of bromine will be lost in the process the bromine make up normally has no flow. Pumps P03 and P17 can also be considered part of this unit.

Bromine evaporation vessel

In evaporation vessel (V06) bromine will be evaporated to be added to the sulphur dioxide gas stream. The energy needed for this process is calculated by the difference in energy of the in- and outgoing streams and this way the duty of the heat exchanger (E10) has been calculated. By simply adding up the streams the mass balance is correct and the heat balance too.

Reactor 2

In the first reactor (R02) the total mass of the in- and outgoing streams is approximately in balance. Berekeningen Jurre? All of the sulphur dioxide will eventually be converted into sulphuric acid. So just as many moles of sulphur dioxide entering the reactor that many moles of sulphuric acid will leave the reactor. There is a difference in the enthalpy of the in- and outgoing streams. This is most likely because of any heat of reaction hasn't been accounted for. That's why there is a difference.

Reactor 1

In the other reactor (R01) the same holds. Berekeningen Jurre? The mass streams are in balance and a small difference in the heat balance exists, most likely because of any heat f reaction, which has not been accounted for by the calculations.

Sulphuric acid concentrator

In the sulphuric acid concentrator (C02) water and hydrogen bromide is being distilled off and the sulphuric acid is concentrated to 96 mass %. The rest of the water and hydrogen bromide is sent to back into the reaction section. The mass balances are easily constructed. Because of the high temperature, which is needed to concentrate the sulphuric acid, a furnace is used for heating. The amount of energy needed has been calculated by the difference in enthalpies of the in- and outgoing streams.

Sulphuric acid cooler

The hot sulphuric acid <501> is pumped (P11) to a heat exchanger where the stream is cooled to down to 298 K to make it suitable for selling. With the calculated enthalpies the duty of the cooler has been determined.

Concentrator top condenser

The top stream from the sulphuric acid stream (<502>) will be condensed in a cooler (E03) and then enters a vessel (V02) from which a small part is sent back to the concentrator, but the major part is sent to a water collection vessel. The duty of the cooler has been calculated by comparing the enthalpies of the in- and outgoing streams.

Water collection vessel

In the water collection vessel (V03) the recycled water and hydrogen bromide is added to the water make-up stream (<103>). The water make up stream is pumped into the vessel with pump P02. These streams combined (<405>) are sent back to the rector section for conversion. This water make up stream is necessary because water reacts in the reactor forming sulphuric acid. The water make up stream has a size of twice the number of moles of sulphuric acid leaving the plant and the amount of water leaving with the sulphuric acid.

Carbon dioxide membrane unit

Stream <406>, which contains undesired carbon dioxide, is contacted with a specific membrane unit to remove the carbon dioxide from the stream to avoid accumulation in the system. In this membrane unit (S03), this stream is contacted with a MEA solution (<603>), which causes the carbon dioxide to dissolve. The carbon dioxide containing MEA stream (<601>) is sent to a regenerator so all carbon dioxide is removed from the stream. There is only a minor difference in the mass balance and this is most probably because of a minor miscalculation. There is also a small difference in values of the enthalpies; this is most likely because of some slight faults in the polynomial from which the enthalpies were calculated.

MEA regeneration vessel small

In the MEA regeneration vessel (V04) the MEA is regenerated to release carbon dioxide from the MEA stream. The mass balance is not completely correct, but the difference in mass is exactly as large as the difference of the MEA membrane unit. Therefore it is most likely that a small mistake was made, but this will have no effect on the overall mass balance. In order to release the carbon dioxide energy is needed. This energy comes from heating with lower pressure steam. From the difference in enthalpies the duty of this heater (E06) has been calculated.

MEA cooler

From this regeneration the bottom stream (<602>) needs to be cooled down to be suitable again for carbon dioxide absorption. The stream is pumped with P12 and is cooled down with a cooler (E07). The duty has been calculated by the difference in enthalpies.

Bromine strippper

The stream, which is now cleansed of carbon dioxide, (<604>) is sent to a bromine stripper unit (CO3). Bromine is stripped from the top and at the bottom quite a large stream containing water and hydrogen bromide (<701>) is sent to an electrolysis cell with pump P13. The mass balance calculations come from Jurre. The stripping unit needs some heating. This is done by heat exchanger E08. The duty of this heater is calculated by the difference in enthalpy of the in- and outgoing streams.

Electrolysis cell

In the electrolysis cell (SO4) a water and hydrogen bromide mixture enters the cell. Hydrogen bromide is partially converted into bromine and hydrogen. The hydrogen gas comes out of the cell and is used in a fuel cell for electricity production. The cell now contains a mixture of water, bromine and hydrogen bromide, which is sent back to the stripping unit where bromine can be stripped of again. The data on mass balances comes from mark 13 article jurre?. The heat balance is calculated by the difference in enthalpies.

Bromine condenser

The top from the bromine stripper is condensed in a heat exchanger E09 to remove water from the stream. The water is sent back to the stripper and the bromine is recycled to the reaction section.

MEA absorber

The flue gas stream that has been cleansed of sulphur dioxide can now be reduced on carbon dioxide content. The specification for which the scrubbing unit (CO4) will be designed is a 6 % carbon dioxide removal. From Ciferno article has been calculated how much MEA is needed to remove the desired amount of carbon dioxide. The streams entering the absorber need to be around 330 K for the carbon dioxide to be absorbed by the MEA. For the mass balance a comparison with the Ciferno article has been made to determine the size of all streams entering and leaving the absorber. The heat balance is based on the enthalpies of incoming and outgoing streams and for this unit it appears to be correct.

MEA heat exchanger

From the MEA absorber comes a cold MEA stream, which needs to be heated up in order to have the carbon dioxide released from the stream. From the MEA regenerator comes a hot stream, which needs to be cooled to be put back into the MEA absorber. Therefore these streams are heat exchanged in a heat exchanger (E11). The mass streams entering will leave the exchanger at the same size since mass is not contacted. The streams entering the heat exchanger are approximately of the same size and the heat capacity is considered to be very much constant over that temperature range. The cold stream will therefore be heated with 25 K and the hot stream cooled down with the same temperature difference. The temperature difference between the leaving streams is 12 K, which is acceptable. The heat balance is almost correct and therefore can be concluded that the assumption that the heat capacity is constant is valid. So for this unit can be concluded that the heat balance is right.

MEA regenerator

In the MEA regenerator (C05) the MEA stream needs to be heated to release carbon dioxide from the MEA. A heater performs this heating of the MEA stream. The duty of this heater is calculated from the enthalpy difference of the in- and outgoing streams. Because of the heat exchanging (E11) this heater has a significantly lower duty and this heat exchangers makes sure the costs for utilities are substantially lower. The mass and heat balances appear to be correct.

MEA cooler

After the hot MEA stream has been heat exchanged it has to be further cooled to be suitable for putting back into the MEA absorber. Because it has been heat exchanged the cooling costs are substantially lower. The duty of the cooler (E14) has been determined by comparing the enthalpy of the ingoing stream with the enthalpy of the outgoing stream.

Carbon dioxide cooler

It is possible that some of the water or MEA in the MEA regenerator unit evaporates and contaminates the carbon dioxide stream. To avoid this from happening a condenser (E12) is put on the top of the MEA regenerator. Any water or MEA will condense and is sent back into the regeneration unit. From the collection vessel (V07) the carbon dioxide stream is ready to be mixed with the other carbon dioxide stream. It is substantially cooled which makes it easier for handling this stream if it needs to be compressed. The duty of the condenser is calculated by the comparison of the enthalpies.

Carbon dioxide

The carbon dioxide coming from the membrane unit and the carbon dioxide from the MEA scrubbing units are added together and are then able to leave the system. The mass balance is a simple adding up pure carbon dioxide streams. Further compressing the carbon dioxide might be necessary but is beyond the scope of this project. For the heat balance the enthalpies of the streams are simply added and this seems to be correct.

19Process Control

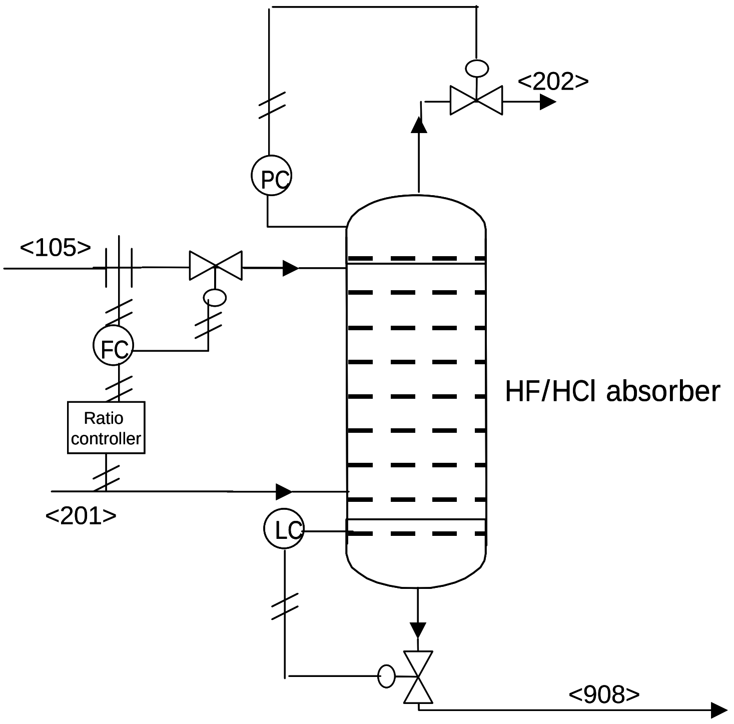


Figure 19-1: HF /HCL Absorber control configuration

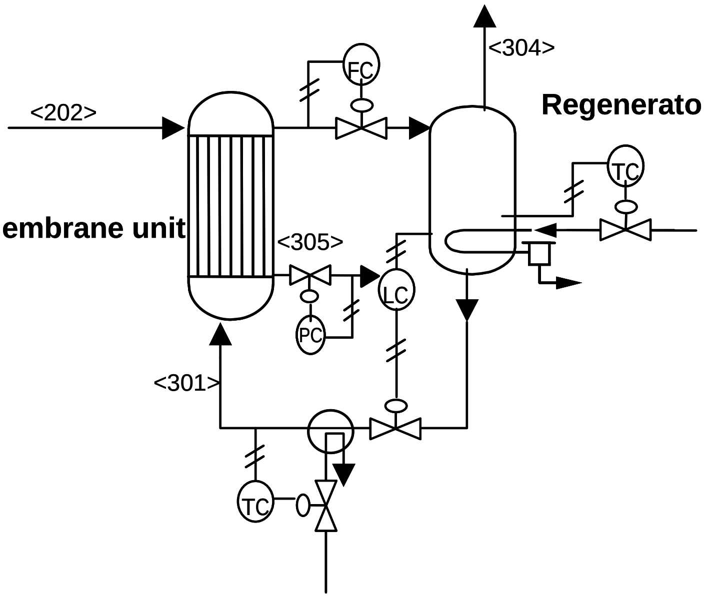


Figure 19-2: Configuration of a membrane unit with absorbent regeneration

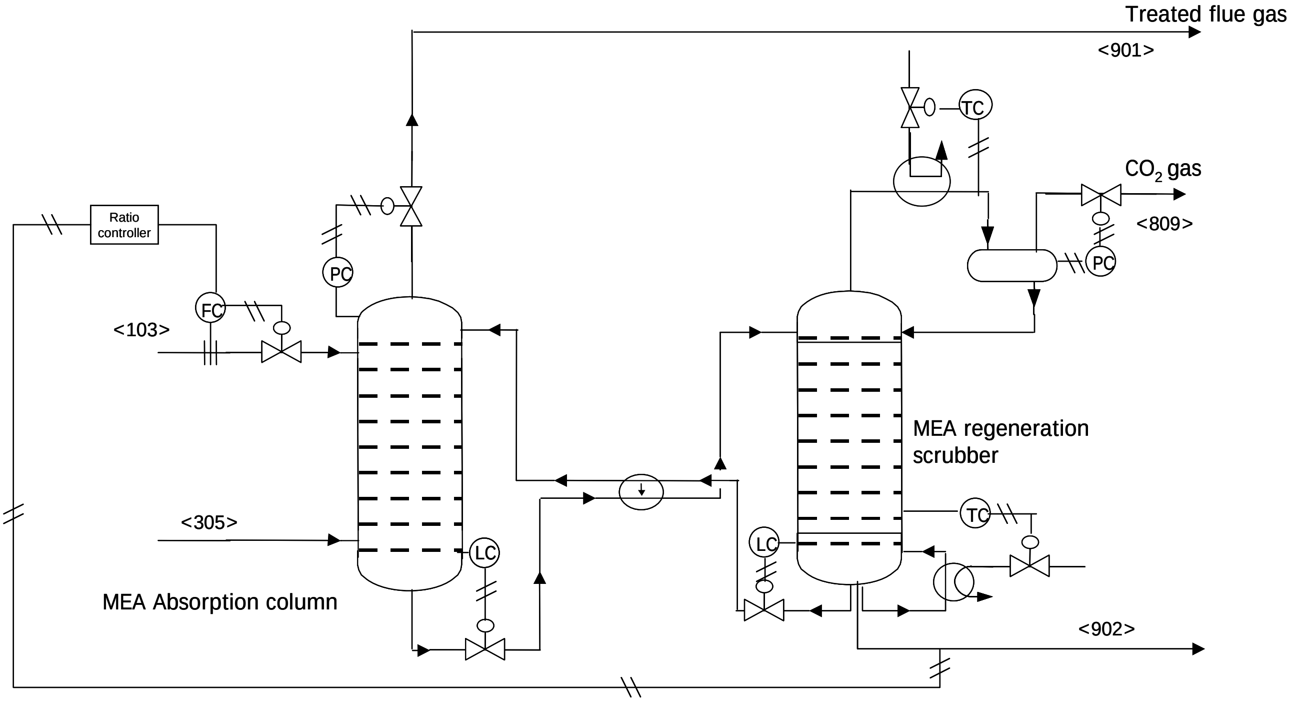


Figure 19-3: MEA absorption and MEA scrubber control

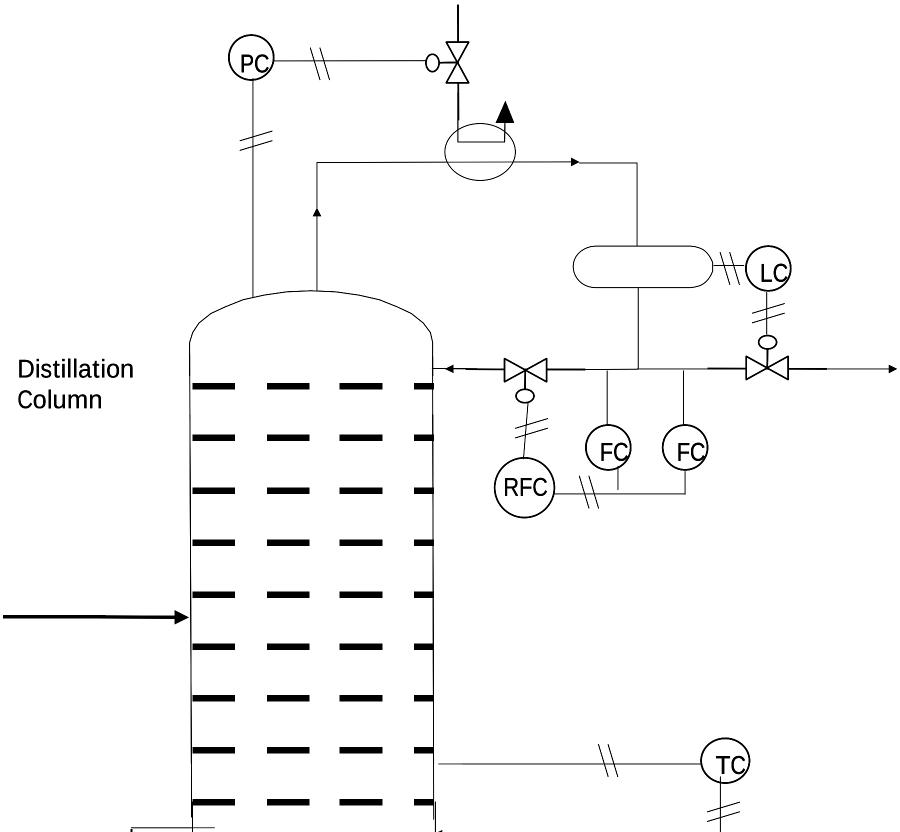


Figure 19-4: Distillation column control

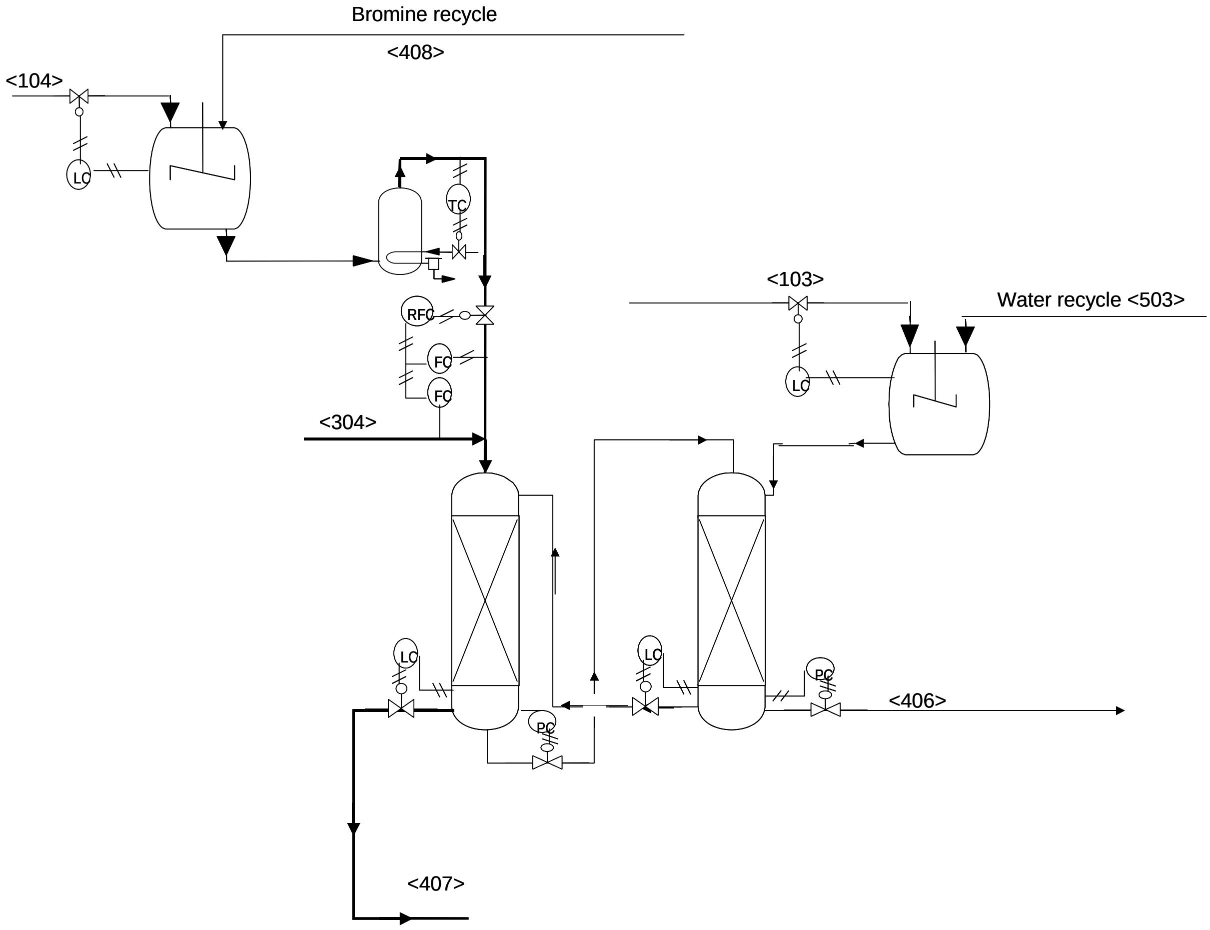


Figure 19-5: Process control configuration of the reaction section

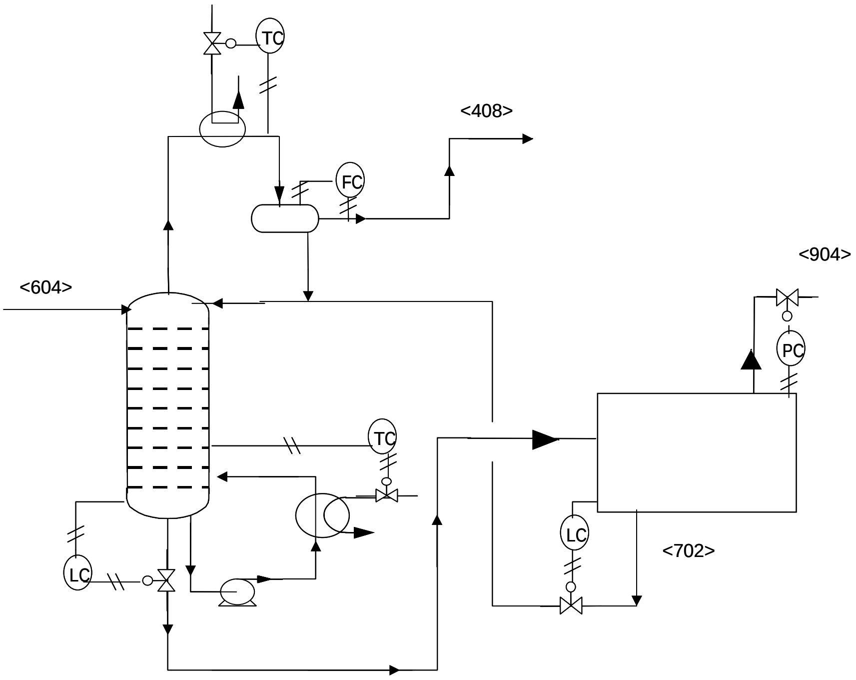


Figure 19-6: Control configuration for the bromine stripper and electrolysis cell

20Process Equipment

20.1 Fly Ash Removal Possibilities

Table 20-1: Composition of fly ash [1]

Major elements	(%)	Trace elements	(mg/kg)
SiO_2	*46.9*	As	*27.7*
TiO_2	*0.2*	B	*308*
Al_2O_3	*24.9*	Ba	*2166*
Fe_2O_3	*8.8*	Co	*66.1*
MnO	*0.1*	Cr	*154*
MgO	*3.8*	Cu	*214*
CaO	*6.9*	Mo	*11.2*
K_2O	*2.1*	Ni	*138*
Na_2O	*1.2*	Pb	*126*
P_2O_5	*0.7*	Sb	*16.1*
SO_3	*1*	Se	*16.1*
LOI	*1.6*	V	*320*
		Zn	*217*

20.1.1 Wet scrubbers

Wet scrubbers use liquid to collect the particulates. The scrubbing liquid (usually water) is brought in contact with a gas stream containing dust or fly ash. Removal efficiencies depend on the contact of the gas and liquid streams, the better the contact the higher the efficiency. The cleaned gases pass through a demister to remove water droplets from the gas stream. The dirty water from the scrubber could be cleaned and discharged or recycled to the scrubber. Fly ash is removed from the scrubber in a so-called clarification unit or a drag chain tank. In both systems solid materials settle on the bottom of the tank. In Figure 20-1 a schematic representation of a wet scrubber is given.

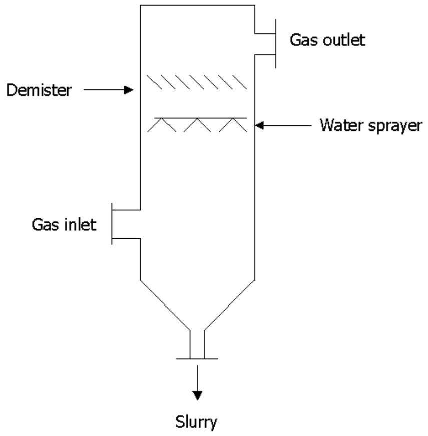


Figure 20-1: Wet scrubber

There is a large variety of wet scrubbers, but it is beyond the scope of this project to describe them all individually. The advantages and disadvantages of wet scrubbers are given in Table 20-2, whereas the common operating problems and solution are given in Table 20-3.

Table 20-2: Advantages and disadvantages of wet scrubbers

Advantages	Disadvantages
Low capital costs and small space requirements	High operating and maintenance costs
Can treat high-temperature and high-humidity gas streams	Require corrosion-resistant materials if used with acidic gases
Collects gases as well as (sticky) particulates	Require precleaner for heavy dust loadings
	Cause water pollution
	Susceptible to erosion at high velocities
	Require freeze protection

Table 20-3: common operating problems and solutions of wet scrubbers

Problem	Solution
Wet/dry build up	**- Keep all areas dry or all areas flooded** - The scrubber should be installed vertically
Dust build up in fan	Install clean water spray at fan inlet

20.1.2 Fabric collectors

Fabric collectors are usually called baghouses see Figure 20-2. The separation process is based on filtration of particulates from dusty gases. They are one of the most efficient and cost effective types of dust collectors and can achieve a collection efficiency of more than 99% for very fine particulates. Dusty gases enter the baghouse and pass through fabric bags that act as filters. The bags are made of woven cotton, synthetic, or glass-fibre material. The high efficiency is due to the dust layer formed on the surfaces of the bags. Also here we limit us to the main features of the baghouse collectors without getting into the details about the mechanisms playing a role and the different types.

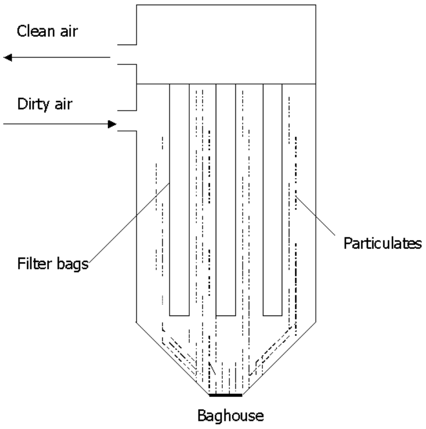


Figure 20-2: Baghouse

The main advantages and disadvantages of baghouses are set in Table 20-4, while the common operating problems and solutions are mentioned in Table 20-5.

Table 20-4: Advantages and disadvantages of baghouses

Advantages	**Disadvantages**
Have high collection efficiency for respirable dust	May not be used at high temperature unless special fabrics are used
Have low pressure drop for equivalent collection efficiency.	Cannot be used if high moisture content levels are present in the exhaust gases
Simple to operate	Require personnel to enter baghouse and replace bag, which can contain toxic dust
Can clean continuously	May consist of many moving parts and require frequent maintenance
	Need large number of filter bags
	Can result in reduced cleaning efficiency if even a slight positive pressure exist inside bags
	Have low air-to-cloth ratio (1.5-2 ft/min)

Table 20-5: Common problems and solutions for baghouses

Symptom	Cause	Solution
High baghouse pressure drop	Baghouse undersized	- Install double bags - Add more compartments
	Not capable of removing dust from bags	- Check for condensation on bag - Dryclean or replace bags - Reduce airflow
Dirty discharge at stack	Bags leaking	- Replace bags - Tie off leaking bags and replace them later
High rate of bag failure, bags wearing out	Cleaning cycle too frequent	Slow down cleaning
	Too much dust	Install primary collector

20.1.3 Electrostatic Precipitator

A typical ESP is depicted in Figure 20-3.

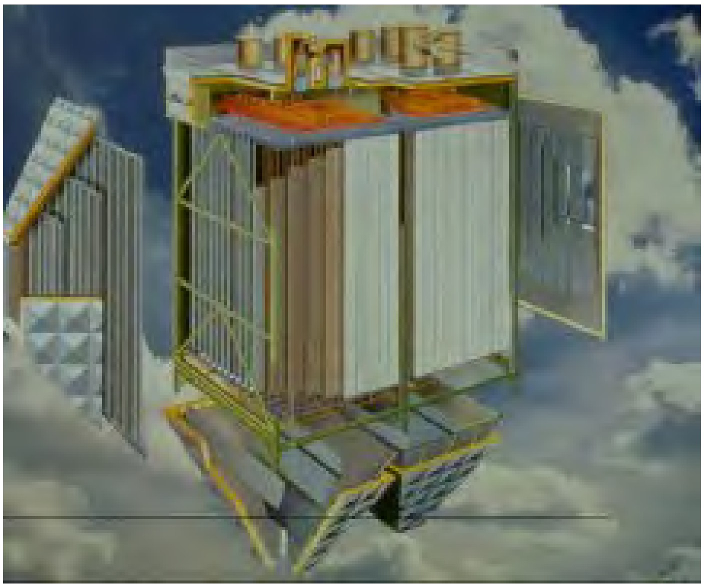


Figure 20-3: Electrostatic precipitator [4]

A schematic of the collecting plates and the discharging electrodes of the plate-type ESP is depicted in Figure 20-4.

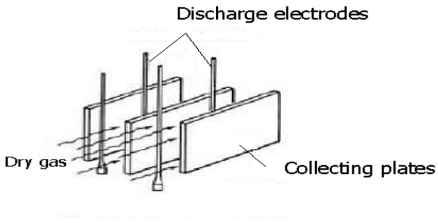


Figure 20-4: Plate-Type precipitator [2]

The collection efficiency is affected by the following factors:

- Larger collection-surface area and lower gas-flow rates extend the residence time of the particles in the ESP increasing the electrical activity to remove the particles.
- Resistivity of the particles to be collected
    - Particles with a moderate resistivity (107-1010ohm-cm) are more easily removed because they are easily charged and slowly loose their charge once deposited on the collecting electrode. Particles with less resistivity loose their charge so rapidly that they do not adhere to the collector, on the other hand particles with high resistivity (greater than 1010 ohm-cm) are not easily charged and are difficult to remove by ESP
- An increase in the fly ash particle migration velocity to the collecting electrodes increases efficiency. The migration velocity could be increased by:
    - Decreasing the gas viscosity
    - Increasing the gas temperature

Increasing the voltage field

Table 20-6: Advantages and Disadvantages of electrostatic precipitators

Advantages	Disadvantages
Collection efficiency can exceed 99.9% for all particulates, including sub-micron particles	High initial investments costs
Collect dust by dry methods	Require highly skilled maintenance personnel
Have lower pressure drop and therefore lower operating costs	Risk of explosion when gas stream contains combustibles
Can operate at high temperatures and in colder climates	Do not respond well to process changes such as gas temperature, gas pressure, gas flow rate, particulate size distribution, gaseous or chemical composition, dust loading
Increase in collection efficiency allowed by increasing ESP size	
Require little power	
Can effectively handle relatively large gas flows (up to $3.5*10^6\ m^3/h$)	
Smaller spare parts costs	
Minimal maintenance requirements	

Table 20-7: Comparison of dust collector characteristics [2]

Device	To control particles greater than (μm)	Pressure drop (Pa)	Water usage (gal/min per $1000ft^3/min$)	Humid air influence	Space requirements	Max. Temperature (1) (°C)	Costs (ft^3/min)
Precipitator	*0.25*	*125*	-	Improve efficiency	Large	*650*	*$0.4-$1.00*
Cyclone	*20-40*	*188-375*	-	May cause condensation and plugging	Large	*400*	*5c-25c*
Shaker baghouse	*0.25*	*750-1250*	-	May make bag cleaning difficult	Large	*82-135*	*30c-$2.50*
Reverse-air baghouse	*0.25*	*750-1500*	-	May make bag cleaning difficult	Moderate	*288*	*30c-$2.50*
Reverse-jet baghouse	*0.25*	*750-2000*	-	May cause bag to blind	Large	*82-135*	*30c-$2.50*
Low-energy scrubber (e.g. centrifugal collector)	*25*	*125-625*	*5*	None	Large	*Unlimited*	*25c-75c*
Low- to medium energy scrubber (e.g. spray tower)	*1-5*	*625-1500*	*3-5*	None	Moderate	*Unlimited*	*25c-75c*
Medium- to high energy scrubber (e.g. packed bed)	*1-5*	*625-3750*	*5-10*	None	Large	*Unlimited*	*25c-75c*
High-energy scrubber (e.g. venture)	*0.5-2*	*3750 and greater*	*5-15*	none	Moderate	*Unlimited*	*25c-75c*

Notes (1) Based on standard construction
(2) Costs based on collector section only, does not include ducting, water and power requirements.
Cost figures should be used only for comparison only. Actual costs may vary.

20.2 Acid Gas Scrubber and Regenerator

Table 0-1: Advantages and disadvantages of wet scrubber to remove HF and HCl [1]

Advantage	**Disadvantage**
Relatively small space requirements	Waste stream
Low capital costs	
Able to process high temperature, acidity and humidity flue gas streams	
Costs are decreasing leading to lower operating costs	
Multi-pollutant control approach	
Low energy costs	
Removes up to 97% of HF and HCl	

The height is defined by:

$$H = \frac{2.3 \cdot N}{E_0} \quad \text{(H2-1)}$$

With H is the height of the tower in [ft], N is the number of trays and E_0 is the efficiency. We include the space at the ends of the column for vapor disengagement and the liquid sump to be *15%.* The efficiency is taken to be *0.5*, which is conservative design estimate for atmospheric columns. The absorber with 6 trays gives a height of *27.6ft* or *8.4m*. The tower cross-sectional area is calculated using the following equation:

$$A_T = \frac{V / \rho_m}{1.5 \cdot (3600) \cdot \sqrt{M_G \rho_m}} \quad \text{(H2-2)}$$

With A_T is the cross-sectional area of the tower in [ft^2], V is the molar rate in [mol/h], P_m is the molar density in [mol/m^3] and M_G is the molecular weight of distillate in [g/mol]. This gives a cross-sectional area of *63.4* ft^2. The tower diameter can now simply be calculated by:

$$D_T = \left(\frac{4 \cdot A_T}{\pi} \right)^{1/2} \quad \text{(H2-3)}$$

This results in D_T = *9ft*, which is equal to *2.75m*

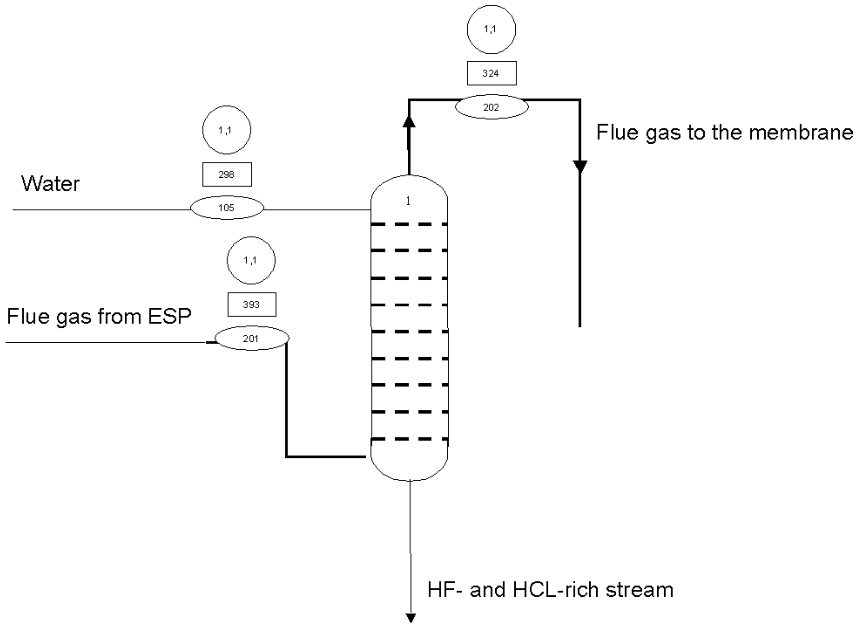


Figure 0-1: HF-HCl absorber

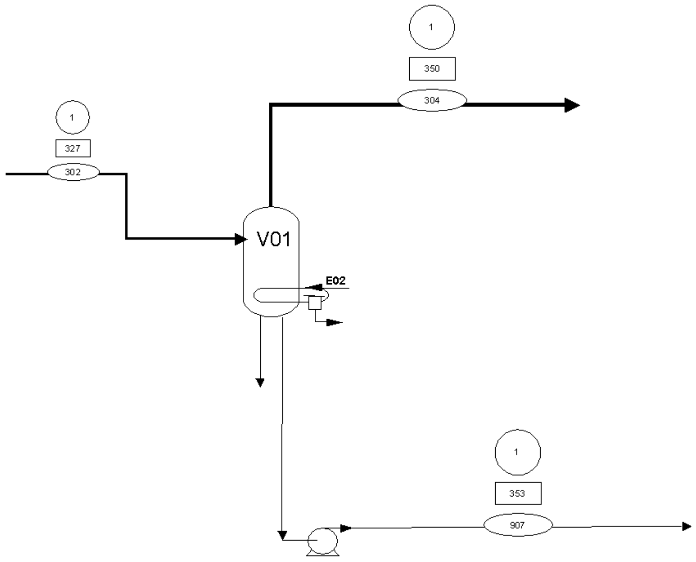


Figure 0-2: Na_2SO_3 regenerator

20.3 Membranes

Table 0-2: Main advantages and disadvantages of membranes

Advantages	Disadvantages
Large surface area	Surface area is more expensive than packed column
No flooding	
Laminar flow	
Higher selectivity	
Selective towards more components	

Table 0-3: Advantages and disadvantages of membranes with alkanolamine

Advantages	Disadvantages
High absorption capacity	High energy requirements for regeneration
High absorption rate	Corrosive
High reaction rate towards CO_2	Degradation at high temperature or when is contacted to oxygen except when inhibitors are used
	Expensive

20.4 SO_2 Reaction Section

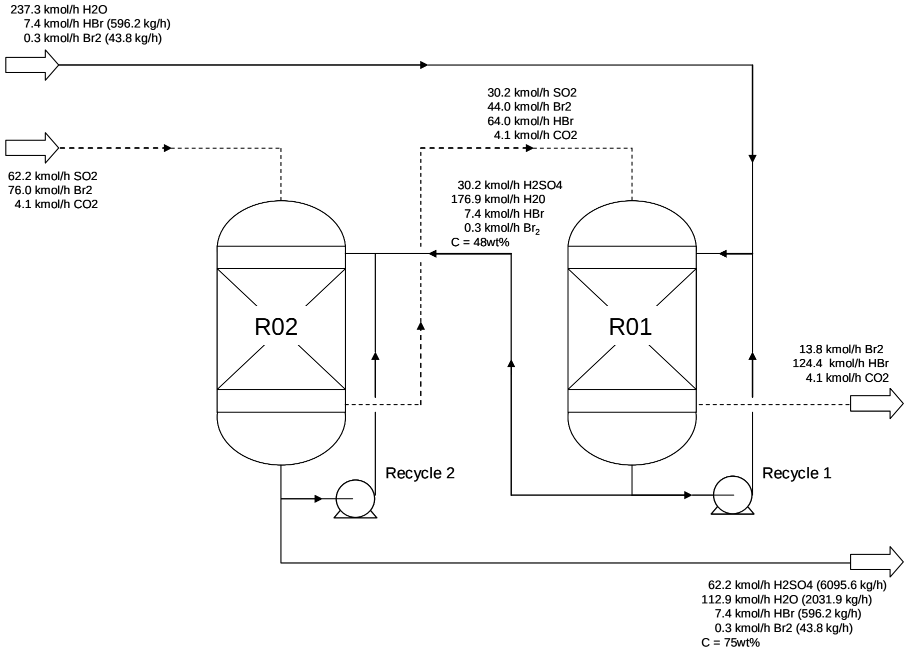


Figure 0-3: Schematic representation of the conversion section

A schematic drawing of the cell that performed best and is used in the conceptual design is shown in Figure 0-4.

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{1}{K_1 (0.82 - C)^2}$$

$$K_g a = 78.8 kmol \cdot m^{-3} \cdot h^{-1}$$

$$N_{og} = \frac{K_g azAP}{G}$$

$$N_{og} = 10.7$$

$$N_{og} = \ln \frac{(21.2 - Y_{eq})_{in}}{(Y - Y_{eq})_{out}}$$

$$Y_{out} = 0.0005\%$$

Resulting in an overall conversion of >>99.99%.

Table 0-4: Viscosities of gas components in the reactors

Viscosity μ / [Pa s]	
SO_2	*1.16E-05*
$C0_2$	*1.37E-05*
HBR	*1.71E-05*
BR_2	*1.24E-05*
Average	*1.37E-05*

20.5 H_2SO_4 Concentration Section

The number of actual stages is calculated from equation L-1.

$$N_{act} = \frac{N}{E_0} \tag{H5-1}$$

Where N_{act} is the actual number of trays, N is the theoretical number of trays and E_0 is the plate efficiency, which is *0.5* as stated in Douglas. The height of the column (H_{C02}) is calculated from equation 8-14. The tray spacing is chosen to be *0.6m* instead of the *2ft* used in Douglas, hence;

$$H_{C02} = \frac{0.6N}{E_0} + H_0 \tag{H5-2}$$

Above and below the trays extra space is added for the vapour disengagement and the liquid sump. Therefore the term H_0 is added and is estimated to be *1.5m* at the top of the column. The liquid sump should be able to hold a supply of liquid product for around 15 minutes. From the product flow rate and the hold-up time the height of the sump can be calculated. The cross sectional area of the column (A_{C02} in [units]) is calculated form equation 8-15.

$$A_{C02} = \frac{V\sqrt{M_G / \rho_m}}{0.88 \cdot 1.5 \cdot 3600} \tag{H5-3}$$

Where V is the molar flow rate of vapour [units], M_G is the average molar mass of the vapour [units] and ρ_G is the molar density of the vapour [units].

Table 0-5: Stream summary of H_2SO_4 concentration unit

Stream Summary			
	Feed	Distillate	Product
Temperature [^oC]	*77*	*108*	*305*
Phase	*Liquid*	*Liquid*	*Liquid*
Total mole flow [kmol/h]	*182.5*	*100*	*82.5*
Total mass flow [kg/h]	*8733*	*2267*	*6466*
		Composition [kmol/h]	
Water	*112.9*	*92.6*	*20.3*
H_2SO_4	*62.2*	*TRACE*	*62.2*
HBr	*7.4*	*7.4*	*0.0001*
Pressure [bar]	*1.1*	*1*	*1*

20.6 Bromine Electrolysis

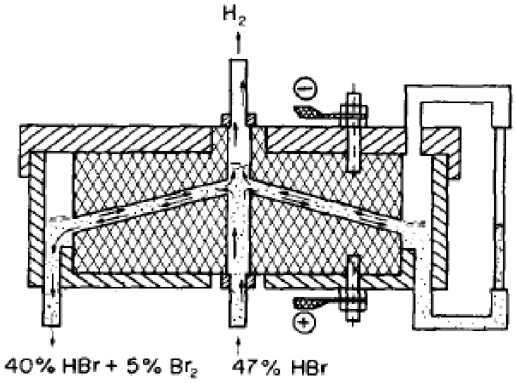


Figure 0-4: Schematic drawing of the HBr electrolysis cell

21Column Specification Sheets

Column - Specification Sheet

EQUIPMENT NUMBER : C01
NAME : HF/HCl absorption

General Data

Service		:	~~distillation~~ /	~~extraction~~ /	absorption /	reaction	
Column Type		:	~~packed~~ /	tray /	spray /		
Tray Type		:	~~cap~~ /	sieve /	~~valve~~ /		
Tray Number		:					
	Theoretical	:	6				
	Actual	:	12				
	Feed	:	12				
Tray Distance (HETP)	[m]	:	N/A	Tray Material	:	SS	(1)
Column Diameter	[m]	:	2.75	Column Material	:	SS	(1)
Column Height	[m]	:	8.4				
Heating		:	none	~~open steam~~	~~reboiler~~		

Process Conditions

Stream Details			Feed <201>		Feed <105>		Product <202>		Product <908>	
Temp	[oC]	:	120		25		51		51	
Pressure	[bara]	:	1.1		1.1		1.1		1.1	
Density	kg/m3	:	N/A		N/A		N/A		N/A	
Mass Flow	kg/h	:	1.96E+6		72E+3		2.01E+6		7056	
Mole Flow	kmol/h	:	65.77E+3		4E+3		69.41E+4		396	
Phase		:	G		L		G		L	
Composition			mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%
Nitrogen			75.04	70.96			71.11	68.66	0.00	3.9655E-04
Carbon dioxide			12.917	19.22			12.24	18.6	0.00	4.9849E-03
Sulphur dioxide			0.11	0.207			0.1037	0.2	0.00	1.8145E-03
Oxygen			4.89	5.4			4.72	5.22	0.00	0.0000E+00
Water			6.9	4.19	100	100	11.46	7.31	95.71	9.2206E+01
Hydrogen chloride			0.021	0.026					3.62	7.0792E+00
Hydrogen fluoride			0.0038	0.00185					0.66	7.0792E-01

Column Interals

Trays					**Packing**	N/A	
Number of					Type		:
	~~caps~~ /	sieve holes		:	Material		:
Active Tray Area		3.5	[m2]	:	Volume	[m3]	:
Weir Length		N/A	[mm]	:	Mass	[kg]	:
Diameter of		N/A			Width	[m]	:
	~~chute pipe~~	hole		:	Height	[m]	:
			[mm]				

Remarks

(1) Stainless Steel

Designers:	Alberts, J.	Tange, C.	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.	Date:	6-12-05
	Gastel, H. van			

Column - Specification Sheet

EQUIPMENT NUMBER	:	C02
NAME	:	H_2SO_4 conectration Column

General Data

Service		:	distillation /	~~extraction~~ /	~~absorbtion~~ /	~~reaction~~		
Column Type		:	~~packed~~ /	tray /	~~spray~~ /			
Tray Type		:	~~cap~~ /	~~sieve~~ /	~~valve~~ /			
Tray Number		:	N/A					
	Theoretical	:	4					
	Actual	:	8					
	Feed	:	2	(Above)				
Tray Distance (HETP)	[m]	:	0.6	Tray Material		:	SS	(1)
Column Diameter	[m]	:	1.29	Column Material		:	SS	(1)
Column Height		:	7.2					
Heating		:	~~none~~	~~open steam~~	reboiler			

Process Conditions

Stream Details			Feed 1		Distillate		Bottom Product	
Temp	[^{o}C]	:	77		108		305	
Pressure	[bara]	:	1.1		1		1	
Density	kg/m3	:	1700		1234		1448	
Mass Flow	kg/h	:	8775.2		2314.2		6461	
Mole Flow	kmol/h	:	182.8		100.3		82.5	
Phase		:	L		L		G	
Composition			mol%	mol%	wt%	wt%	mol%	wt%
Bromine			0.2	0.5	0.3	0.2		
Hydrogen bromide			4	6.8	7.4	25.8		
Water			61.8	23.2	92.3	72.0	24.6	5.7
Sulpuric Acid			34	69.5			75.4	94.3

Column Interals

Trays			Not Known		**Packing**		Not Applicable
Number of					Type		:
	caps /	sieve holes /		:	Material		:
Active Tray Area			[m2]	:	Volume	[m3]	:
Weir Length			[mm]	:	Mass	[kg]	:
Diameter of					Width	[m]	:
	chute pipe	/ hole /	[mm]	:	Height	[m]	:

Remarks

(1) Stainless Steel

Designers:	Alberts, J.	Tange, C.	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.	Date:	6-12-05
	Gastel, H. van			

Column - Specification Sheet

EQUIPMENT NUMBER : C03
NAME : Br_2 Stripping/HBr Absorbing Column

General Data

Service : ~~distillation~~ / ~~extraction~~ / absorbtion / stripping
Column Type : packed / ~~tray~~ / ~~spray~~ /
Tray Type : ~~cap~~ / ~~sieve~~ / ~~valve~~ /
Tray Number : N/A
Theoretical :
Actual :
Feed : (Above)
Tray Distance (HETP) [m] : Tray Material : SS (1)
Column Diameter [m] : Column Material : SS (1)
Column Height :
Heating : ~~none~~ ~~open steam~~ reboiler

Process Conditions

Stream Details			Feed 1		Feed 2		Bottom Product		Top Product	
Temp	[^{o}C]	:	40				130		55	
Pressure	[bara]	:	1.1		1		1		1	
Density	kg/m3	:								
Mass Flow	kg/h	:	12284.4		215786.5		251910.9		10526.2	
Mole Flow	kmol/h	:	138.2		9034.6		9096.8		92	
Phase		:	G		L		L		G	
Composition			mol%	mol%	wt%	wt%	mol%	wt%	mol%	wt%
Bromine			10.0	18.0	0.7	4.0			67.6	94.5
Hydrogen bromide			90.0	82.0	14.1	41.0	15.4	45.0	6.5	0.5
Water					85.2	55.0	84.6	55.0	31.7	5.0
Sulpuric Acid										

Column Interals

Trays Not Known
Number of
caps / sieve holes / :
Active Tray Area [m2] :
Weir Length [mm] :
Diameter of
chute pipe / hole / [mm] :

Packing
Type : Rashig rings 5mm
Material :
Volume [m3] : 6.8
Mass [kg] :
Width [m] :
Height [m] :

Remarks

(1) Stainless Steel

Designers:	Alberts, J.	Tange, C.	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.	Date:	6-12-05
	Gastel, H. van			

Column - Specification Sheet

EQUIPMENT NUMBER		:	C04
NAME		:	MEA/CO_2 Absorber

General Data

Service		:	~~distillation /~~	~~extraction /~~	absorption /	reaction	
Column Type		:	packed /	~~tray /~~	~~spray /~~		
Tray Type		:	~~cap /~~	~~sieve /~~	~~valve /~~		
Tray Number		:	N/A				
	Theoretical	:					
	Actual	:					
	Feed	:					
Tray Distance (HETP)	[m]	:		Tray Material	:		
Column Diameter	[m]	:		Column Material	:	SS	(1)
Column Height	[m]	:					
Heating		:	none	~~open steam~~	~~reboiler~~		

Process Conditions

Stream Details			Feed <102>		Feed <305>		Product <901>		Product <801>	
Temp	[oC]	:	25		54		54		79	
Pressure	[bara]	:	1		1		1		1	
Density	kg/m3	:	N/A		N/A		N/A		N/A	
Mass Flow	kg/h	:	N/A		2.01E+6		1.822E+6		2.0E+6	
Mole Flow	kmol/h	:	N/A		69336		65088		82224	
Phase		:	L		G		G		L	
Composition			mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%
Nitrogen					71.20	68.81	75.86	75.88	0.00	0.00
Carbon dioxide					12.26	18.62	6.53	10.27	7.18	12.97
Sulphur dioxide					0.00	0.00	0.00	0.00	0.00	0.00
Oxygen					4.74	5.23	5.05	5.77	0.00	0.00
Water				70	11.79	7.33	12.57	8.08	82.40	60.92
Hydrogen chloride										
Hydrogen fluoride										
Bromine										
Hydrogen bromide										
Sulphuric Acid										
Hydrogen										
MEA				30					10.42	26.09
MEA CO2salt										0.02

Column Interals

Trays					**Packing**			
	Not Applicable							
Number of					Type		:	CMR (2)
	caps /	sieve holes /		:	Arrangement			Random
Active Tray Area			[m2]	:	Packing specific surface area	m^2/m^3	:	144.0
Weir Length			[mm]	:	Void fraction		:	0.971
Diameter of					Diameter	[m]	:	9.8
	chute pipe	/ hole /	[mm]	:	Height	[m]	:	15

Remarks

(1) Stainless Steel

(2) Cascade Mini Rings

Designers:	Alberts, J.	Tange, C.	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.	Date:	6-12-05
	Gastel, H. van			

Column - Specification Sheet

EQUIPMENT NUMBER : C05
NAME : CO_2/MEA stripper

General Data

Service		:	~~distillation /~~	~~extraction /~~	~~absorption /~~	~~reaction~~	stripping
Column Type		:	packed /	~~tray /~~	~~spray /~~		
Tray Type		:	~~cap /~~	~~sieve /~~	~~valve /~~		
Tray Number		:	N/A				
	Theoretical	:					
	Actual	:					
	Feed	:					
Tray Distance (HETP)	[m]	:		Tray Material	:		
Column Diameter	[m]	:		Column Material	:	SS	(1)
Column Height	[m]	:					
Heating		:	~~none~~	~~open steam~~	reboiler		

Process Conditions

Stream Details			Feed <802>		Feed <808>		Product <803>		Product <902>	
Temp	[oC]	:	79		116		91		116	
Pressure	[bara]	:	1		1		1		1	
Density	kg/m3	:	N/A		N/A		N/A		N/A	
Mass Flow	kg/h	:	2.0E+6		259632		1.8E+6		1116	
Mole Flow	kmol/h	:	82224		5904		77940		36	
Phase		:	L		L		L		L	
Composition			mol%	wt%	mol%	wt%	mol%	w%	mol%	wt%
Nitrogen										
Carbon dioxide			7.18	12.97	100	100	2.12	4.00		
Sulphur dioxide										
Oxygen										
Water			82.40	60.92			86.89	67.20	88.77	57.55
Hydrogen chloride										
Hydrogen fluoride										
Bromine										
Hydrogen bromide										
Sulphuric Acid										
Hydrogen										
MEA			10.42	26.09			10.99	28.80		
MEA CO2salt			0.01	0.02					11.23	42.45
Na_2SO_3										
$NaHSO_3$										
NaHCO3										
Flyash										

Column Interals

Trays			Not Applicable		**Packing**			
Number of					Type		:	CMR (2)
	caps /	sieve holes /		:	Packing arrangement			Random
Active Tray Area			[m2]	:	Diameter	[m]	:	5.5
Weir Length			[mm]	:	Height	[m]	:	9.6
Diameter of								
	chute pipe	/ hole /	[mm]	:				

Remarks

(1) Stainless Steel
(2) Cascade mini rings

Designers:	Alberts, J.	Tange, C.	Gastel, H. van	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.		Date:	6-12-05

Column - Specification Sheet

EQUIPMENT NUMBER	:	R01
NAME	:	Trickle bed reactor 1

General Data

Service		:	~~distillation~~ /	~~extraction~~ /	~~absorbtion~~ /	reaction		
Column Type		:	packed /	~~tray~~ /	~~spray~~ /			
Tray Type		:	~~cap~~ /	~~sieve~~ /	~~valve~~ /			
Tray Number		:	N/A					
	Theoretical	:						
	Actual	:						
	Feed	:						
Tray Distance (HETP)	[m]	:	N/A	Tray Material		:	SS	*(1)*
Column Diameter	[m]	:	2.11	Column Material		:	SS	*(1)*
Column Height		:	7.87					
Heating		:	none	~~open steam~~	~~reboiler~~			

Process Conditions

Stream Details			Feed 1		Feed 2		Product 1		Product 2	
Temp	[oC]	:								
Pressure	[bara]	:	1.1				1.1			
Density	kg/m3	:								
Mass Flow	kg/h	:	14330.8		4911.4		12464.8		6783.8	
Mole Flow	kmol/h	:	142.3		245		142.3		214.8	
Phase		:	G		L		G		L	
Composition			mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%
Sulphur dioxide			21.2	13.5						
Bromine			30.9	49.1	0.1	0.9	9.7	17.7	0.1	0.6
Hydrogen bromide			45.0	36.2	3.0	12.1	87.4	80.8	3.4	8.8
Carbon dioxide			2.9	1.3			2.9	1.4		
Water					96.9	87.0			82.4	46.9
Sulpuric Acid									14.1	43.6

Column Interals

Trays		Not Applicable			**Packing**			
Number of					Type		:	Raschig rings 5mm
	caps /	sieve holes /		:	Material		:	
Active Tray Area			[m2]	:	Volume	[m3]	:	20.55
Weir Length			[mm]	:	Mass	[kg]	:	18491
Diameter of					Width	[m]	:	2.11 *(2)*
	chute pipe /	hole /	[mm]	:	Height	[m]	:	5.87

Remarks

(1) Stainless Steel

(2) Diameter of packed bed

Designers:	Alberts, J.	Tange, C.	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.	Date:	6-12-05
	Gastel, H. van			

Column - Specification Sheet

EQUIPMENT NUMBER	:	R02
NAME	:	Trickle bed reactor 2

General Data

Service		:	~~distillation~~ /	~~extraction~~ /	~~absorbtion~~ /	reaction		
Column Type		:	packed /	~~tray~~ /	~~spray~~ /			
Tray Type		:	~~cap~~ /	~~sieve~~ /	~~valve~~ /			
Tray Number		:	N/A					
	Theoretical	:						
	Actual	:						
	Feed	:						
Tray Distance (HETP)	[m]	:	N/A	Tray Material	:	SS	(1)	
Column Diameter	[m]	:	2.11	Column Material	:	SS	(1)	
Column Height		:	7.87					
Heating		:	none	~~open steam~~	~~reboiler~~			

Process Conditions

Stream Details			Feed 1		Feed 2		Product 1		Product 2	
Temp	[oC]	:					77		77	
Pressure	[bara]	:	1.1				1.1		1.1	
Density	kg/m3	:							1700	
Mass Flow	kg/h	:	16321.2		6783.8		14330.8		8775.2	
Mole Flow	kmol/h	:	142.3		214.8		142.3		182.8	
Phase		:	G		L		G		L	
Composition			mol%	wt%	mol%	wt%	mol%	mol%	mol%	wt%
Sulphur dioxide			43.7	24.4		0.2	0.5	13.5		
Bromine			53.4	74.5	0.1	4	6.8	49.1	0.2	0.5
Hydrogen bromide					3.4	61.8	23.2	36.2	4	6.8
Carbon dioxide			2.9	1.1		34	69.5	1.3		
Water					82.4	46.9			61.8	23.2
Sulpuric Acid					14.1	43.6			34	69.5

Column Interals

Trays		Not Applicable			**Packing**			
Number of					Type		:	Raschig rings 5mm
	caps /	sieve holes /		:	Material		:	
Active Tray Area			[m2]	:	Volume	[m3]	:	20.55
Weir Length			[mm]	:	Mass	[kg]	:	18491
Diameter of					Width	[m]	:	2.11 *(2)*
	chute pipe	/ hole /	[mm]	:	Height	[m]	:	5.87

Remarks

(1) Stainless Steel

(2) Diameter of packed bed

Designers:	Alberts, J.	Tange, C.	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.	Date:	6-12-05
	Gastel, H. van			

Column - Specification Sheet

EQUIPMENT NUMBER	:	V01
NAME	:	Heated solvent regeneration

General Data

Service		:	~~distillation /~~	~~extraction /~~	~~absorption /~~	~~reaction~~	regeneration
Column Type		:	~~packed /~~	tray /	~~spray /~~		
Tray Type		:	~~cap /~~	sieve /	~~valve /~~		
Tray Number		:					
	Theoretical	:	4				
	Actual	:	8				
	Feed	:	8				
Tray Distance (HETP)	[m]	:	N/A	Tray Material	:	SS	(1)
Column Diameter	[m]	:	2.0	Column Material	:	SS	(1)
Column Height	[m]	:	5.6				
Heating		:	~~none~~	~~open steam~~	reboiler		

Process Conditions

Stream Details			Feed <302>		Product <304>		Product <303>		Product	
Temp	[oC]	:	54		90		80			
Pressure	[bara]	:	1		1		1			
Density	kg/m3	:	N/A		N/A		N/A			
Mass Flow	kg/h	:	940320		4284		936036			
Mole Flow	kmol/h	:	51444		72		51444			
Phase		:	L		L		L		L	
Composition			mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%
Nitrogen										
Carbon dioxide					9.09	6.42				
Sulphur dioxide					90.91	93.58				
Oxygen										
Water			99.69	98.17			99.82	98.75		
Hydrogen chloride										
Hydrogen fluoride										
Bromine										
Hydrogen bromide										
Sulphuric Acid										
Hydrogen										
MEA										
MEA CO2salt										
Na_2SO_3			0.05	0.32			0.18	1.25		
$NaHSO_3$			0.25	1.45						
NaHCO3			0.01	0.06						
Fly ash										

Column Interals

Trays					**Packing**			
Number of					Type		:	
	~~caps /~~	sieve holes /		:	Material		:	
Active Tray Area		1.2	[m2]	:	Volume	[m3]	:	
Weir Length		N/A	[mm]	:	Mass	[kg]	:	
Diameter of		N/A			Width	[m]	:	
	chute pipe /	hole /	[mm]	:	Height	[m]	:	

Remarks

(1) Stainless Steel

Designers:	Alberts, J.	Tange, C.	Gastel, H. van	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.		Date:	6-12-05

Column - Specification Sheet

EQUIPMENT NUMBER	:	V04
NAME	:	Heated solvent regeneration

General Data

Service		:	~~distillation /~~	~~extraction /~~	~~absorption /~~	~~reaction~~	regeneration	
Column Type		:	~~packed /~~	tray /	~~spray /~~			
Tray Type		:	~~cap /~~	sieve /	~~valve /~~			
Tray Number		:						
	Theoretical	:	4					
	Actual	:	8					
	Feed	:	8					
Tray Distance (HETP)	[m]	:	N/A	Tray Material		:	SS	(1)
Column Diameter	[m]	:	2.2	Column Material		:	SS	(1)
Column Height	[m]	:	5.6					
Heating		:	~~none~~	~~open steam~~	reboiler			

Process Conditions

Stream Details			Feed <601>		Feed <605>		Product <602>		Product <905>	
Temp	[oC]	:	54		115		116		116	
Pressure	[bara]	:	1		1		1		1	
Density	kg/m3	:	N/A		N/A		N/A		N/A	
Mass Flow	kg/h	:	3132		N/A		2952		10.3	
Mole Flow	kmol/h	:	144		N/A		144		0.36	
Phase		:	L		G		L		L	
Composition			mol%	wt%	mol%	wt%	mol%	w%	mol%	wt%
Nitrogen										
Carbon dioxide			4.77	8.79		10	2.12	4.00		
Sulphur dioxide										
Oxygen										
Water			84.51	63.75		90	86.89	67.20	88.77	57.55
Hydrogen chloride										
Hydrogen fluoride										
Bromine										
Hydrogen bromide										
Sulphuric Acid										
Hydrogen										
MEA			10.69	27.32			10.99	28.80		
MEA CO2salt			0.03	0.14					11.23	42.45
Na_2SO_3										
$NaHSO_3$										
NaHCO3										
Flyash										

Column Interals

Trays					**Packing**			N/A
Number of					Type		:	
	~~caps /~~	sieve holes /		:	Material		:	
Active Tray Area		1.5	[m2]	:	Volume	[m3]	:	
Weir Length		N/A	[mm]	:	Mass	[kg]	:	
Diameter of		N/A			Width	[m]	:	
	chute pipe	/ hole /	[mm]	:	Height	[m]	:	

Remarks

(1) Stainless steel

Designers:	Alberts, J.	Tange, C.	Gastel, H. van	Project ID number:	**CPD3330**
	Braber, J-H.	Zubeir, L.		Date:	6-12-05

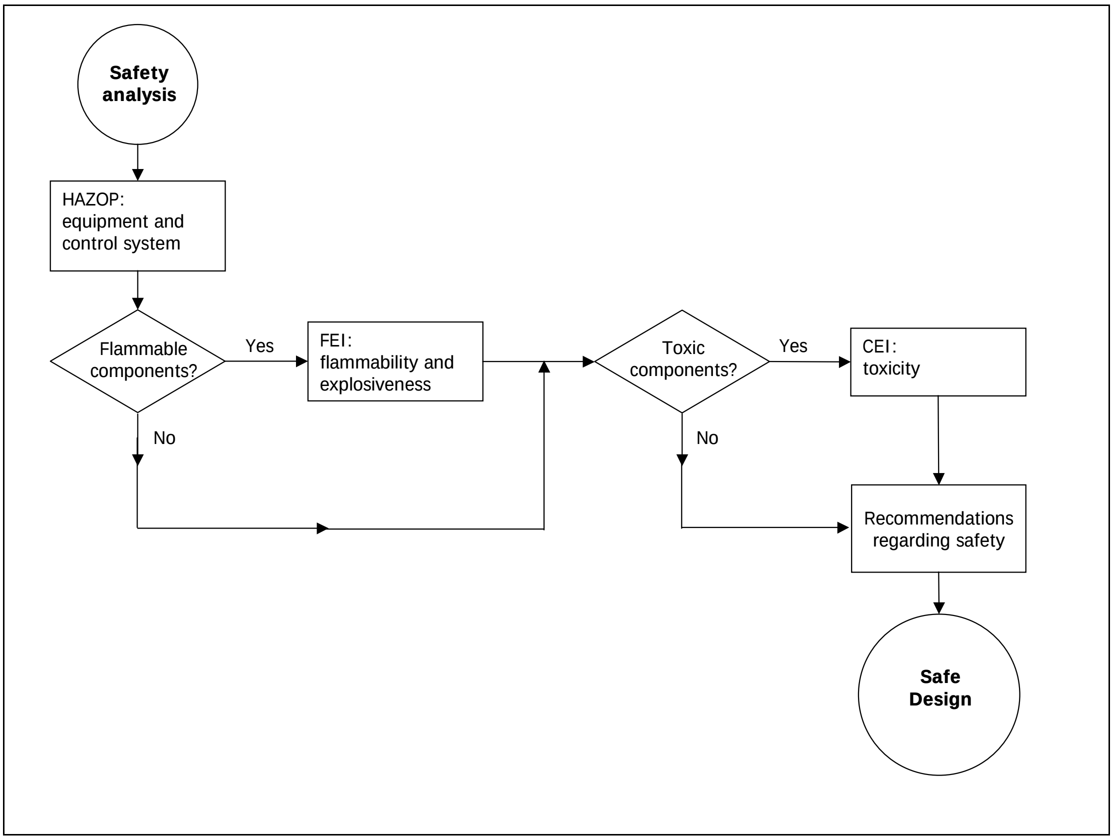
22Wastes

Waste (S/L/G)	Composition				Effect	Disposal	Discussion of risk
Fly ash (S)	Major elements	[%]	Trace elements	[mg/k	Dry fly ash can become airborne in moderate winds, and should be stored in silos. While it is not particularly harmful for human health, it should be handled with care, according to normal safety measures.	The dry product can be sold for use as additive in cement.	Dry fly ash can be difficult to store, if not contained in silos. Uncontained it can lead to inhalation problems. However, when fly ash is slightly moisturized, it is easy to handle and contain. Furthermore, it is not flammable, explodable or toxic to human health and therefore is not very risky to handle. Fly ash can be sold for use as/ in cements.
	SiO2	*46.9*	As	*27.7*			
	TiO2	*0.2*	B	*308*			
	Al2O3	*24.9*	Ba	*2166*			
	Fe2O3	*8.8*	Co	*66.1*			
	MnO	*0.1*	Cr	*154*			
	MgO	*3.8*	Cu	*214*			
	CaO	*6.9*	Mo	*11.2*			
	K2O	*2.1*	Ni	*138*			
	Na2O	*1.2*	Pb	*126*			
	P2O5	*0.7*	Sb	*16.1*			
	SO3	*1*	Se	*16.1*			
	LOI	*1.6*	V	*320*			
			Zn	*217*			
	Source: H.W. Nugteren, M. Janssen-Jurkovicova, B. Scarlett, "*Removal of heavy metals from fly ash and the impact on its quality,* TU Delft, KEMA, 2001.						

Insoluble MEA salts (S)	Salts formed with impurities in flue gas, oxygen, sulphur oxide and nitrogen dioxide.	MEA is very harmful, insoluble MEA salts not. When contained in landfill sites, the effect is neglegible.	The separated salts contain some process water, and might contain some unconverted MEA. This should be suficiently dried however, since MEA is very harmful to humans. The MEA can be neutralized by reaction with HCl, which leads to salt formation. Specialized companies take care of further disposal of these salts, which can be by means of landfill.	No large risks are involved in the handling of these salts, if sufficiently dried to remove MEA. The salts can easily be contained, and since specialized companies take care of further disposal of these components, no further risks exist.
Treated flue gas (G)	The treated flue gas consists mainly of CO_2, H_2O, N_2 and O_2, but can still contain traces of HCl, HF, SO_2 and Fly ash.	The effect of the treated flue gas is low; hazardous substances are removed from this waste stream, CO_2 however can have an adverse effect on the greenhouse effect, however at a removal rate of 50%, this stream falls well withing legal requirements.	The treated flue gas is within regulation specifications and therefore can be disposed of via the plant stack.	Due to the very low content of potentially hazardous materials, this stream can be considered unharmful. Furthermore it is not combustible or odorous.
Hydrochloric and hydrofluoric acid	The waste stream of the first absorber is a mixture of water, HCl and HF.	HCl and HF both are potentially very dangerous substances, and therefore have to be contained and treated in order to become harmless.	The disposal of the HCl and HF containing aqqueous stream can be achieved via a waste water treatment plant. When the concentrations of both substances in the waste water are within legal requirements, this waste water can be discarded in surface water.	While HF and HCl both can be very dangerous chemicals, when present in concentrated form, the risk they present in the waste water of the absorber is minimal due to the low concentrations. This water can be treated in a wastewater treatment plant up to legal requirements and can be discarded without risk into the surface water.

23Process Safety

23.1 Procedure of Safety Analysis



23.2 Hazard and Operability Analysis

Table 23-1: HAZOP analysis of the reaction section

Guide Word	Deviation	Possible Causes	Consequences	Action Required
Not/No	No flow	(1) Pump fails (#X) (2) Line fracture (3) Line blockage	- Loss of feed to reaction section and reduced output. - As for (1) with discharge into surroundings. - As for (1).	(a) Check design pumps. (b) Regular controlling of pipelines. (c) Dikes around reactors. (d) Level controller in reactor.
More	More flow	(4) Ratio control fails (5) Flow control fails (6) Outlet valves fail	- More water causing more reflux in distillation column. - As for (4). - Chance of drying out of column.	(e) Reflux capable of coping with large amounts of water. (f) Level controller in the bottom.
	More pressure	(7) Outlet valves blocked	- Pressure builds up possibly causing an explosion.	(g) Pressure valve with buffer vessel.
	More temperature	(8) Temperature control reactors fail (9) Flow water reduced (10) High storage temperature	- Run away possible. - As for (8). - As for (8).	(h) Excess water controls the temperature.
Less	Less flow	(11) Failure in outlet valves (12) Leakage in pipeline(s)	- Blockage causing too much pressure. - Loss of feed causing discharge into surroundings.	(i) Covered by (f). (j) Covered by (b) and by (f).
	Less temperature	(13) Winter conditions	- Water freezes up in pipelines.	(k) Suitable heater for buffer vessel.
As well as	Contaminations	(14) Excess CO_2 (15) HF & HCl present	- Less conversion of SO_2 -	
Part of	Change in composition	(16) High Br_2 concentration (17) High SO_2 concentration	- Br_2 in outlet stream, which leads to highly contaminated waste stream. - Larger gas outlet stream, which leads to contamination in CO_2 product.	(l) Excess of water used. (m) Check that design of tanks and pipes can cope with harsh conditions.

Other than	Maintenance	(18) Equipment failure; leaks in tanks etc…	- Pipelines cannot be drained or emptied. - Loss of feed.	(n) Install purges.

23.3 Fire and Explosion Index

Table 23-2: Fire and explosion index

Fire & Explosion Index					Mark-13 Process	Calcination Process
Material Factor					*24.00*	*40.00*
1. General Process Hazards						
			Penalty Factor Range		Penalty Factor Used	
Base factor				*1.00*	*1.00*	*1.00*
A	Exothermic Chemical Reactions			*0.30-1.25*	*1.00*	*1.00*
B	Endothermic Processes			*0.20-0.40*	*0.00*	*0.00*
C	Material Handling and Transfer			*0.25-1.05*	*0.00*	*0.00*
D	Enclosed or Indoor Process Units			*0.25-0.90*	*0.00*	*0.50*
E	Access			*0.20-0.35*	*0.00*	*0.00*
F	Drainage and Spill Control			*0.25-0.50*	*0.00*	*0.00*
General Process Hazards Factor (F1)					*2.00*	*2.50*
2. Special Process Hazards						
Base factor				*1.00*	*1.00*	*1.00*
A	Toxic Materials			*0.20-0.80*	*0.80*	*0.00*
B	Sub-atmospheric pressure			*0.50*	*0.00*	*0.00*
C	Operation in or near flammable range					
	1	Tanks farms storage flammable liquids		*0.50*	*0.00*	*0.00*
	2	Process upset or Purge failure		*0.30*	*0.00*	*0.00*
	3	Always in flammable range		*0.80*	*0.00*	*0.00*
D	Dust Explosion			*0.25-2.00*	*0.00*	*1.00*
E	Pressure	Operating pressure	110 kPa		*0.00*	*0.00*
		Relief setting			*0.00*	*0.00*
F	Low temperature			*0.20-0.30*	*0.00*	*0.00*
G	Quantity of flammable/unstable material		Quantity	*145 kg/s*	*0.00*	*0.00*
			H_c	*32.5 kcal/kg*	*0.00*	*0.00*
	1	Liquids or gases in process			*0.00*	*0.00*
	2	Liquids or gases in storage			*0.00*	*0.00*
	3	Combustible solids in storage			*0.00*	*0.00*
H	Corrosion and Erosion			*0.10-0.75*	*0.75*	*0.00*
I	Leakage - joints and packing			*0.10-1.50*	*0.00*	*0.00*
J	Use of fired equipment				*0.00*	*0.00*
K	Hot oil heat exchange system			*0.15-1.15*	*0.00*	*0.00*
L	Rotating equipment			*0.50*	*0.00*	*0.00*
Special Process Hazards Factor F2					*2.55*	*2.00*
Process Units Hazards Factor F1xF2=F3					*5.10*	*5.00*
Fire and Explosion Index = F3xMF					*122.40*	*200.00*

23.4 Toxicity of Bromine

$$LC_{50m} = \frac{1}{\left({C_i}/{LC_{50i}} \right)} \qquad \text{(K4-1)}$$

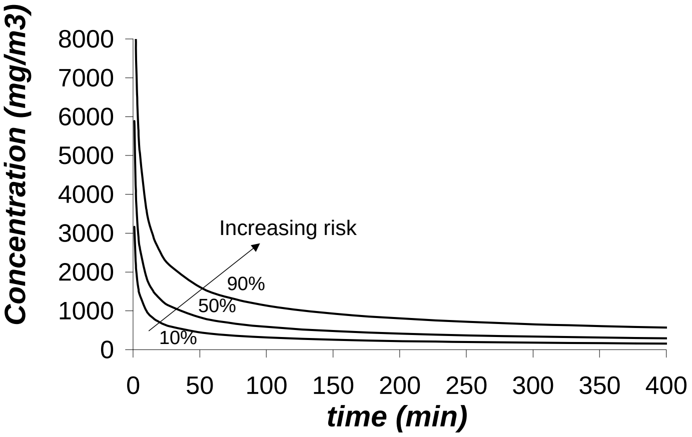


Figure 23-1: Concentration-time exposure plot for bromine, based on the data of Bibo *et al.* in [30]

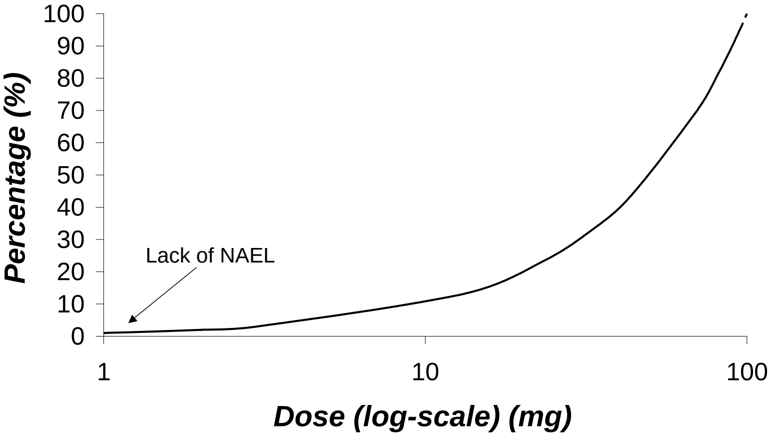


Figure 23-2: Log-normal distribution of the dose vs percentage, based on data of Bibo *et al.* in [30]

23.5 Chemical Exposure Index

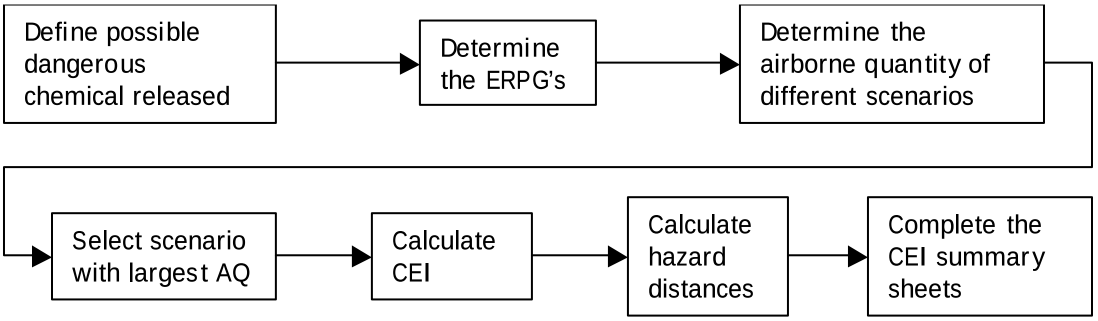


Figure 23-3: Procedure for the calculation of the CEI, taken from [33]

Table 23-3: Chemical Exposure Index for bromine

	Br_2 (mg/m^3)	H_2SO_4 (98%) (mg/m^3)	MEA (mg/m^3)	HBr (mg/m^3)	Explanation
ERPG-1	*1*	*2*	*15*	*7*[5]	Maximum airborne concentration below which it is believed that nearly all individuals could be exposed for one hour without experiencing other than mild transient adverse health effects.
ERPG-2	*7*	*10*	*75*	*17*	Maximum airborne concentration below which it is believed that nearly all individuals could be exposed up to one hour without developing irreversible or serious health effects and symptoms.
ERPG-3	*33*	*30*	*75*	*85*[6]	Maximum airborne concentration below which it is believed that nearly all individuals could be exposed up to one hour without developing life-threatening health effects.

In this case it is assumed that the flow is choked and that the hole is ragged, which results in C_d=0,85. This leads to the following result in equation K5-1 for the liquid mass flow rate:

$$G_l = 9.44 * 10^{-7} D^2 \rho \left(\frac{P_g}{\rho} + gh \right)^{\frac{1}{2}} \qquad \text{(K5-1)}$$

The total amount of liquid released W_T is given in equation K5-2: (K5-2)

When the temperature difference between the boiling point and the operating temperature is large enough, it is possible that there will be no liquid pool formed, but that the system will behave like a flash. The amount of liquid flashed can then be calculated with equation 10-5. When the fraction flashed exceeds *20%*, the airborne quantity produced by the flash (AQf) is equal to the liquid flow rate L and no pool is formed. This is only the case for the bromine in the first reactor, but the fraction flashed F_v=*0.023* so a pool will be formed.

$$F_v = \frac{C_p}{H_v}(T_s - T_b) \qquad \text{(K5-3)}$$

$$F_v \geq 0.2 \rightarrow AQf = L$$

The heat of vaporisation H_v is estimated with equation X in appendix X/chapter4.

Equations K5-1 to K5-3 are all necessary to calculate the hazard distance X, which is an estimate for the CEI. Equation K5-4 shows the hazard distance and equation K5-5 indicates the possible range. The source strength SS is given in equation K5-6, but in this case the source strength is taken as the vapour flow rate from the pool AQ_p in equation K5-7.

---

[5] Not available so estimated with the odor threshold value of 2 ppm

[6] Not available so calculated as ERPG-3 = 5 x ERPG-2

$$X = 17.5\left(\frac{Cm}{C_0}\right)^{-1/2}\left(\frac{q_0}{Vrf}\right)^{1/2} \qquad \text{(K5-4)}$$

$$X = 0 \le \left(\frac{g_0^2 q_0}{V^5 rf}\right)^{1/5} \le 3 \qquad \text{(K5-5)}$$

$$SS = q_0 \cdot \rho \qquad \text{(K5-6)}$$

$$AQ_p = 9.0\cdot 10^{-4}\left(A_p{}^{0.95}\right)\left(\frac{(MW)P_v}{T+273}\right) \qquad \text{(K5-7)}$$

Combining equation K5-4 and K5-6 and expressing the density by means of the ideal gas law ($\rho = PM_w/RT$) results in equation K5-8:

$$X = C\sqrt{\frac{SS}{ERPG * Mw}} \qquad \text{(K5-8)}$$

The parameter C is assumed to be *C=38702*, with the ERPG expressed in PPM. Converted to mg/m^3 results in *C=6552*. The CEI is then estimated as *10%* of the hazard distance at ERPG-2 concentration.

24Economy

24.1 Operational Costs

Table 24-1: Operational cost

Fixed		
Maintenance		*€ 12,192,599.88*
Operating labour		*€ 600,000.00*
Laboratory cost		*€ 120,000.00*
Supervision		*€ 120,000.00*
Plant overheads		*€ 300,000.00*
Capital charges		*€ 18,288,899.82*
Rates/Local taxes		*€ 2,438,519.98*
Insurance		*€ 1,219,259.99*
Licence fees and royalty payments		*€ 1,219,259.99*
total		*€ 36,498,539.65*
Variable		
Raw materials		*€ 344,314.63*
Miscellaneous operating materials		*€ 1,219,259.99*
Utilities		*€ 8,837,984.47*
Shipping and packaging		*€ 0.00*
total		*€ 10,401,559.09*
Direct production cost	total	*€ 46,900,098.74*
Sales expense		
General overheads		
R&D		
total		*€ 9,380,019.75*
Annual production cost		*€ 56,280,118.49*

Table 24-2: Cost of raw materials

Name	ton/h		price	price/year ($)	price/year (euro)
	IN	OUT	$/ton		
INGOING STREAMS					
flue gas	*1948*		*$0.00*	*$0.00*	*€ 0.00*
MEA make up	*0.03*		*$408.35*	*$87,828.94*	*€ 73,117.59*
water make-up	*2.49*		*$0.50*	*$9,972.00*	*€ 8,301.69*
bromine make-up	*0*		*$992.00*	*$0.00*	*€ 0.00*
water to hcl scrubber	*72*		*$0.50*	*$288,000.00*	*€ 239,760.00*
SO3 make up	*0*		*$100.00*	*$0.00*	*€ 0.00*
small MEA make-up	*0.009*		*$408.35*	*$27,790.21*	*€ 23,135.35*
			total	*$413,591.15*	*€ 344,314.63*

Table 24-3: Cost of utilities

Name	ton/h	kWh/h	price /(ton or kWh) pound(1998)	price euro (2005)	
LP steam	*54.2*		*£7.00*	*€ 12.71*	*€ 5,505,327.66*
Natural gas		*348*	*£0.01*	*€ 0.03*	*€ 72,766.69*
Cooling water	*75.8*		*£0.02*	*€ 0.03*	*€ 16,506.08*
Electricity		*5170*	*£0.04*	*€ 0.08*	*€ 3,243,384.03*
total					*€ 8,837,984.47*

24.2 Process Equipment Costs

The process equipment can be divided in several groups for a clearer view on the costs of certain types of process equipment.

24.2.1 Heat exchangers

The first group of equipment are the heat exchangers. Very important for the cost of a heat exchanger is the area of the piece of equipment. To calculate the areas this formula is used:

$$Q = \frac{A}{U * \Delta T_{lm}} \qquad \text{(L2-1)}$$

In which Q is the duty in W, A is the area of the heat exchanger in m^2, U is the heat transfer coefficient in $W/(K*m^2)$ and ΔT_{lm} is the log mean of temperature in K.

The heat duties of all heat exchangers have been calculated in chapter 7. In all the heat exchangers liquids are being heat exchanged and as a typical value for U has been taken 300 $W/(K*m^2)$. ΔT_{lm} has been calculated with the formula:

$$\Delta T_{lm} = \frac{(T_2 - T_3) - (T_1 - T_4)}{\ln\left(\frac{(T_2 - T_3)}{(T_1 - T_4)}\right)} \qquad \text{(L2-2)}$$

With these data the areas of the heat exchangers can be calculated:

Table 24-4: Calculation of areas of heat exchangers

	U (W/(m2*K)	Q (W)	T1 (K)	T2 (K)	T3 (K)	T4 (K)	deltaTlm	A (m2)
E01	300	-23840.15	313	293	353.00	330.00	88.60465	896.8736
E02	300	27600.51	406.5	463	327.00	353.00	-216.273	425.3964
E03	300	-189.258	313	293	390.00	298.00	60.63052	10.40496
E04	300	184.53						
E05	300	-120.595	313	293	565.00	298.00	145.0867	2.770642
E06	300	163.46						
E07	300	-216.08	313	293	389.00	298.00	60.07563	11.98947
E08	300	144.90	406.5	463	313.00	353.00	-233.774	2.066038
E09	300	-58.1284	313	293	353.00	298.00	38.75583	4.999539
E10	300	11.42	406.5	463	298.00	333.00	-273.838	0.138981
E11	300	4449.80	364	389	352	327	-70.1055	211.5761
E12	300	-264.584	313	293	389.00	340.00	138.945	6.347463
E13	300	6598.152	406.5	463	352.00	389.00	-146.798	149.8234
E14	300	-5873.64	313	293	364.00	330.00	100.4531	194.9049

E04 and E06 are furnaces, but are listed in the above table.

Table 24-5: Cost of heat exchangers

Name	Equipment	M of C Sh/tubes	Surface (m2)	Cost ($) 2003	Type	Cost (Euro) 2003	Cost (Euro) 2005
E01	Heat exchanger	SS/SS	896.87	$503,100.00	floating head	€ 418,830.75	€ 444,337.54
E02	Heat exchanger	SS/SS	425.40	$274,800.00	floating head	€ 228,771.00	€ 242,703.15
E03	Heat exchanger	SS/SS	10.40	$18,800.00	floating head	€ 15,651.00	€ 16,604.15
E04	Furnace	SS		$72,900.00	box	€ 60,689.25	€ 64,385.23
E05	Heat exchanger	SS/SS	2.77	$9,800.00	floating head	€ 8,158.50	€ 8,655.35
E06	Furnace	SS		$67,200.00	box	€ 55,944.00	€ 59,350.99
E07	Heat exchanger	SS/SS	11.99	$20,600.00	floating head	€ 17,149.50	€ 18,193.90
E08	Heat exchanger	SS/SS	2.07	$5,000.00	floating head	€ 4,162.50	€ 4,416.00
E09	Heat exchanger	SS/SS	5.00	$12,900.00	floating head	€ 10,739.25	€ 11,393.27
E10	Heat exchanger	SS/SS	0.14	$2,400.00	floating head	€ 1,998.00	€ 2,119.68
E11	Heat exchanger	SS/SS	211.58	$156,100.00	floating head	€ 129,953.25	€ 137,867.40
E12	Heat exchanger	SS/SS	6.35	$14,400.00	floating head	€ 11,988.00	€ 12,718.07
E13	Heat exchanger	SS/SS	149.82	$117,600.00	floating head	€ 97,902.00	€ 103,864.23
Total							€ 1,126,608.96

With the calculated areas the prices can be estimated on an Internet site www.matche.com [35]. This is an American website, which uses non SI-units and therefore all units have to be converted. For the area calculations m^2 has to be converted into ft^2. To do this the area in m^2 has to be multiplied by 10.76. For the equipment has to be stated what it is made of. Because all equipment needs to be able to handle water-containing streams all equipment will be made of stainless steel. All heat exchangers have been chosen being floating head heat exchangers. The furnaces are taken as box-type furnaces. The cost of the equipment calculated by the website are prices in \$ in 2003. First the \$ will be converted into €; to do this it has to be multiplied with the current exchange rate of 0.8325. To convert this to € in 2005 it has to be multiplied with an annual inflation of 3 %. So it has to be multiplied with 1.0609.

A total heat exchanger cost of 1.13 million euros has been calculated. The majority of the cost is from the heaters and coolers of the sulphur dioxide capturing units. If some heat integration would be implemented these costs would most probably be reduced.

24.2.2 Columns

Table 24-6: Cost of columns

Columns	Mass (ton)	Cost ($) 2003	Cost (Euro) 2003	Cost Euro (2005)
C01	*100*	*$914,300.00*	*€ 761,154.75*	*€ 807,509.07*
C02	*10*	*$119,900.00*	*€ 99,816.75*	*€ 105,895.59*
C03	*10*	*$119,900.00*	*€ 99,816.75*	*€ 105,895.59*
C04	*100*	*$914,300.00*	*€ 761,154.75*	*€ 807,509.07*
C05	*100*	*$914,300.00*	*€ 761,154.75*	*€ 807,509.07*
total				*€ 2,634,318.40*

To calculate the costs of the columns also [35] has been used. To determine the costs the cost estimator demanded the weight of the units. It is really difficult to estimate these values, but it has been taken that columns C02 and C03 have to deal with a significantly smaller stream and have therefore been taken as ten times less heavy than the other three columns.
The small columns are assumed to have a mass of about 10 ton, the big columns are assumed to have a mass of 100 ton. From Table 24-6 can be concluded that the total costs of the columns are about € 2.63 million.

24.2.3 Reactors

Table 24-7: Cost of reactors

Name	Equipment	diam(m) curve volume (m3)	Height cost	Material of construction Factor	Cost equipment (UK pounds)	cost total 1998 (UK pounds)	cost 1998 (Euro)	Cost 2005 (euro)
R01	Vessel	*2.11* *3*	*8.37* *£10,000.00*	SS *2*	*£20,000.00*			
	Raschig rings	*20.5*	*50814.621*	SS *2*	*£101,629.24*	*£121,629.24*	*€ 179,500.44*	*€ 190,432.01*
R02	Vessel	*2.11* *3*	*8.37* *£10,000.00*	SS *2*	*£20,000.00*			
	Raschig rings	*20.5*	*50814.621*	SS *2*	*£101,629.24*	*£121,629.24*	*€ 179,500.44*	*€ 190,432.01*
total								*€ 380,864.02*

The costs of the reactors can be calculated with tables from [coulson and Richardson]. The reactors are made of basically two things: a vessel, which is filled with Raschig rings. To determine the vessel cost the height and the diameter must be known. From chapter eight these are known for both reactors: both reactors are vertical ones with a reactor height is 8.37 m and the reactor diameter is 2.11 m. Since the diameter is 2.11 m in [coulson and Richardson] in figure 6.5 line 3 must be taken. With a reactor height of 8.37 m the basic vessel cost is £ 10000. Since the vessels will be made of stainless steel the basic vessel cost must be multiplied with two.

The cost of the Raschig rings can be taken from [Douglas] The volume of the Raschig rings is 20,5 m^3 per reactor from chapter eight. The Raschig rings will also be made of stainless steel and the cost will have to be doubled from the basis cost. The total cost calculated is in pound sterling in 1998. The exchange rate is 1.4758 and to get the cost in euros in 1998 it has to be multiplied with that number With an annual inflation the converted cost has to be multiplied with $(1.03)^7$ to get the 2005 cost. The total reactor price is about 380 thousand euros.

24.2.4 Separators

Table 24-8: Cost of separators

Name	equipment	type area (m2)	diameter (m)	height number of units	Material of Construction cost per unit	Cost $ (2003) / pound (1998)	Cost euro (2003)/(1998)	cost euro 2005
S01	ESP					$103,336.27	€ 86,027.44	€ 91,266.52
S02	Vessel		1	2 177	SS £8,000.00	£2,832,000.00	€ 4,179,465.60	€ 5,140,215.51
	Membrane	1613.92		177	Hollow fibre € 80,696.13			€ 14,283,214.13
S03	Vessel		1	2 13	SS £8,000.00	£208,000.00	€ 306,966.40	€ 377,529.95
	Membrane	228.26		13	Hollow fibre € 11,413.00			€ 148,369.00
S04	Vessel							€ 10,000.00
	Electrodes							€ 50,000.00
total								€ 20,100,595.11

You gotta keep ‘em separated. The next types of equipment that will be evaluated are the separators. It exists out of the electrostatic precipitator (S01), two membrane separators (S02 and S03) and a electrolysis cell (S04). The electrostatic precipitator has been calculated with the aid of [35]. The flow rate had to be converted from m^3/s to gallons/min. After this had been done it could be filled in the website. The cost calculates was in $ dollars in 2003 and had to be converted to € in 2005.

The membrane units consist of vessels of 2 meters high and with a diameter of 1 meter. The costs of these vessels have been determined using [coulson and richarson]. The vessels are made of stainless steel and therefore the basic cost has to be doubled. To reach the current costs it has to be converted from pound sterling in 1998 to euros in 2005. These vessels are both filled with hollow fiber membranes of different diameters. Therefore the vessels can be filled with different areas of membrane. The cost of the membranes has been estimated at € 50 / m^2. The number of units for the sulphur dioxide capturing membranes is 177 and for the carbon dioxide capturing membranes is 13.

The last separating unit is the electrolysis cell (S04). No information on cost could be found and therefore the size of the unit is approximately the same as the smaller vessels and is estimated to cost € 10000. The cost of the electrodes is not known either but is estimated to be € 50000.

The total cost for the separators is € 20.1 million. This is, relative to the other types of equipment, very high. The main costs are the membrane units, which are very expensive at this moment.

24.2.5 Vessels

Table 24-9: Cost of vessels

Name	equipment	material	type	volume (gallons)	cost ($) 2003	cost 2003 (euro)	cost 2005 (euro)
V01	Vessel	SS	vert shop fab, mediu	13068	$33,500.00	€ 27,470.00	€ 29,142.92
V02	Vessel	SS				€ 0.00	€ 10,000.00
V03	Vessel	SS				€ 0.00	€ 10,000.00
V04	Vessel	SS	vert cone top/small	5558	$11,900.00	€ 9,758.00	€ 10,352.26
V05	Vessel	SS				€ 0.00	€ 10,000.00
V06	Vessel	SS				€ 0.00	€ 10,000.00
V07	Vessel	SS				€ 0.00	€ 10,000.00
V08	Vessel	SS					€ 10,000.00
total							€ 99,495.19

Of all the vessels only the size of two are known (V01 and V04). The size of these vessels has been calculated in chapter eight. With the aid of [35] the costs of these units can be

calculated. These units are relatively large and all the other units are much smaller. Therefore the costs for the other units have all been estimated to be € 10000.
The total cost of the vessels is about € 100000, which is relatively low.

24.2.6 Pumps

Table 24-10: Cost of pumps

	mass flow rate					number of		
	kg/s	gallon/min	type	material	seal type	pumps	cost per unit ($)	cost euro 2005
P01	0.01	0.118295		SS	packing	1	$100.00	€ 86.99
P02	0.69	10.9692	rotary	SS	packing	1	$1,200.00	€ 1,043.93
P03	0	0	rotary	SS	packing	1	$0.00	€ 0.00
P04	20.00	316.8	rotary	SS	packing	1	$14,700.00	€ 12,788.09
P05	0	0	rotary	SS	packing	1	$0.00	€ 0.00
P06	0.00	0.03743		SS	packing	1	$200.00	€ 173.99
P07	1.96	31.0768	rotary	SS	packing	1	$2,600.00	€ 2,261.84
P08	260.01	4118.525	rotary	SS	packing	13	$14,800.00	€ 167,376.07
P09	0	0	rotary	SS	packing	1	$0.00	€ 0.00
P10	2.44	38.577	rotary	SS	packing	1	$3,000.00	€ 2,609.81
P11	1.77	27.96473	rotary	SS	packing	1	$2,400.00	€ 2,087.85
P12	0.82	13.04009	rotary	SS	packing	1	$1,300.00	€ 1,130.92
P13	0.00	0.04553		SS	packing	1	$200.00	€ 173.99
P14	75.41	1194.51	rotary	SS	packing	4	$14,800.00	€ 51,500.33
P15	0.04	0.634159		SS	packing	1	$200.00	€ 173.99
P16	75.38	1193.956	rotary	SS	packing	4	$14,800.00	€ 51,500.33
P17	3.37	53.42938	rotary	SS	packing	1	$3,900.00	€ 3,392.76
P18	66.74	1057.107	rotary	SS	packing	4	$14,800.00	€ 51,500.33
P19	60.46	957.7458	rotary	SS	packing	3	$14,800.00	€ 38,625.25
P20	2.8894	45.76811	rotary	SS	packing	1	$3,400.00	€ 2,957.79
P21	0.04	0.591865		SS	packing	1	$200.00	€ 173.99
total								€ 389,558.24

To determine the cost of the pumps **[35]** first the flow rate will have to be converted from kg/s to gallons per minute. Almost all streams mainly consist of water and therefore for all conversion the density of water has been taken. The pumps are rotary pumps made of stainless steel, which have a maximum capacity of 320 gallons. So some ‘pumps’ actually are several pumps to be able to pump around all fluids. The seal type of all pumps are taken as packing and by filling in these values in on [35] the cost of the pumps in $ in 2003 can be calculated and this has to be converted to € in 2005.

The total cost of pumps is almost € 400000 and this is primarily because some very large liquid streams have to be pumped around.

25Creativity

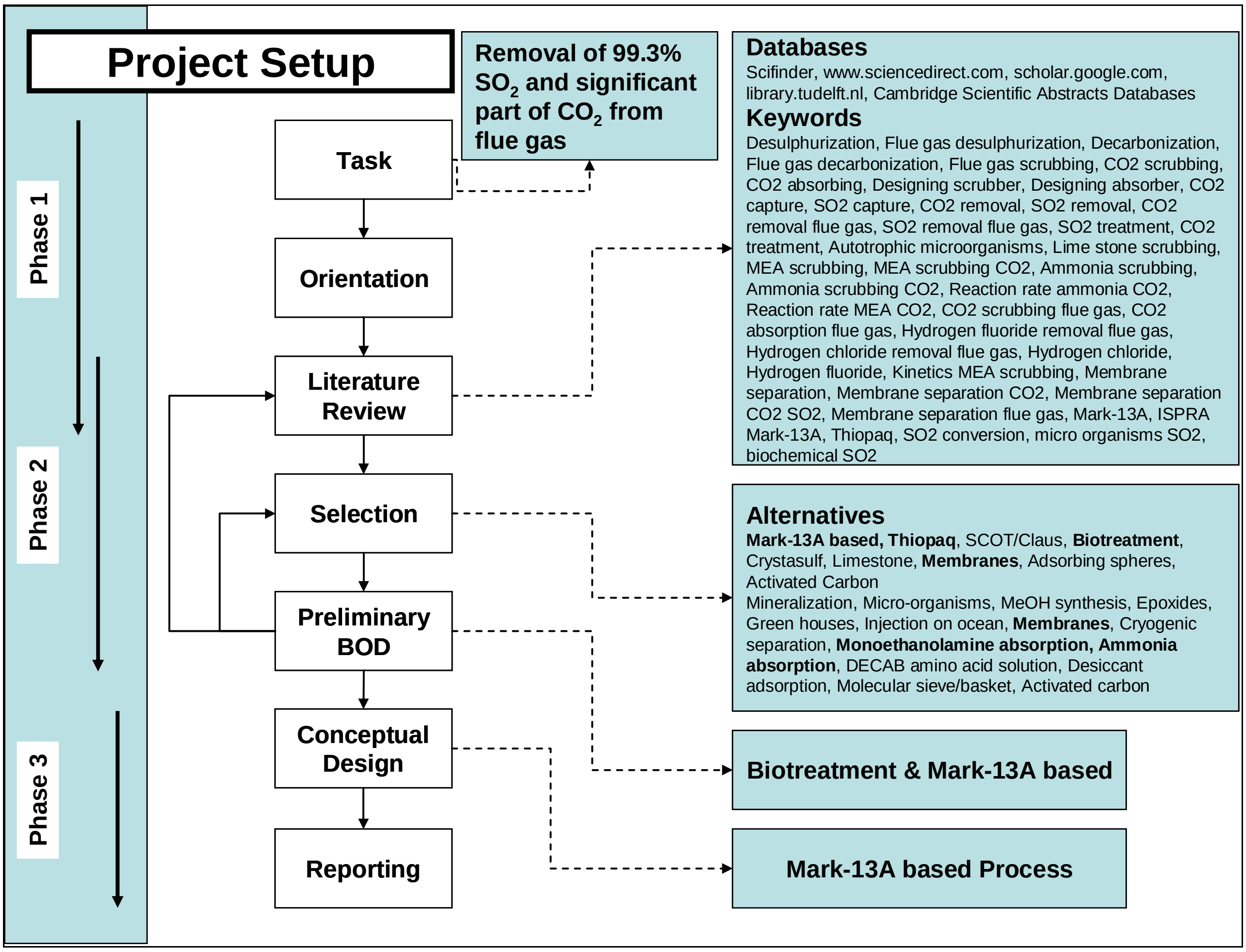


Figure 25-1: Project setup

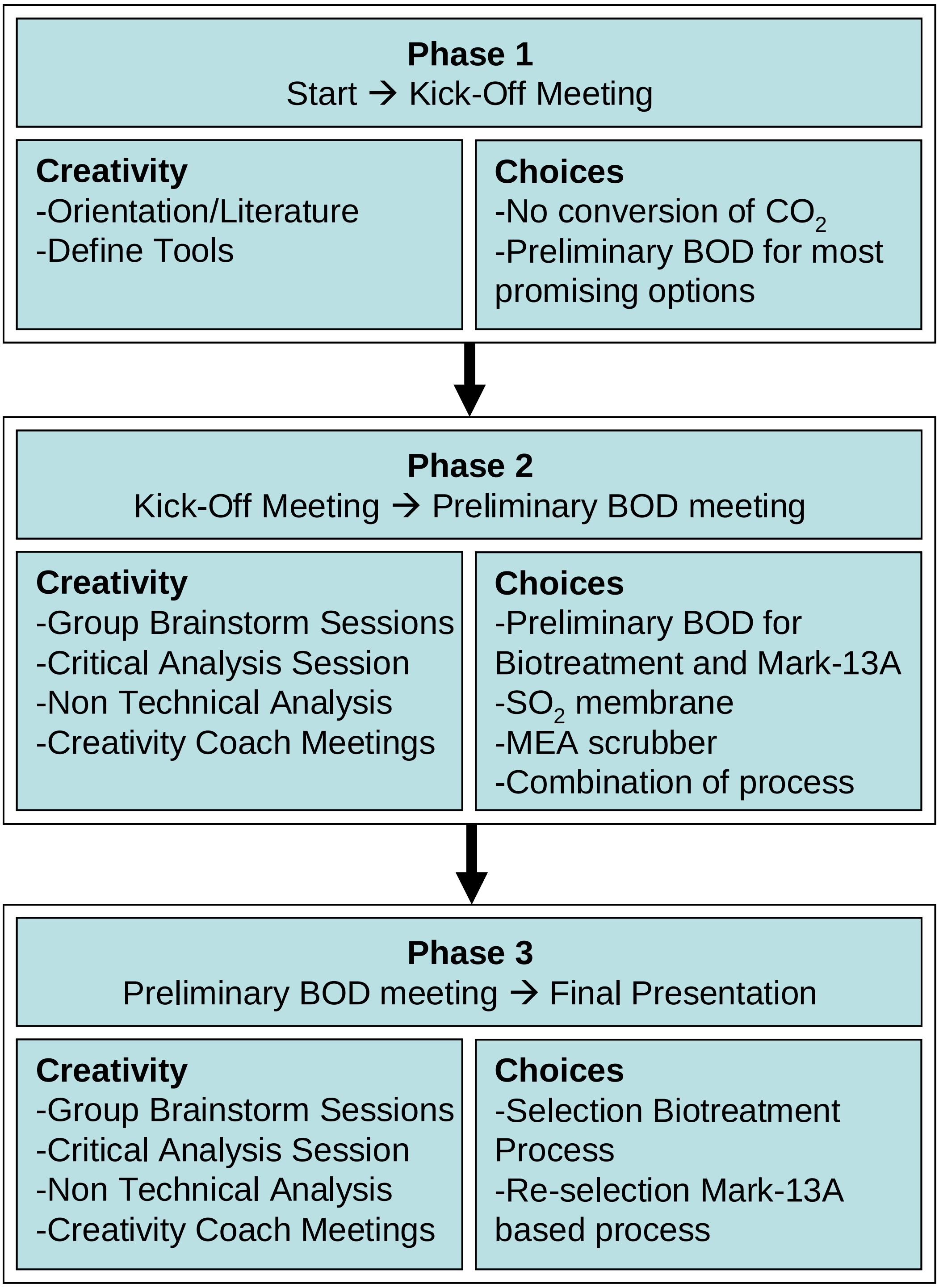


Figure 25-2: Project phases diagram

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