**Subject**
Design of a magnesium removal process for an electrolytic zinc plant

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Summary

Framework of the project

In the electrolytic zinc production sulphuric acid is used to leach zinc from roasted zinc concentrate. Unfortunately the acid also leaches a lot of other metal ions, one of which is magnesium. These metals, except for magnesium, are successively removed in purification steps after which the zinc is produced by electrolysis. The magnesium doesn’t cause huge problems during the zinc production process, but since the sulphuric acid is being recycled it has to be removed somewhere in the process to prevent accumulation.

Usually the magnesium is removed by addition of calcium carbonate, yielding contaminated gypsum, which has to be dumped. Due to environmental regulations, dumping of gypsum has become prohibited several years ago in the Netherlands.

The Dutch zinc producer, Budel Zinc, located at Budel-Dorplein [36] currently uses a biological process (SRB process) to remove the magnesium from the sulphuric acid stream. Since this method of magnesium removal is a costly matter, Budel Zinc is still looking for other possibilities.

One alternative method, proposed by J.L. Booster [P8] who has done extensive research on this method at the section of Applied Earth Sciences at the Delft University of Technology in cooperation with Budel Zinc, uses a combination of magnesium fluoride precipitation and a membrane reactor to regenerate the fluoride ions.

Aim of the project

The aim of this project is twofold:
- First of all a conceptual process design will be made of the process proposed by J.L. Booster, to which will be referred as the membrane process. This includes detailed design of the process, improving the process if possible and, providing solutions to known problems such as the fact that there remains to much fluoride in the stream which goes back to the zinc plant as well as in the magnesium product.
- Secondly, using creative methods, alternative solutions for the removal of magnesium will be created, one of which will be selected and conceptually designed.

The conceptual designs of these two processes will be assessed on economic performance. Furthermore a health and safety analysis will be carried out, process control will be designed and wastes will be discussed.
**Creativity**

Throughout the project the use of creativity is focused on. Different methods for stimulating creativity were used, some of which the group members were already familiar with and some new methods. The use of creative methods was assisted by dr. Grunwald, psychologist.

Furthermore the way the team members work together as a group is assessed.

The use of creativity appeared to be very fruitful and resulted in numerous alternative processes of variable quality. The promising ideas were selected and research was done in order to be able to evaluate the ideas. The most promising idea appeared to be the evaporation process. This will be described below.

**Results**

**Membrane process**

The fluoride problem in the solution that is led back to the plant was solved by precipitation using silicate and aluminium sulphate. The fluoride present in magnesium hydroxide is removed by calcination, yielding magnesium oxide.

Another problem described is the uncertainty about the performance of the membranes. From the research of Booster and Schrader [7, 5] most of the uncertainties are taken away. However the membrane lifetime, which can be achieved in industrial practice, and the operational performance (i.e. fouling) is still not completely known.

When considering the stream, which is led back to the plant as main product, the yield of the feed stream to the product stream is 0.995 t/t. Furthermore, the yield of magnesium product is 0.015 t/t.

The loss of zinc is on average 155 kg zinc per ton magnesium removed. This can be considered to be quite high.

If possible, recommendations coming from the HAZOP-analysis have been taken up into the design.
The Fire and Explosion Index indicated that the process has an intermediate degree of hazard (degree 3 on a scale of 1 to 5).

The investment costs for the membrane process are 3523 k€. The operational costs are calculated to be 3753 k€/a. While removing 234 t/a the costs per kg magnesium will be 14.6 €. This price is too high to compete with the existing SRB process.
Evaporation process

In the evaporation process water in the incoming solution is evaporated in order to achieve precipitation of the metal salts. In the first part of the evaporation no precipitation occurs, which makes it possible to use simple falling film evaporators. In the stages where precipitation does occur, forced circulation evaporators are used. After the evaporation, the mixture of zinc, magnesium and manganese sulphate is heated in a rotary kiln. All metal sulphates except magnesium decompose to oxides and sulphides that are insoluble in water. By dissolving in water followed by evaporation, pure magnesium sulphate is obtained. All other fractions are led back to the zinc plant.

Again the stream led back to the plant is regarded as being the product. The yield with respect to the feed is 1.07 t/t. The magnesium sulphate yield is 0.0335 t/t product.

In evaporation process there a negligible zinc loss.

One of the most important issues in the evaporation process is the use of heat integration. To maximise the efficiency of the used steam, multi-effect evaporation is used.

The evaporation process appears to be very robust. The only uncertainty is the process of decomposition in the rotary kiln. Due to unexpected big particles there may be zinc and manganese sulphate that does not decompose. Grinding of the particles or heating the rotary kiln above the melting temperature of magnesium sulphate may bring an outcome.

If possible, recommendations coming from the HAZOP-analysis have been taken up into the design.
The Fire and Explosion Index indicated that the process has a limitedly degree of hazard (degree 2 on a scale of 1 to 5).

The investment costs for the evaporation process are 6256 k€. The operational costs are calculated to be 2470 k€/a. In the plant 268 tonne magnesium is removed each year, which leads to the price of 7.7 € for each kg of magnesium removed. This price is lower than the price for the existing SRB process, and can even be lowered by increasing the heat integration. This makes the evaporation a very promising concept.

For the zinc refinery in Budel, the evaporation has an additional advantage. In the roasting unit at the site one tonne 6 bar steam is produced per hour. Up to now, this steam is not used. The amount of steam produces should be enough to supply the multi-effect evaporators, which reduces the costs even further.
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1 Introduction

Budel Zink B.V., a company owned by Pasminco Ltd, has operated a zinc refinery since 1973 at Budel-Dorplein in the Netherlands. A few years ago the process that was used to remove magnesium from the process stream became forbidden in the Netherlands because of new environmental regulations. Budel Zink B.V. therefore started using a biological process to remove the magnesium [4]. This method to remove the magnesium is rather expensive. Therefore, during this project, two alternatives to the existing magnesium removal process will be designed that might present a more cost-effective solution to the magnesium removal problem.

Around 80 percent of the world zinc production is processed by the so-called roast-leach-electrowinning (RLE) process [5] (figure 1.1).

In this process, ore (mostly zinc-sulphide) is roasted to mostly zinc oxide and sulphur dioxide [eq 1.1].
\[
\text{ZnS (s) + 1.5 O}_2 (g) \rightarrow \text{ZnO (s) + SO}_2 (g) \quad [\text{eq. 1.1}]
\]

The acquired zinc oxide is leached in several steps by adding sulphuric acid [eq 1.2], which was formed out of the sulphur dioxide in a sulphuric acid plant.
\[
\text{ZnO (s) + H}_2\text{SO}_4 (l) \rightarrow \text{ZnSO}_4 (aq) + \text{H}_2\text{O} \quad [\text{eq. 1.2}]
\]

After purification, the metallic zinc is obtained by electrolysis [eq. 1.3].
\[
\text{ZnSO}_4 (aq) + \text{H}_2\text{O}(l) \rightarrow \text{Zn(s) + 0.5 O}_2 (g) + \text{H}_2\text{SO}_4(l) \quad [\text{eq. 1.3}]
\]

The big advantage of the RLE process over the pyrometallurgic process [6] is the high purity of the produced zinc (> 99.9%), while the zinc produced by the pyrometallurgic process contains a lot of lead (0.7-3 wt%).
In the electrolytic process, after the leaching step, other metals, which are present in the ore, have to be removed. Some metals can be recovered to obtain valuable by-products (e.g. cobalt, nickel and copper), while others (iron, magnesium) cause difficult waste streams.

In this project, we will design a process to remove magnesium from the electrolyte circuit. The source of magnesium is the incoming ore, which contains about 0.2 wt% magnesium. Accumulation occurs in the process, as the natural magnesium bleed in the system is insufficient. A high concentration of magnesium in the zinc-electrolyte causes significant energy losses in the plant due to the increased solution viscosity (pumping requirements) and lower electrolysis efficiency. We assume a magnesium concentration below 15 g/l doesn’t give serious problems [P8].

A common method to remove magnesium is the so-called ‘basics’ process [5]. In this process CaCO₃ is added to the process stream, which causes precipitation [eq. 1.4].

\[
3 \text{CaCO}_3(s) + 4 \text{ZnSO}_4(aq) + 13 \text{H}_2\text{O}(l) \rightarrow \text{ZnSO}_4 \cdot 3\text{Zn(OH)}_2 \cdot 4\text{H}_2\text{O}(s) + 3[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](s) + 3 \text{CO}_2 (g)
\]

In this way, contaminated gypsum is formed, which has to be dumped. Due to environmental regulations, dumping of gypsum is now prohibited in the Netherlands.

The environmental regulations forced Budel Zink to design a new process. The production of gypsum is avoided with a biological sulphate-reduction process, described by Copini [4]. This process is economically unfavourable though. This is the reason we are trying to find an alternative way to remove magnesium.

Booster et al. [P8] have suggested a new approach [7]. Looking at the difference in thermodynamic solubility constants of zinc fluoride and magnesium fluoride, it should be possible to precipitate the magnesium fluoride out of the zinc sulphate solution. In this report, this possibility will be worked out in more detail. Throughout this report, this process will be referred to as membrane process.

Furthermore, we will design a new alternative to the existing processes ourselves. The chosen alternative consists of using an evaporator to concentrate the process stream in order to precipitate MgSO₄, ZnSO₄ and MnSO₄. This solid mixture will be separated, in order to obtain purified MgSO₄. Calculations and experiments have to be done to investigate the solubility products of zinc sulphate, manganese sulphate and magnesium sulphate in sulphuric acid.

In this report, all alternatives we thought about will be discussed. Arguments and relevant information obtained about this process are given for the choice made between these alternatives. After the justification of the choice for the evaporation process, the two processes will be worked out. The membrane process in chapters 5 until 11, and the evaporation process in chapters 12 until 18.

There are two boxes with a number in it in the block scheme (figure 1.1). These boxes stand for the optional locations in the process where we have chosen to place the magnesium removal step. The box with number 1 is the location where the membrane process will be implemented, while the evaporation process will be implemented at the place of box 2.
2 Process Option and Selection

2.1 Process Concept chosen

As proposed by Booster et al. [P8] a process will be worked out in detail for removal of magnesium from purified zinc sulphate solution by precipitation of magnesium ions as magnesium fluoride in a zinc production plant. Additionally, a second process concept, proposed by this CPD team will be worked out. In this process we concentrate the process stream using evaporation. Due to the increased concentration of ions, all metal sulphates will precipitate, which can then be separated. Both options will be discussed in this chapter in more detail.

It is decided to carry both processes out in continuous mode. For the evaporation process that choice was not very difficult, because the start-up of evaporators, which will be the most important part of the process, is not economically favourable. For the membrane process the choice is made to carry it out continuously, too. One of the most important reasons for this is the fact that the whole zinc plant works continuously, so it seems very logical to maintain this type of operation.

In both processes there will be a magnesium removal of approximately 250 ktpa.

2.1.1 Membrane Process

In this process part of the stream of the purified zinc sulphate solution entering the electrolysis unit will be redirected to the membrane process. A block scheme of the process is shown in figure 2.2.

In a precipitation tank, zinc fluoride is added. As a result, magnesium fluoride will precipitate while zinc sulphate remains dissolved [eq. 2.1].

\[
\text{ZnF}_2(\text{aq}) + \text{MgSO}_4(\text{aq}) \leftrightarrow \text{MgF}_2(\text{s}) + \text{ZnSO}_4(\text{aq}) \quad \text{[eq. 2.1]}
\]

To separate the formed solid from the process liquid a solid-liquid separator is necessary. In order to make saleable product MgF₂ is converted to MgO, using a 2-step process. In the first step MgF₂ is converted to Mg(OH)₂ following equation 2.2.

\[
\text{MgF}_2(\text{s}) + 2\text{NaOH}(\text{aq}) \leftrightarrow \text{Mg(OH)}_2(\text{s}) + 2\text{NaF}(\text{aq}) \quad \text{[eq. 2.2]}
\]
Magnesium hydroxide cannot be sold because part of the fluoride remains in the product. To overcome this problem and obtain a valuable product, decided is to add an extra reaction step in which magnesium oxide is formed [eq. 2.3]

\[
\text{Mg(OH)}_2 (s) \rightarrow \text{MgO} (s) + \text{H}_2\text{O} \quad \text{[eq. 2.3]}
\]

The sodium fluoride from the conversion process is recycled to the magnesium precipitation vessel via electrolysis. A schematic picture of the electrolytic cell is shown in figure 2.1.

In the electrolytic cell the following reactions take place:

\[
\text{Zn} (s) \rightarrow \text{Zn}^{2+} (aq) + 2e^- \quad \text{[eq. 2.4]}
\]
\[
2 \text{H}_2\text{O} (l) + 2e^- \rightarrow 2 \text{OH}^- (aq) + \text{H}_2 (g) \quad \text{[eq. 2.5]}
\]

Equation 2.4 takes place at the zinc anode (left compartment) and equation 2.5 takes place at a steel cathode (right compartment). Sodium fluoride is led into the middle compartment where the fluoride ion goes to the left and the sodium ion to the right.

![Figure 2.1: Electrolytic cell for membrane process](image)

After the ZnF$_2$-precipitation the purified zinc sulphate solution has a too high fluoride concentration, 137 ppm at reaction temperature of 356K [7]. This is far above the acceptable 10 ppm. Fluoride concentration increases as more magnesium is removed and with decrease of pH [7]. It is also observed that the fluoride concentration decreases with higher reaction temperature [7]. In order to remove the fluoride from the solution, an extra process step has to be inserted.

The loss of zinc in the MgF$_2$ precipitation step is on average 20 kg zinc per ton magnesium removed, and is dependant of the washing of the precipitate with diluted acid, unwashed precipitates contain much higher zinc concentration.

The membrane process has some advantages. The selectivity for magnesium of the process is very large. Furthermore the amount of magnesium removal is relatively
easily controllable. There are no severe process conditions required. And a final advantage lies in the fact that precipitation processes are well understood in chemistry.

But unfortunately the process also has some weak points. One important drawback is the removal of the remaining fluoride from the zinc sulphate stream to an acceptable level. Fluoride is harmful for the electrolysis cell in concentrations above 10 ppm [7]. Without additional fluoride removal, the concentration will go beyond this limit (about 20 ppm). Another disadvantage is the presence of fluoride in the magnesium product, Mg(OH)₂, as there is no market for impure Mg(OH)₂. This has been solved by converting Mg(OH)₂ to MgO. There are also some uncertainties about the electrodialysis reactor that contains membranes, which have been investigated. These include the membrane replacement due to fouling, the decrease and control of fouling, and recycling loops for chemicals not 100 % converted.

---

**Figure 2.2: Block scheme of the membrane process**
2.1.2 Evaporation

In the evaporation process, the incoming stream is heated to the point where water starts to evaporate from the water/sulphuric acid mixture, as water has a lower boiling point than sulphuric acid. Due to the evaporation of water the ion concentrations of magnesium, zinc, manganese and sulphate increase. If enough water is evaporated this will lead to precipitation. For this purpose, solubility data from [8] are used.

The block scheme for the proposed process is shown in figure 2.3. The evaporator will be placed behind the electrolysis step of the zinc plant to minimize the amount of zinc sulphate, which has to be precipitated.

This process has a big advantage over the other alternatives. There are no additional chemicals necessary to separate the metal ions, so there are no additional separation steps required.

As usual there are also some disadvantages. The solubility products of the metal sulphates in sulphuric acid are unknown. This data is very important for the feasibility of the evaporation process. We have tried to overcome this difficulty by a combination of experiments and computer simulations.

Furthermore, the evaporation of water may be very costly. From a XRF analysis, it was concluded that about 48 % of the water has to be evaporated until solid metal sulphates are formed. In the models used, 70% of the water has to be evaporated until precipitation begins.

The last problem to be solved is the winning of pure magnesium sulphate to make it sellable.
2.2 Other Alternatives

During the first weeks of the project a lot of ideas have been generated. Most alternatives are obtained using Brainwriting pool method (see Appendix 6). Of all the generated alternatives a number of promising ideas have been looked upon in more detail. The other alternatives are summarized below:

- Zeolites
- Complex formation
- Selective membranes
- Ion exchanger
- Crown ethers
- Electrolysis of magnesium
- Calixarenes

Down here, we will discuss the advantages and the drawbacks of each alternative.

2.2.1 Zeolites [P1,P2,P3]

In this process, zeolites are used as ion exchanger. The zeolites may exchange the cations in solution for calcium cations or maybe even protons. In this particular case, zeolites are not easy to apply. Zeolites are silicium-aluminium structures. At the pH of 2.2 the aluminium in the zeolite will be ion-exchanged for protons. The solution has to be neutralized solution to at pH of about 5. This won’t be a very big problem, but finding a zeolite, which is selective enough to separate magnesium and zinc ions is. Furthermore the recovery of the used zeolites will be very difficult.

2.2.2 Selective membranes [P4,P5]

In this process, a selective membrane is used, which is impermeable for zinc but allows magnesium ions to pass. As a result, the membrane will function as an ion exchanger. The magnesium ions will be exchanged for a small cation, such as H⁺. In theory it’s possible to design such a membrane, but research would take a very long time, approximately 10 years, so it’s not an option here [P4]. Membranes are also expensive and there might be problems with fouling and scaling.
2.2.3 Ion exchanger [1,2,P6]

To separate magnesium ions from the zinc solution, ion exchangers could be useful. There are two options: the ion exchangers could be integrated in the process either before or after the electrolysis step. The stream leaving the electrolysis unit contains less zinc ions but has a pH of about 0.

There appears to be no ion exchanger for selective removal of magnesium [P6]. However, ion exchangers selectively removing zinc out of a zinc sulphate solution exist (type Duolite ES-63) [1]. As the zinc concentration is much higher than magnesium concentration and we want to avoid any loss of zinc, the option of removing zinc from a solution that contains in comparison to zinc very little magnesium is not a workable solution.

Another phenomena could be of importance here: in an acidic environment, zinc will form multivalent anionic complexes, which can be captured by an anion exchanger. Three types of exchangers are known that are suitable for this task [2].

2.2.4 Electrolysis of magnesium

This unit should be integrated in the system in the stream leaving the zinc electrolysis unit. The target is here to remove magnesium out of this stream since less zinc is present. The main problem here is the fact that Mg$^{2+}$ is a very weak oxidant. Even water and sulphate will be reduced before magnesium is; in the zinc electrolysis step this problem is solved by the use of specially designed electrodes, but it is unlikely that a similar electrode for specific magnesium removal exists.
2.2.5 Complex formation [3,P7]

In this process, a selective complex forming agent is added to the purified zinc sulphate solution. The metallic complex could be separated from the main stream using a two-phase system (organic-inorganic). The complex ion will be recovered from the organic phase, while the complex formation agent will be recycled to the reactor.

As a complex forming agent, EDTA looks promising since the dissociation constants for the complexes of the two ions differ by a factor $10^8$, for magnesium EDTA complex $2.0 \times 10^{-9}$ mol/l and for zinc EDTA complex $3.2 \times 10^{-17}$ mol/l [3].

This process also has a number of disadvantages:

- The pH of the purified zinc solution is about 2.2. Because protons will compete for ligand positions, complexes are highly unstable at such a low pH. Only at pH 4 or higher, stable complexes will form [P7]. This means the solution has to be diluted or a basic agent has to be added, such as ZnO.
- Since zinc has electrons in its d-orbital and magnesium has not, the affinity for complexation of zinc is much higher than of magnesium. Therefore no selectivity towards magnesium can be obtained. Again it is not a workable solution to remove all zinc from a solution that contains 0.2 wt% magnesium.
- It is still unclear how the organic phase could be regenerated. The only option here seems to be a back extraction, but a lot of steps (>100) will be needed [P7]

2.2.6 Crown ethers and Calixarenes [P5]

In contrast to the complexation mentioned above, crown ethers and calixarenes have a somewhat heightened affinity for alkali and earth-alkali cations. Having a fixed ring size, a crown ether can selectively form a complex with cations with a matching ion radius. Both crown ethers and calixarenes can be used in the following ways:

- Immobilization in an ion exchange resin [P5], or
- Using a supported liquid membrane extraction [P5].

This is carried out by impregnating the membrane pores with extractant solution and feeding the solution that needs to be purified at one side of the membrane and the strip solution at the other.

Using calixarenes, sufficient selectivity towards magnesium can be achieved.

Some problems here are:

- Crown ethers are highly toxic and expensive, so they need to be recycled to reduce costs and environmental damage [P5].
- Calixarenes are even more expensive than crown ethers [P5].
- The availability of crown ethers and calixarenes is limited [P5].
- The ionic radii of zinc and magnesium are about the same, so the selectivity in the case of using crown ethers could be questioned [P5].
- An extra unit has to be included for regeneration of the crown ether/calixarene [P5].
2.2.7 Comparison of the different options

All different options are compared with respect to the following selection criteria:

1. Is it technically achievable?
2. Is it economically achievable?.
3. Innovativity
4. Certainty
5. Environmental impact
6. Safety

By each alternative and criteria minuses, zeros and pluses have been awarded. The summation of minuses, zeros and pluses for each alternative is called \( W_1 \). As the technical achievability is most important criteria it has been given a weighing factor 2. After the application of the weighing factor for technical achievability the corresponding summation is called \( W_2 \) (see table 2.1).

Table 2.1: Selection of alternatives based on different selection criteria

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Because the evaporation process is the best alternative besides the membrane process, this process will be worked out in detail.
3 Basis of Design

3.1 Plant capacity

3.2.1 General

The zinc plant in Budel produces more than 200,000 t/a zinc [4]. In our design, we assumed a production of 220,000 t/a. Therefore the electrolytic zinc plant uses 400,000 t/a zinc concentrate. The typical cell house input for an electrolytic zinc plant is 300 m³/h [7].

Booster calculates the amount of magnesium to be removed, using the assumption of 0.2 wt.% magnesium in zinc sulphide concentrates [7]. In a plant, which processes 400,000 t/a zinc concentrates, the amount of magnesium that has to be removed is 400,000*0.2=800 t/a (91 kg/h). In this approach the natural bleed streams of the process are neglected.

Copini [4] takes only 0.5 m³/h of the process stream to remove the magnesium. Assuming this stream contains 10 kg/m³ magnesium, the total removal will be 43.8 t/a (5.0 kg/h).

To design a robust process, we decided to choose the total amount of magnesium to be removed at 250 t/a.

3.1.2 Membrane

In the membrane process we will assume to remove 50% of the incoming magnesium. Following this assumption, we will need a purified solution stream of (28.5/0.5)/10=5.7 m³/h. (However, in the design of the process the magnesium removal is mistakenly set to 100%, while the purified solution stream was still 5.7 m³/h. Therefore all equipment is designed twice as large as needed.)

For the membrane process as base chemicals ZnF₂(s), NaOH (aq), Zn(s) and water will be used. As there will be loss of fluoride in the process, it can be supplied in form of ZnF₂ (s). NaOH (aq) will be supplied in the start up of the process. Water has to be supplied, as there is conversion of water in the electrolytic cell. The Zn anode in the electrolytic cell also has to be replaced from time to time.

In the membrane process the magnesium from the purified zinc sulphate solution will be converted from MgF₂ to Mg(OH)₂. Then the Mg(OH)₂, which is contaminated with a small amount of MgF₂ will be calcined so MgO (s) and HF (g) are formed. The MgO will be sold while the HF will be recycled. Dependent on the bleed stream mentioned above our aim is to produce 415 t/a MgO.

The membrane process will be done in continuous mode. We assume the membranes have to be changed each 9 months. This will cause a down time of 3 days. Furthermore due to fouling the membrane has to be cleaned each 3 months. This can be done by mechanical removal, by changing the acidity or by changing stream direction. The time needed for cleaning is assumed to be 1 day. Hereby we will get a
processing time of \((365-3 \times 12/9-4 \times 1) \times 24 = 8568\) h/a. When we take into account some unforeseen down time (about 4\%), the process will run 8225 h/a.

A common estimate for the economical plant life of a petrochemical process is 15 years. The economical plant life for this process is assumed to be 10 years, due to uncertainties about the membrane reactor.

3.1.3 Evaporation

In the evaporation process we assume a removal of 70\% of the incoming magnesium. This will give a stream of \((28.5/0.7)/10.0 = 4.1\) m\(^3\)/h.

In the evaporation process no additional chemicals are used. The magnesium will be sold as MgSO\(_4\), which is produced at a rate of 1238 t/a.

Heat integration with the current plant units is possible. 1 Ton steam/h of 200 °C and 6 bara is produced and available in the roasting process. Furthermore 300 m\(^3\)/h steam of a lower quality is produced at the leaching process. This lower quality steam is not used in the design.

This process will also be in continuous mode. This is the most efficient way to use and recycle the energy, which is necessary. Taking into account a downtime of 4\%, the process runs 8410 h/a.

For this process we estimate the economical plant life to be 15 years.

3.4 Location

The processes that are being worked out in this CPD project will be incorporated in the Budel Zink B.V., a metallurgical-chemical company that is located in Budel-Dorplein, (Municipality Cranendonck) in the Netherlands.
3.5 Battery Limit

In order to place the battery limit of the magnesium removal process within the complete zinc plant, see figure 1.1. The block marked 1 is the place where the membrane process will be implemented (between purification and electrolysis), whereas the evaporation process will be located between electrolysis and leaching (block marked 2).

As the current biological process part of the purified solution is redirected to the SRB plant already, we assume no new splitter is needed in our design.
3.6 In and out going streams

In the following tables information about the streams crossing the above mentioned battery limit will be provided for the precipitation and the evaporation process.

3.7.1 Membrane process

Table 3.1: Membrane process, incoming purified solution

<table>
<thead>
<tr>
<th>Stream Name:</th>
<th>Available Design</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Units</td>
<td>Specification</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>g/l</td>
<td>419.8</td>
<td>Design data are taken from [7].</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>g/l</td>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>MnSO₄</td>
<td>g/l</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>g/l</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>g/l</td>
<td>820.6</td>
<td></td>
</tr>
<tr>
<td>Traces: Ca, Si, K, Al, C</td>
<td>g/l</td>
<td>&lt; 0.5</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1301.2</td>
<td></td>
</tr>
</tbody>
</table>

Process Conditions and Price

| Temp. ºC | 35-80 |
| Press. Bar | 1 |
| Phase V/L/S | L |
| Price | - |

Table 3.2: Membrane process, ZnF₂

<table>
<thead>
<tr>
<th>Stream Name:</th>
<th>Available Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Units</td>
<td>Specification</td>
</tr>
<tr>
<td>ZnF₂ kg/h</td>
<td>33.6</td>
</tr>
<tr>
<td>Total</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Process Conditions and Price

| Temp. ºC | 20 |
| Press. Bar | 1 |
| Phase V/L/S | S |
| Price €/kg   | 2.8 |
### Table 3.3: Membrane process, \( \text{H}_2\text{O} \)

<table>
<thead>
<tr>
<th>Comp. Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} ) kg/h</td>
<td>58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

| Temp. | \( ^\circ\text{C} \) | 20 | |
| Press. | Bar | 1 | |
| Phase | V/L/S | L | |
| Price | €/ton | 0.60 | (49) |

### Table 3.4: Membrane process, Zn templates

<table>
<thead>
<tr>
<th>Comp. Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn kg/h</td>
<td>132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>132</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

| Temp. | \( ^\circ\text{C} \) | 20 | |
| Press. | Bar | 1 | |
| Phase | V/L/S | S | |
| Price | €/kg | 0.85 | |

### Table 3.5: Membrane process, NaOH

<table>
<thead>
<tr>
<th>Comp. Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NaOH} ) kg/h</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

| Temp. | \( ^\circ\text{C} \) | 20 | |
| Press. | Bar | 1 | |
| Phase | V/L/S | L | |
| Price | €/kg | 0.22 | |
### Table 3.6: Membrane process, ZnO

<table>
<thead>
<tr>
<th>Stream Name: ZnO</th>
<th>Comp. Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>kg/h</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

- Temp. °C: 20
- Press. Bar: 1
- Phase V/L/S: S
- Price €/kg: 1.9

### Table 3.7: Membrane process, Fuel, CH₄

<table>
<thead>
<tr>
<th>Stream Name: CH₄</th>
<th>Comp. Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>kg/h</td>
<td>14.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>14.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

- Temp. °C: 20
- Press. Bar: 1
- Phase V/L/S: V
- Price €/MJ: 0.0064

### Table 3.8: Membrane process, Air

<table>
<thead>
<tr>
<th>Stream Name: Air</th>
<th>Comp. Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>kg/h</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>kg/h</td>
<td>208</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

- Temp. °C: 20
- Press. Bar: 1
- Phase V/L/S: V
- Price €/kg: -
### Table 3.9: Membrane process, SiO$_2$

<table>
<thead>
<tr>
<th>Stream Name: SiO$_2$</th>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>kg/h</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>S</td>
</tr>
<tr>
<td>Price</td>
<td>€/kg</td>
<td>107.4</td>
</tr>
</tbody>
</table>

### Table 3.10: Membrane process, Al$_2$(SO$_4$)$_3$

<table>
<thead>
<tr>
<th>Stream Name: Al$_2$(SO$_4$)$_3$</th>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>kg/h</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>-</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>S</td>
</tr>
<tr>
<td>Price</td>
<td>€/kg</td>
<td>0.257</td>
</tr>
</tbody>
</table>

### Table 3.11: Membrane process, purified solution back to plant

<table>
<thead>
<tr>
<th>Stream Name: Purified Solution back to plant</th>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnSO$_4$</td>
<td>g/l</td>
<td>419.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgSO$_4$</td>
<td>g/l</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MnSO$_4$</td>
<td>g/l</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$SO$_4$</td>
<td>g/l</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>g/l</td>
<td>820.6</td>
<td></td>
</tr>
<tr>
<td>Traces: Ca, Si, K, Al, C</td>
<td>Traces: Ca, Si, K, Al, C</td>
<td>g/l</td>
<td>&lt; 0.5</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>Total</td>
<td>1276.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>L</td>
</tr>
<tr>
<td>Price</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1) The manganese concentration should be at least 4 g/l (to prevent pyrolusite, MnO$_2$, formation), which corresponds to 11 g/l manganese sulphate.
### Table 3.12: Membrane process, magnesium to be sold

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>kg/h</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>kg/h</td>
<td>94.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>kg/h</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>kg/h</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>kg/h</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>112.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>K</th>
<th>293.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>S</td>
</tr>
<tr>
<td>Price</td>
<td>€/kg</td>
<td>0.388</td>
</tr>
</tbody>
</table>

[43]

### Table 3.13: Membrane process, Off-gas

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>kg/h</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>kg/h</td>
<td>94.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>kg/h</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>141.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>V</td>
</tr>
<tr>
<td>Price</td>
<td>€/kg</td>
<td>-</td>
</tr>
</tbody>
</table>

[43]

### Table 3.14: Membrane process, Alumina silicate fluoride

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>kg/h</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>kg/h</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSO₄</td>
<td>kg/h</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂(SiF₆)₃</td>
<td>kg/h</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>S</td>
</tr>
<tr>
<td>Cost</td>
<td>(€/year) x1000</td>
<td>18</td>
</tr>
</tbody>
</table>
### 3.7.2 Evaporation Process

#### Table 3.15: Evaporation process, incoming purified solution

<table>
<thead>
<tr>
<th>Stream Name:</th>
<th><strong>Incoming Purified Solution</strong></th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄</td>
<td>g/l</td>
<td></td>
<td>74.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSO₄</td>
<td>g/l</td>
<td></td>
<td>49.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSO₄</td>
<td>g/l</td>
<td></td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>g/l</td>
<td></td>
<td>210.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>g/l</td>
<td></td>
<td>820.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Traces:</td>
<td></td>
<td></td>
<td>&lt; 0.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ca,Si,K,</td>
<td>g/l</td>
<td></td>
<td></td>
<td></td>
<td>Design data are taken</td>
</tr>
<tr>
<td>Al,C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>from [7].</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1165.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Process Conditions and Price

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>°C</td>
<td>42</td>
</tr>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>L</td>
</tr>
<tr>
<td>Price</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In the evaporation process it is assumed that 70% of the incoming magnesium will be removed. We use a bleed stream of 4.1 m³/h.

#### Table 3.16: Evaporation process, incoming steam

<table>
<thead>
<tr>
<th>Stream Name:</th>
<th><strong>Steam</strong></th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>kg/h</td>
<td></td>
<td>949</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>949</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Process Conditions and Price

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>°C</td>
<td>200</td>
</tr>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>6</td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>V</td>
</tr>
<tr>
<td>Price</td>
<td>€/kg</td>
<td>0.0112</td>
</tr>
</tbody>
</table>
### Table 3.17: Evaporation process, incoming fuel

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>kg/h</td>
<td>112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>112</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Price</td>
<td>€/MJ</td>
<td>0.0064</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.18: Evaporation process, incoming Air

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>kg/h</td>
<td>447</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>kg/h</td>
<td>1565</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>2012</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Price</td>
<td>€/kg</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.19: Evaporation process, purified solution back to plant

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Units</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄</td>
<td>g/l</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSO₄</td>
<td>g/l</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSO₄</td>
<td>g/l</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>g/l</td>
<td>957</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>kg/h</td>
<td>3144</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Traces:</td>
<td>g/l</td>
<td>&lt; 0.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ca,Si,K,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AI, C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>4173</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>°C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Press.</td>
<td>Bar</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>V/L/S</td>
<td>L</td>
<td></td>
</tr>
<tr>
<td>Price</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.20: Evaporation process, magnesium sulphate to be sold

<table>
<thead>
<tr>
<th>Stream Name: Magnesium to be sold (from evaporation process)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comp.</strong></td>
</tr>
<tr>
<td>MgSO₄</td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

| Temp. | °C | 20 |
| Press. | Bar | 1 |
| Phase | V/L/S | S |
| Price | €/kg | 0.419 |

[42]

### Table 3.21: Evaporation process, exiting water

<table>
<thead>
<tr>
<th>Stream Name: Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comp.</strong></td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

| Temp. | K | 300 |
| Press. | Bar | 1 |
| Phase | V/L/S | L |
| Price | €/kg | - |

### Table 3.22: Evaporation process, off-gas

<table>
<thead>
<tr>
<th>Stream Name: Off-gas</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comp.</strong></td>
</tr>
<tr>
<td>CO₂</td>
</tr>
<tr>
<td>N₂</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

| Temp. | K | Different T’s |
| Press. | Bar | 1 |
| Phase | V/L/S | V |
| Price | €/kg | - |
Table 3.23: Evaporation process, ZnO back to roasting

<table>
<thead>
<tr>
<th>Stream Name: Water</th>
<th>Specification</th>
<th>Notes</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp.</td>
<td>Units</td>
<td>Available</td>
<td>Design</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>kg/h</td>
<td></td>
<td>949</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>949</td>
</tr>
</tbody>
</table>

**Process Conditions and Price**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Press.</th>
<th>Phase</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>Bar</td>
<td>V/L/S</td>
<td>€/kg</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>L</td>
<td>-</td>
</tr>
</tbody>
</table>
4 Thermodynamic Properties

The pure component properties of the substances which are used are available in appendix 4.1.

4.1 Aspen

Aspen is a simulation program very suitable for calculations of a chemical plant. However, Aspen is not that suitable when certain inorganic compounds are involved. In our case where electrolytes are involved, Aspen is not able to deal with streams that contain both electrolytes and solid phase with particle size distribution. Crucial equilibrium data of different hydrates where missing, it has been tried to use the data from International Critical Tables [8], but without success.

4.2 Estimation of total precipitation and precipitant composition

For the evaporation process, a Matlab script (appendix 4.2) has been used to determine the amount of metal sulphate precipitated related to the fraction of water evaporated. In this script, the influence of sulphuric acid on the equilibrium is taken into account. From [8] and [9], two sets of equilibrium constants have been taken. For both cases, the resulting concentrations and amount of metal sulphates precipitated have been calculated. In figures 4.1 and 4.2, the resulting concentrations are shown using the data obtained from [8], in figures 4.3 and 4.4 from [9]. The dashed lines represent the solubility; the solid lines represent the actual concentration.
As different sources gave different solubility data, see figures above, the worst-case scenario have been . The worst-case scenario will be when zinc sulphate precipitates first. For this reason, the data taken from [8] will be used for further calculations.

There are 2 options worked out for separating the solid metal sulphates. The first one is to add water, and to use the difference in water solubility to completely dissolve zinc and manganese sulphate, while part of the magnesium sulphate will still be in the solid phase when equilibrium is reached. To determine whether this is possible, the ratio of the solubility’s has been determined as a function of temperature (see figure 4.5). Data are taken from [8].
However, there are a number of assumptions made:
- solubility data from different hydrates have been combined, because the temperature ranges given for the different hydrates were limited.
- data are only limited to 100 °C, while the operating conditions are at higher temperatures.

For this reason, an analysis of the solubility’s for the anhydrates has been made, as shown in figure 4.6. Data are taken from [9]

Figure 4.6: solubility ratio of the different anhydrous salts in water

Again, the temperature range is limited to 100 °C. Because above 100 °C it is likely that anhydrous salts will precipitate, figure 4.6 seems more reliable.
From figure 2, it is clear that, when all water has been evaporated, the relative amount of zinc sulphate precipitated compared to magnesium sulphate, will be about 3:1. This value will only be higher when only part of the water is evaporated. From figure 4.6, it is clear that no good separation between zinc and magnesium sulphate can be achieved by adding water, because zinc sulphate and magnesium sulphate will dissolve in a maximum ratio of 3.3:1 at 20 °C. In theory this would yield 0.11 g solid MgSO4 (assuming the data used are accurate enough) per liter process stream treated, but this value is so low, that very large quantities of water would have to be evaporated.

Another option is to design a two-stage evaporator; the first unit is used to precipitate ZnSO4, which will be recycled back to the leaching step. The remaining solution will then be further evaporated in a second evaporator; the ratio at which the metal sulphates will precipitate will be about Zn:Mg:Mn = 5:2.5:1, according to data from [8]. Of course, this ratio is equal to the solubility’s of the 3 metal sulphates (because the sulphate concentration which determines the solubility in our process will cancel out when the ratio is taken). A separation using water is only possible if the ratio of the equilibrium constants changes with temperature, and according to figure 4.6, it does not.

From figure 4.4, it is clear that it might be possible to obtain solid magnesium sulphate by evaporation of 70 % water per litter process stream. This would yield about 2 g solid MgSO4 per litter. To remove the desired amount of magnesium, 14.3 m³/h has to be evaporated. Because evaporating water is very costly, the amount of process stream treated should be kept to a minimum. Also, because the two salts will begin to precipitate at about the same time, a minor change of the value of equilibrium constant may result in earlier precipitation of zinc sulphate instead of magnesium sulphate.

In general, the process is not robust enough to cope for small changes in the process stream and/or operating conditions.

Some basic experiments have also been done. These are described in (Appendix 4.3). When the results are compared to the mathematical model used, the following conclusions could be drawn:

- In the experiment, salts began to precipitate when about 40 to 45 % of the water was evaporated; according to the mathematical models, precipitation should not occur until about 65% of the water is evaporated.
- From the experiment, it is unknown which salt(s) precipitate first; at the first measuring point (48% water evaporated), all three metal sulphates were present in the precipitant.
- The composition of the precipitated salts from the experiments is roughly the same as calculated with both models.

In general, it is still unsure which model comes closest to reality.
4.3 Calculating the enthalpy of flows

In the stream summary every flow has an enthalpy given in kW. Calculations of these enthalpies can be found in appendix 4.4: Enthalpy calculations.

On the lower left side of the file (appendix 4.4) the stream data for the flow of which the enthalpy has to be calculated can be found.
On the right side of this table the heating enthalpies can be found. Here for each component the enthalpy (kW) is calculated, using \( T=298.15 \) K as a reference temperature.
The parameters A, B, C and D have been used in formula 2:

\[
dH = c_p dT = (A + BT + CT^{-2} + DT^2) dT
\]  
\[\text{[eq.4.1]}\]

Which, if integrated, becomes:

\[
\Delta H = \left( AT + \frac{1}{2} BT^2 - CT^{-1} + \frac{1}{3} DT^3 \right)_{298.15}
\]  
\[\text{[eq.4.2]}\]

A reference temperature of 298.15 Kelvin has been used.
If \( \Delta H \) is multiplied by the size of the stream from the table containing the stream data enthalpy can be converted to kW for each component.

Below the table with heating enthalpies the formation enthalpy of the entire flow (in kW) is calculated by multiplying the formation enthalpies of each component with the flow size of that component.

\[
\Delta H_{\text{formation}} = \Delta H_{f,H_2O} n_{H_2O} + \Delta H_{f,H_2SO_4} n_{H_2SO_4} + \ldots.
\]  
\[\text{[eq.4.3]}\]

\( \Delta H_{\text{heating}} \) and the \( \Delta H_{\text{formation}} \) yield the enthalpy of the entire stream which can be found in the stream summary.

Because there is a difference in enthalpy between vapours and liquids/solids due to the evaporation enthalpy, an extra parameter ‘\( n \)’ is introduced. If this is 0 it makes the enthalpy calculations without evaporation enthalpies. If it is 1, it takes into account the evaporation enthalpy in calculating the formation enthalpy.

It should be noted that the difference between solid and solved compounds is being neglected because the solvation enthalpy is almost equal to the lattice enthalpy. So taking these two enthalpies into account would make the calculations more difficult with only a very limited or even no influence on the final result.
4.4 Density

Throughout the design, a rough estimation is made to estimate the density of the streams. We have assumed a density of all liquid streams equal to 1000 kg/m³. The densities of all solid streams are set equal to 3500 kg/m³. The density of streams containing solids is estimated with the following equation.

\[ \rho_{\text{slurry}} = x_{\text{liquid}} \rho_{\text{liquid}} + x_{\text{solid}} \rho_{\text{solid}} \]  

[eq.4.4]

In this equation \( x_{\text{liquid}} \) and \( x_{\text{solid}} \) are the mass fraction liquid and solid present in the slurry.

This assumption is used throughout the report unless mentioned otherwise.
Membrane Process
5 Process Structure and Description

Starting with the block scheme as given in chapter 2.2 we will now translate the operations per block to unit operations constituting the flow sheet. The stream numbers and unit numbers refer to the flow sheet given in chapter 5.2.

5.1 Criteria and Selection of equipment

5.1.1 MgF₂ precipitation

The precipitation reaction is performed in a mixing unit. A hopper does addition of zinc fluoride.

5.1.2 Liquid solid separation

Thickener V101

The stream <102> leaving the mixer M101 in which MgF₂ has precipitated has following composition:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>ρ (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>3.777E+04</td>
<td>1301*</td>
<td>29.03</td>
<td>98.05</td>
</tr>
<tr>
<td>Solid</td>
<td>7.53E+02</td>
<td>3141**</td>
<td>0.24</td>
<td>1.95</td>
</tr>
</tbody>
</table>

* calculated from stream <101> with size of 5.7 m³/h
** density of MgF₂ as most of the solids is MgF₂.

One part of the precipitated MgF₂, the smallest particles, will be needed in the membrane cell, the remaining larger particles will be converted to Mg(OH)₂. The small particles solid are needed to prevent fouling in the membrane cell [5]. As the stream contains very low amount solid the most suitable type of liquid/solid separators are the thickeners before any other type of liquid/solid separator can be used [10]. Thickeners are also most suitable for handling large streams.

Hydrocyclone S101

Stream <105> leaving the thickener V101 has the following composition:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>ρ (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>2.259E+03</td>
<td>1301*</td>
<td>1.74</td>
<td>75</td>
</tr>
<tr>
<td>Solid</td>
<td>7.53E+02</td>
<td>3141**</td>
<td>0.24</td>
<td>25</td>
</tr>
</tbody>
</table>

* calculated from stream <101> with size of 5.7 m³/h
** density of MgF₂ as most of the solids is MgF₂.
The concentrated solid, MgF₂, from thickener V101 needs to be classified as small particles are needed in the membrane cell for scrubbing of the membranes in order to prevent fouling [5]. The larger particles will be converted to Mg(OH)₂. In order to classify solids on their size the choice can be made between filters and hydrocyclones. As solid MgF₂ will be converted in the next step to Mg(OH)₂, it is important that the solid MgF₂ contains as less liquid as possible to prevent to much impurities in the Mg(OH)₂. Filters normally produce solids with 40 wt% liquid and solids leaving hydrocyclones will contain 25 wt% liquid, for that reason the choice has been made for hydrocyclone.

5.1.3 MgF₂ - Mg(OH)₂ conversion

Mixing unit M104

The conversion of MgF₂ to Mg(OH)₂ by addition of NaOH takes place in a mixing unit. The solid Mg(OH)₂ is then filtered in S102.

5.1.4 Liquid Solid separation

Sedimentation Centrifuge S102

Stream <117> with precipitated Mg(OH)₂ to be treated has the following composition:

Table 5.3: Composition of stream <117> from the membrane process

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>(\rho) (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.53E+02</td>
<td>1301*</td>
<td>0.31</td>
<td>84</td>
</tr>
<tr>
<td>Solid</td>
<td>1.39E+02</td>
<td>2370**</td>
<td>0.059</td>
<td>16</td>
</tr>
</tbody>
</table>

*calculated from stream <101> which has size of 5.7 m³/h
** density of Mg(OH)₂

All of the solid Mg(OH)₂ which constitutes 16wt% of the stream <117> needs to be removed. The solids should be as dry as possible to reduce the loss of sodium, which is present in the liquid as NaF and NaOH. The more liquid remains in the solids, the more heat needs to be supplied in the rotary kiln R102. However if solid to be treated in the rotary kiln wouldn’t contain liquid, the outgoing gasses would contain more concentrated HF at high temperatures. For treatment of streams containing more than 10wt% solids centrifuges and filters are mostly used [10]. As the solids entering the rotary kiln shouldn’t contain to much liquid which needs to be evaporated and shouldn’t be very dry because of the presence of HF in the gas leaving rotary kiln at high temperatures, the choice has been made for sedimentation centrifuge for which is assumed that the solids will contain 25 wt% liquid.

Scroll discharge decanter type sedimentation centrifuge, a continuous operating centrifuge seems to be the best choice for the above mentioned stream characteristics, as the treated stream contains 16 wt % solid and continues operation is required [10]. To justify the choice of scroll discharge decanter type sedimentation centrifuge a sigma value of the centrifuge can be calculated and compared with the desired values from the literature:
Sigma theory

\[ Q = u_g \Xi \quad [\text{eq.5.1}] \]

\[ u_g = \frac{\Delta \rho d_s^2 g}{18 \mu} \quad [\text{eq.5.2}] \]

From the data of stream <117> of the membrane process \( Q/\Xi \) can be calculated:

Data and assumptions:

- particle size varies from 20 \( \mu \)m till 400 \( \mu \)m
- \( \mu = 4.0 \times 10^{-3} \) Pa*s
- \( d_s = 5 \times 10^{-6} \) m

\[ Q/\Xi = \frac{2 \Delta \rho (d_s)^2 g}{18 \mu} = 7.23 \times 10^{-6} \text{ m/s} \quad [\text{eq.5.3}] \]

The normal operating range of solid bowl scroll discharge is 0.7 m\(^3\)/h at 1.5E-06 m/s to 15 m\(^3\)/h at 1.5E-05 m/s [10]. For stream <117> flow is equal to 0.37 m\(^3\)/h at \( Q/\Xi \) of 7.23E-06 m/s. As the calculated values falls just outside normal operating range of a solid bowl scroll discharge type, scroll discharge decanter type can be used.

To obtain the idea of the size of the machine needed the sigma value is calculated where efficiency for solid bowl scroll discharge type centrifuges is equal to 0.6 [10].

\[ \Xi = \frac{Q}{(\text{eff}) 2 u_g} = \frac{1.705E-4}{(0.6 \times 2 \times 3.64E-06)} = 24 \text{ m}^2 \quad [\text{eq.5.4}] \]

The sigma value is the equivalent area of a gravity settler that would perform the same separation as the centrifuge.

5.1.5 Mg(OH)\(_2\) - MgO conversion

*Rotary kiln R102*

In order to calcinate the solids, process of heating solid material to drive out the volatile chemically combined component, high temperatures are required. The best-known furnaces for this kind of operation are the Herreshoff furnaces. As the Herreshoff furnaces date from twenties of the preceding century, they have made the way for Rotary kiln furnaces with much better energy saving. Rotary kiln furnaces are more flexible. Different variables can be changed to process different feeds, such as the inclination of the furnace and the rotational speed. However the residence time for different particle size in the Herreshoff furnace is same as the furnace is operated vertically in contrast to Rotary kiln, which is operated under inclination and where the larger particles will roll faster down the reactor. Rotary kilns are easier to design for processing smaller feeds.

*Air-cooled heat exchanger E101*

The stream <129> from rotary kiln containing hot gasses at 520 K needs to be cooled down, before entering fluidised bed FB101. As the gasses will be cooled down to 338
K, air-cooled heat exchangers are the best choice in contrast to cooling water heat exchangers [10]. Cooling water heat exchangers are used for process temperatures below 323 K [10].

**Cooling unit FB101**

The way of cooling of solid material depends much of the particle size. Granulates can be cooled by flowing liquid through a plate heat exchanger, while particles with a size of about 100 µm can best be cooled by using a fluidised bed with a cooling coil [11]. The particle size of the products of the rotary kiln is assumed to be between 20 to 200 µm. Therefore a fluidised bed is the best option for cooling the solid.

**Flue gas cleaning M105**

Flue gas, stream <129>, is formed in the rotary kiln (R102). It contains, besides reaction products of the methane combustion, sulphuric acid, sulphur trioxide and hydrofluoric acid. The gases should be removed from the flue gas before venting. Besides the hazardous nature of these gases recycling them is also profitable. The location where this recycle is closed can be chosen at two points in the process.

First of all the gas can be stripped by using stream <101>. Hereby the fluoride can be used directly in the precipitation step. However sulphuric acid, sulphur trioxide (forming sulphuric acid in water) and hydrofluoric acid decrease the pH of the solution to a value of 0.9. This is an unwanted effect while a low pH (below 2) results in too high a zinc loss [12]. Even if the magnesium removal were set to 50% instead of 100% (as stated in the Basis Assumptions) the pH would have a value of 1.2. A second option to recycle the gases is to strip the flow using stream <119>. The hydrofluoric acid reacts with unconverted sodium hydroxide to form sodium fluoride. A disadvantage of this recycle is the fact that the amount of sodium fluoride, which needs to be converted in the membrane reactor, increases somewhat. The amounts of sulphuric acid and sulphur trioxide are very small, so this doesn’t influence the choice for recycling the gasses by stream <119>.

**Filtration Centrifuge S103**

Stream <134> to be treated has the following composition:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>ρ (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.174E+01</td>
<td>1000*</td>
<td>0.072</td>
<td>40</td>
</tr>
<tr>
<td>Solid</td>
<td>1.067E+02</td>
<td>3600**</td>
<td>0.030</td>
<td>60</td>
</tr>
</tbody>
</table>

* as most of the liquid is water  
** density of MgO

The stream <134> contains mostly solid MgO 60 wt% and dissolved NaOH that needs to be removed. The solids should be as dry as possible. The solid liquid...
separator, which produces very dry cake, is the filtration centrifuge. The solids will contain 5 wt% liquid. The option to use a dryer is more costly and as the water is evaporated the dissolved NaOH would remain in the solid and reduce the purity.

5.1.6 Electro dialysis

Membrane Reactor R101

In order to regenerate sodium fluoride a membrane reactor is the only option. The use of membranes has, however, quite some disadvantages. These are:
- high investment costs
- short operational period
- high operational costs
- difficult in scaling
- little knowledge of operation

5.1.7 Fluoride removal

There are several ways to remove the fluoride from the zinc electrolyte solution, below some fluoride removing methods are summarized from Appendix 5.1:

Natural bleed:
- jarosite

Additional fluoride removal:
- Use of fluosilicic acid
- Use of silica, followed by addition of aluminium sulphate
- Use of titanyl sulphate dehydrate

The amount jarosite needed to remove fluoride will be small and could be sent to waste treatment facility, however it is not clear if this option can be implemented, as the plant is not allowed to produce jarosite. For that reason this option will not be worked out.

Of the three remaining options the last one is the most promising. The three options will be mentioned in more detail below.

Use of fluosilicic acid

Fluosilicic acid, H₂SiF₆ decomposes under influence of heat to volatile SiF₄ and HF. By heating the zinc electrolyte solution it will be very easy to remove the fluoride from the solution in this way. However the decomposition reaction is too slow. The equilibrium constant at room temperature is 4.7E-15 and 4.5E-7 at 900 °C.

Use of silica, followed by addition of Al₂(SO₄)₃

The reaction of silica with fluoride is notorious. The following reactions take place between fluoride ions from a zinc electrolyte en SiO₂:
SiO₂ (s) + 6F⁻ (aq) + 4H⁺ (aq) → SiF₆²⁻ (aq) + 2H₂O (aq) \[\text{eq.5.5}\]

According to Rakhmankulov et al (Appendix 5.1), removal of fluoride can be accomplished by addition of Al₂(SO₄)₃ to zinc electrolyte in the presence of dissolved SiO₂. Experiments are described in which the reaction temperature was 333K and the addition of aluminium sulphate was followed by neutralisation with zinc oxide to pH=5.1. Thus, aluminium hydroxide was formed and the removal of fluoride was explained by a chemisorption mechanism. The fluoride level could be reduced to 10.6 ppm. At such a fluoride level, solutions can be returned to a zinc plant without causing problems in the cellhouse. The fluoride removal efficiency reportedly decreases from 8.5 ppm/gram Al(OH)₃/l solution at high fluoride levels (500-700 ppm) to 1.6 ppm/gram Al(OH)₃/l solution at low fluoride levels (10-50 ppm). The form of aluminium hydroxide determines the effectiveness of fluoride removal (amorphous aluminium hydroxide being most effective and crystalline gibbsite being hardly effective).

Direct addition of aluminium hydroxide to the solution is not effective as when aluminium compounds are freshly precipitated.

The following reaction takes place by addition of Al₂(SO₄)₃ in presence of SiO₂:

\[
\text{Al}_2(\text{SO}_4)_3 (\text{aq}) + 3 \text{SiF}_6^{2-} (\text{aq}) \leftrightarrow \text{Al}_2(\text{SiF}_6)_3 (\text{s}) + 3 \text{SO}_4^{2-} (\text{aq}) \quad \text{[eq.5.6]}
\]

Direct addition of aluminium hydroxide to the solution is not effective as when aluminium compounds are freshly precipitated.

The following reaction takes place by addition of Al₂(SO₄)₃ in presence of SiO₂:

\[
\text{Al}_2(\text{SO}_4)_3 (\text{aq}) + 3 \text{SiF}_6^{2-} (\text{aq}) \leftrightarrow \text{Al}_2(\text{SiF}_6)_3 (\text{s}) + 3 \text{SO}_4^{2-} (\text{aq}) \quad \text{[eq.5.6]}
\]

**Figure 5.1: Fluoride removal with Al₂(SO₄)₃**

*Use of titanyl sulphate dehydrate (TiOSO₄)*

Oohara (Appendix 5.1) proposes a method to remove fluoride from zinc sulphate solutions by addition of titanyl sulphate dehydrate (TiOSO₄) instead of an aluminium compound. The addition is followed by adjusting the pH with zinc oxide to 2.1-4.2 (but preferably 2.7). Fluoride ions are adsorbed to the hydrolysis product and separated from solution by filtration. The fluoride content could be reduced to 10 ppm (at pH=2.7).

We assume, the following reaction will take place by addition of TiOSO₄ to a zinc electrolyte solution:

\[
\text{TiOSO}_4(s) + 2\text{OH}^- (\text{aq}) + x\text{F}^- (\text{aq}) \leftrightarrow \text{TiO(OH)}_{2-x}\text{F}_x (\text{s}) + \text{SO}_4^{2-}(\text{aq}) + x\text{OH}^- (\text{aq}) \quad \text{[eq.5.7]}
\]
Figure 5.2: Fluoride removal with TiOSO₄

Justification for the chosen option

The usage of fluosilicic acid is not a good option. As mentioned above the reaction constant is too small to design a practical process.

The other two options do not have such obvious disadvantages. We assume both methods follow the principle of chemisorption. The aluminium sulphate process is more effective, because adding SiO₂ clusters six fluoride ions. The disadvantage is the need for two reaction steps in the process.

To compare the two processes, a rough cost estimation is made in appendix 5.2. Calculated are the costs for the chemicals necessary, which are summarized in table 5.5.

Table 5.5: Comparison of costs of different fluoride removal processes

<table>
<thead>
<tr>
<th></th>
<th>SiO₂/Al₂(SO₄)₃-process</th>
<th>TiOSO₄-process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical costs (euro/year)</td>
<td>105848</td>
<td>245975</td>
</tr>
</tbody>
</table>

From the table 5.5 follows that the SiO₂/Al₂(SO₄)₃-process is less costly than TiOSO₄-process and for that reason it will be implemented for fluoride removal.

Mixing units M102 and M103

The mixing units M102 and M103 are not combined while first the reaction of fluoride and SiO₂ should be completed. Then by lowering the pH the reaction of formation of the aluminum complex can be completed.

Clarifier V105

Stream <113> coming from mixer M103 has following composition:
Table 3.6: Composition of stream <113> from the membrane process

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>Flow (m$^3$/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.459E+03</td>
<td>1385*</td>
<td>5.4</td>
<td>100</td>
</tr>
<tr>
<td>Solid</td>
<td>1.10</td>
<td>negligible</td>
<td>negligible</td>
<td>negligible</td>
</tr>
</tbody>
</table>

* calculated from the composition of liquid phase and known densities of different components
** not available

Stream <113> contains precipitated Al$_2$(SiF$_6$)$_3$, which needs to be removed to prevent accumulation, as the liquid will be returned to the zinc plant. However the amount of solid present is negligible. In order to remove such low percentage solid from the liquid stream clarifiers are the best choice between liquid/solid separators. Clarifiers are low-cost, easy to design and easy to operate.
5.2 Process Flow Scheme

On the following pages the flow scheme of the membrane process can be found, with units mentioned in the preceding chapter 5.1 and designed in chapter 8, Process and Equipment Design.
page 1 flow sheet membrane process
back side page 1 flowsheet membrane
back side page 2 membrane flowsheet
5.3 Process Stream Summary

Process stream summary has been calculated using a Matlab script (Appendix 7.3), the accompanying assumptions can be found in appendix 7.2.
5.4 Utilities

The complete summary of the utilities required for the membrane process can be found in Appendix 5.3. In the table 5.7 the required utilities in the membrane process are summarized. Fuel and steam is not included in the utilities because they are already mentioned in the stream summary.

Table 5.7: Utilities, membrane process

<table>
<thead>
<tr>
<th>Utility</th>
<th>Process Unit(s)</th>
<th>Load (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>M101-106</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>P101-118</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>R101</td>
<td>0.4</td>
</tr>
<tr>
<td>Cooling water</td>
<td>FB101</td>
<td>38.2</td>
</tr>
<tr>
<td></td>
<td>M106</td>
<td>9.3</td>
</tr>
<tr>
<td>Air Cooler</td>
<td>E101</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Electricity is needed for the mixers, the pumps and the membrane reactor. Furthermore, cooling water is used in the fluidised bed, in order to cool the hot solid particles leaving the rotary kiln and in M106.

The last utility needed is air. Air is used to cool hot gases leaving the rotary kiln.
5.5 Process Yields

A quick overview of the overall process performance, in terms of process yields, is given in appendix 5.4.

There is one existing process that removes magnesium out of the purified solution, being the biological USB process [4]. In chapter 20, the membrane process will be compared to the biological process, and to the evaporation process as well.

The object of the membrane process is to remove 250 t Mg/a or 415 t MgO/a. However the membrane process has been designed to remove 100 % magnesium. The amount of pure MgO removed in this process is \((94.49(\text{kg/h})/1000)\times24\times365= 830\text{ t/a}\). The amount MgO produced is double the amount if the membrane process has been designed to remove 50 %.

The loss of zinc for 100 % removal of magnesium is 80 t/a or 40 t/a if the membrane process has been designed to remove 50 %. The loss of zinc is on average 155 kg zinc per ton magnesium removed.
6 Process Control

In the membrane process, hazardous chemicals as well as exothermic chemical reactions are involved. Fluctuations in pressure, temperature, flow will have their effect on conversions, and unit efficiencies. A good process control is inevitable here.

In the following table, a summary of the controllers used is given.

Table 4.1: Type of controllers used in the membrane process

<table>
<thead>
<tr>
<th>Controller</th>
<th>Symbol</th>
<th>Controlled variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow controller</td>
<td>FC</td>
<td>Mass flow of process stream (can also be used to measure density)</td>
</tr>
<tr>
<td>Pressure controller</td>
<td>PC</td>
<td>Pressure of process stream or unit</td>
</tr>
<tr>
<td>Temperature controller</td>
<td>TC</td>
<td>Temperature of process stream or unit</td>
</tr>
<tr>
<td>Level controller</td>
<td>LC</td>
<td>Height of liquid-gas interface in certain unit</td>
</tr>
<tr>
<td>Ratio controller</td>
<td>RC</td>
<td>Ratio of two mass flows</td>
</tr>
<tr>
<td>Density controller</td>
<td>DC</td>
<td>Density of process stream (ratio of mass flow and volume flow)</td>
</tr>
<tr>
<td>Composition analyser</td>
<td>CA</td>
<td>Composition of process stream (mostly vapour flow)</td>
</tr>
</tbody>
</table>

A description of all controllers is given in [13].

All controllers are included in the flowsheet of the membrane process. In the following chapters, for all units the control system (if needed) will be described and explained briefly.

6.1 Feed stream

The feed stream is pumped into mixer M101. Because the total mass flow determines the amount of zinc fluoride that has to be added, a flow controller is needed here.

6.2 Mixer (M101, M102, M103, M104, M106)

For M101, it is important to control the incoming ZnF2 flow, because a too high fluoride concentration will be very costly. Theoretically, to control this, a mass flow meter measuring the density of the outgoing slurry could be installed. The density measurement, which is easily converted to a solids content, could be used to increase or decrease the incoming stream <123>. A density meter is described in [14]. The amount of fluoride in stream <108> is directly related to the electrical current measured in the membrane unit (chapter 6.14). Measuring the amount of fluoride in stream <114> (fluoride waste) and adapting the ZnF2 flow to changes is not an option either, because of the large residence time (approximately a few hours, especially in unit V105) between the fluoride waste stream and the ZnF2 inlet, so a change in the
amount of fluoride leaving the mixer will only have an effect on the fluoride waste a few hours later. The amount of fluoride needed in M101 is related to the incoming purified solution. To control the amount of fluoride needed from stream <123>, a ratio controller should be installed, that adjusts the total mass flow of stream <123> to changes in the incoming purified solution, also taking into account the amount of fluoride in stream <108> (using the signal from the current controller).

For M102, the same residence time problem occurs. A 3-flow ratio controller should be installed though; for measuring the total mass flow of stream <109>, adjusting the total mass flow of stream <140>; and to keep the ratio of streams <110> and <140> constant.

For M103, a ratio controller between stream <110> (or <109> or <140>) and <112> should be installed, as the amount of ZnO to be added in M103 is directly related to the mass flow of stream <109>.

For M104, a ratio controller between streams <116> and <122> should be installed, to keep a constant slurry composition.

For M106, Na₂O and water are mixed; NaOH is formed, and heat is released. To respond to changes in the solid flow, the cooling water flow will be adjusted if the temperature of the cooling water exit becomes too high or too low. Also, a ratio controller is needed, adjusting stream <133> to respond to changes in stream <132>, keeping a constant ratio.

For all five mixers, a level control is necessary as well. Therefore, a level controller is installed correcting the outgoing slurry mass flow.

### 6.3 Rotary kiln (R102)

This unit is used to convert MgF₂ and Mg(OH)₂ to MgO (plus a number of other reactions). To ensure full conversion, and to minimise energy costs, a good control system is essential. The following parameters should be controlled: airflow, fuel flow, reactor temperature, exit vapour composition, and dust control.

To react to changes in the slurry mass flow, a flow controller should be installed to adapt the fuel flow; a ratio controller could then be installed to ensure a fixed ratio between the air inflow and the fuel flow.

Also, a cascade control loop should be designed: a temperature controller, placed at the reactor gas flow exit, could control the fuel feed flow. The ratio controller then adjusts the air inflow, overruling changes in the slurry feed flow. However, if the airflow becomes too high, an increasing number of small dust particles leave the reactor. To prevent this, a maximum value should be assigned for the incoming gas flows.
6.4 **Bubble column (M105)**

This column is used to strip the gas flow leaving unit R201. To make sure all SO$_3$ is converted to H$_2$SO$_4$ and all HF is removed from the flue gas, a simple control system is required. The flue gas should be analysed by a composition analyser; if there is too much HF present, then the stirrer power is increased to improve gas-liquid transfer. A second control loop is used to increase the liquid level if faster stirring is insufficient, thereby increasing the residence time of the gas. This can be done by changing the outgoing liquid flow.

6.5 **Thickener (V101)**

![Figure 6.1: control system for thickener](image)

In general, two simple discrete control loops are used to:

- maintain a constant bed mass by varying underflow withdrawal rate (see fig. 6.1; pressure controller)
- maintain a constant bed level by varying flocculant addition rate (see fig. 6.1; level controller)

However, in our process the incoming mass is already controlled, so the bed level will be kept constant by the overflow.

6.6 **Cyclone (S101)**

This cyclone has been designed for certain flow rate and particles size, for that reason no control is possible.
6.7 Fluidised bed (FB101)

This unit is needed to cool the solid dust particles leaving the rotary kiln. The amount of solid in the bed doesn’t have to be controlled, because it will just flow over the edge, into the hopper section (see fig. 8.7). To control the temperature of the bed and the cooling water, a cascade control loop could be installed. If the outgoing cooling water temperature deviates from its regular value, the coolant flow is adjusted. If the bed temperature deviates from its regular value, the cooling water flow is also adjusted, overruling the former adjustments if necessary.

6.8 Hoppers (V102, V103, V104)

These are equipped with a solid mass flow controller, described in [16], ensuring constant flow.

6.9 Clarifier (V105)

Because the residence time is so large, any short time scale control loop would not have any effect. A level controller could be installed though correcting the liquid outlet flow, to keep the total mass within the clarifier constant.

6.10 Air cooled heat exchanger (E101)

There are two ways to control the outgoing gas temperature in an air-cooled heat exchanger:
- Vapour (air) flow recompression (VPR)
- Air flow adjustment

In the membrane process, airflow adjustment will be used, as this is the most common method in industry [17]. A few methods mentioned to change the airflow are usage of an adjustable power engine, fan shut-off in sequence, or usage of adjustable louvers. Fan shut-off is most commonly used for simple systems because energy is saved when the airflow reduces, and it will be sufficient for our process as well.

6.11 Sedimentation centrifuge (S102)

A density meter will be used, to adjust scroll discharge if the slurry is not concentrated enough. The incoming flow is already controlled.

6.12 Filtration centrifuge (S103)

This centrifuge will be operated in batch mode. Because it is located between 3 storage tanks, no control system is needed here.
6.13 **Splitter (Y101)**
A ratio controller is set between the 2 outgoing flows (<104> and <109>).

6.14 **Membrane reactor (R101)**
This is not a very complex reactor to control; the control system will not be very complicated either.
For the left compartment, the liquid level will be controlled by adjusting the mass flow of stream <108>. For the right compartment, the level will be controlled by adjusting the total ingoing stream <126> (stream <122> is already regulated). For the middle compartment, liquid level control can be achieved by adjusting pump flow rate to the right compartment (P111).
The ion flux through the membranes can be controlled by adjusting the voltage (shown as EP in the PFS); a current meter can be used to estimate for the total flux.

6.15 **NaOH Storage (T103)**
A level controller is needed here to prevent overload, controlling stream <125>. 
7 Mass and Heat balances

The mass and heat balances can be found in appendix 7.1. The incoming and outgoing stream differ only a fraction. The heat balance is only calculated for the rotary kiln part of the process. All other streams are expected to have a temperature of 298 K and therefore the enthalpy differences are not calculated.

In appendix 7.2 the assumptions made by constructing the mass and heat balances are available.

In appendix 7.3 a MATLAB file is included which is used for the calculation of the stream summary.
8 Process and Equipment Design

8.1 Membrane Reactor R101

In the design of the membrane reactor the following assumptions have been made:

- The conversion of NaF is set to 90%. Unconverted NaF is being pumped to the catholyte section.
- Anode efficiency equals 100% [5].
- The recycle in stream 107/108 is set to 30,000 kg/h [5]. This recycle is needed to decrease fouling of the membrane.
- The residence time in the ampholyte and catholyte compartments is very high. Therefore an internal recycle stream is made, i.e. liquid is pumped from the bottom to the top of the compartments.
- The periodic addition of acid in order to decrease fouling of the membranes is neglected. [5]

The amount of ions transported from one side of the membrane to another depends on the electric potential between the cathode and anode and the area of the membrane. Increasing the area of the membrane leads, at a certain performance of the membrane reactor needed, to a decrease in electric potential needed. While the membranes as well as the electric power are very expensive we need to find an optimum between these costs. The optimum electric potential is believed to be about 3.5 V [5,P8].

The size of pool in which the membranes should be placed is assumed to have about the same dimensions as the electrolysis pools which are currently operated at Budel Zink. The width of the pools is 3 meter in which three electrodes are placed of 0.95 meter width, 1.95 meter in height. The thickness of the zinc electrode is 8 mm and can be operated until the thickness has decreased to 3 mm. The cathode is made of steel and should hardly ever be renewed. A periodic cleaning of the cathode surface might however be necessary. The fact that almost permanently one of the 180 pools is out of operation for renewing the cathodes is neglected in the calculation of amount of pools needed. Renewing of the membranes occurs every 9 months, as stated in the chapter 3.

The hydrogen gas produced in the catholyte section is being redirected to the rotary kiln. The hydrogen content in the gas stream should be outside the explotion limits (4%-76%). When the amount of hydrogen is very small i.e. <4% however, the recycle to the rotary kiln is less profitable. Therefore we have chosen to make sure the hydrogen content should exceed 76%. In order to accomplish this it is necessary to cover the catholyte section of all membrane cells with some sort of extractor fan.
Table 8.1: Design of membrane reactor

<table>
<thead>
<tr>
<th>Anode dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
</tr>
<tr>
<td>Height</td>
</tr>
<tr>
<td>Thickness start</td>
</tr>
<tr>
<td>Thickness end</td>
</tr>
<tr>
<td>Amount of anodes</td>
</tr>
<tr>
<td>Material</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cathode dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
</tr>
<tr>
<td>Height</td>
</tr>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Material</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zinc consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

In appendix 8.1 a detailed calculation of the design is given. In the schematic drawing below an impression is given of how to operate the membrane reactor.

Figure 8.1: Schematic representation of a membrane pool (true to scale)

Figure 8.2: Detailed representation of a membrane cell (true to scale)

Figure 8.3: Schematic representation of membrane pools
8.2 Mixing units M101 – M106

The following reactions take place in the mixing units:

M101
\[ \text{MgSO}_4 + \text{ZnF}_2 \rightarrow \text{MgF}_2 + \text{ZnSO}_4 \] [eq. 8.1]

M102
\[ \text{SiO}_2 (s) + 6\text{F}^- (aq) + 4\text{H}^+ (aq) \rightarrow \text{SiF}_6^{2-} (aq) + 2\text{H}_2\text{O} (aq) \] [eq. 8.2]

M103
\[ \text{ZnO} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 \] [eq. 8.3]
\[ \text{Al}_2(\text{SO}_4)_3 (aq) + 3\text{SiF}_6^{2-} (aq) \rightarrow \text{Al}_2(\text{SiF}_6)_3 (s) + 3\text{SO}_4^{2-} (aq) \] [eq. 8.4]

M104
\[ \text{MgF}_2 + 2\text{NaOH} \rightarrow \text{Mg(OH)}_2 + 2\text{NaF} \] [eq. 8.5]

M105
\[ \text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O} \] [eq. 8.6]
\[ \text{H}_2\text{SO}_4 (g) \rightarrow \text{H}_2\text{SO}_4 (aq) \] [eq. 8.7]
\[ \text{SO}_3 (g) + \text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{SO}_4 (aq) \] [eq. 8.8]

M106
\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \] [eq. 8.9]
\[ \text{NaOH} (s) \rightarrow \text{NaOH(aq)} \] [eq. 8.10]

The mixing units are designed to have a sufficient residence time.

Table 8.2: Design Mixing units

<table>
<thead>
<tr>
<th>Unit</th>
<th>Height (m)</th>
<th>Diameter (m)</th>
<th>Volume (m³)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M101</td>
<td>1.37</td>
<td>3.41</td>
<td>5.00</td>
<td>607</td>
</tr>
<tr>
<td>M102</td>
<td>0.63</td>
<td>1.58</td>
<td>0.50</td>
<td>314</td>
</tr>
<tr>
<td>M103</td>
<td>0.63</td>
<td>1.58</td>
<td>0.50</td>
<td>314</td>
</tr>
<tr>
<td>M104</td>
<td>0.47</td>
<td>1.17</td>
<td>0.20</td>
<td>1452</td>
</tr>
<tr>
<td>M106</td>
<td>0.37</td>
<td>0.93</td>
<td>0.10</td>
<td>3839</td>
</tr>
</tbody>
</table>

Mixing unit M105 is described below.

Stirring power

The following assumptions are made to calculate the stirring power needed:

Turbulent flow: \( \text{Re}>10^3 \) [eq. 8.11]
Impeller diameter / Tank diameter ratio: \( \text{D/D}_T=0.33 \) [eq. 8.12]
Blade pitch / Impeller diameter ratio: \( \text{p/D}=1.4 \) [eq. 8.13]
Revolutions per sec: \( \text{N} \)
Density liquid\(^1\): \( \rho \)
Viscosity\(^1\): \( \mu \)

\(^1\) calculated as stated in chapter on Thermodynamic Properties
Power number [10]: \[ N_p = \frac{P}{(D^5 N^3 \rho)} \]  
\[ N_p = 0.5 \]  
[eq. 8.14]

The stirring power therefore equals: \[ P = N_p D^5 N^3 \rho \]  
[eq. 8.15]

The most important results are shown in the following table. The complete calculation can be found in appendix 8.3.

Table 8.3: Stirring power needed per mixing unit.

<table>
<thead>
<tr>
<th>Mixer</th>
<th>D [m]</th>
<th>N [1/s]</th>
<th>P [W]</th>
<th>Re [-]</th>
<th>P [kW/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M101</td>
<td>0.46</td>
<td>2</td>
<td>156.9</td>
<td>8.2E+05</td>
<td>0.031</td>
</tr>
<tr>
<td>M102</td>
<td>0.21</td>
<td>3</td>
<td>10.8</td>
<td>2.6E+05</td>
<td>0.022</td>
</tr>
<tr>
<td>M103</td>
<td>0.21</td>
<td>3</td>
<td>10.8</td>
<td>2.6E+05</td>
<td>0.022</td>
</tr>
<tr>
<td>M104 (D/Dt=0.5)</td>
<td>0.24</td>
<td>7</td>
<td>387.2</td>
<td>9.5E+02</td>
<td>1.945</td>
</tr>
<tr>
<td>M105</td>
<td>0.66</td>
<td>1.5</td>
<td>655.1</td>
<td>2.0E+06</td>
<td>0.058</td>
</tr>
<tr>
<td>M106 (D/Dt=0.56)</td>
<td>0.21</td>
<td>7</td>
<td>171.5</td>
<td>3.9E+02</td>
<td>1.715</td>
</tr>
</tbody>
</table>

The impeller-diameter ratio is chosen larger than initially assumed. This is caused by the thickness of the slurry, which requires a lot of stirring power.

8.3 Rotary kiln furnace R102

The stream <118> from the membrane process to be treated by Rotary kiln contains mostly Mg(OH)₂ with following impurities: MgF₂, Zn(OH)₂, ZnSO₄, MnSO₄, ZnF₂, NaOH and NaF.

The following reactions take place:

\( \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \)  
[eq. 8.16]

\( \text{MgF}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HF} \)  
[eq. 8.17]

\( \text{NaF} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Na}_2\text{O} + \text{HF} \)  
[eq. 8.18]

\( \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \)  
[eq. 8.19]

\( \text{ZnSO}_4 \rightarrow \frac{1}{2}\text{ZnS} + \frac{1}{2}\text{ZnO} + \text{O}_2 + \frac{1}{2}\text{SO}_3 \)  
[eq. 8.20]

\( \text{MnSO}_4 \rightarrow \frac{1}{2}\text{MnO} + \frac{1}{2}\text{MnS} + \text{O}_2 + \frac{1}{2}\text{SO}_3 \)  
[eq. 8.21]

\( \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{O} + \text{SO}_3 \)  
[eq. 8.22]

\( \text{NaOH (s)} \rightarrow \text{NaOH (l)} \)  
[eq. 8.23]

\( \text{ZnF}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{HF} \)  
[eq. 8.24]

\( \text{H}_2\text{SO}_4 (l) \rightarrow \text{H}_2\text{SO}_4 (l) \)  
[eq. 8.25]

\( \text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)} \)  
[eq. 8.26]

\( \text{CH}_4 + 2\text{O}_2 + \text{N}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2 \)  
[eq. 8.27]

The stream 118 is 185,8 kg/h large with 25wt% liquid. With assumption that the density of liquid is 1000 kg/m³ and that of the solid is equal to the density of Mg(OH)₂ 2370 kg/m³, the density of the total stream is calculated:
\[ \rho = \frac{185.835}{\left( \frac{0.75 \times 185.835}{2370} + \frac{0.25 \times 185.835}{1000} \right)} = 1782 \text{ (kg/m}^3\text{)} \]  
\[ \text{[eq. 8.28]} \]

For the determination of the size of Rotary kiln the residence time of the solid has been set to 1 hour.
The required volume is determined by:
\[ t = \frac{V_s}{\phi_v} \]  
\[ \phi_v = \frac{185.835}{1782} = 0.104 \text{ (m}^3/\text{h)} \]  
\[ \text{[eq. 8.29]} \]
\[ \text{[eq. 8.30]} \]

From the above data follows a required volume of 0.104 m\(^3\).

However the incoming feed doesn’t occupy the entire volume of Rotary kiln, only 30 %, in order to have enough exchange area between the outgoing gasses and incoming solids.

The real volume of the required Rotary kiln is:
\[ V_{\text{tot}} = \frac{V_s}{0.3} = 0.35 \text{ m}^3 \]  
\[ \text{[eq. 8.31]} \]

The ratio between length and diameter of a Rotary kiln is assumed to be equal to 10 [18]. Under this assumption the Rotary kiln has the following dimensions:

L=3.5m  
D=0.35m

As the thickness of the wall is approximately 0.25m [19] the outer diameter is 0.85m.

The rotary kiln will be operated under inclination of 3% as most of the rotary kilns are operated between 1% and 6% [20]. Three per cent inclination is equal to a triangle with horizontal side of 100 and vertical side of 3 that corresponds with 1.72°.

Rotary kilns, which operate feeds between 20kg/h and 200 kg/h, are rotated at speeds between 3 and 6 rpm [19]. Under these typical values the rotary kiln with stream size of 186 kg/h is rotated at 5 rpm.

The gas velocity through the rotary kiln is calculated on the basis of gas production from the rotary kiln, 349 kg/h, density of air at 700°C of 0.5 kg/m\(^3\) [21] (as gas leaving the rotary kiln is mostly composed of N\(_2\) at 793°C) and the area trough which the gas passes, which is equal to 70 % of the cross section of the rotary kiln.

From the above data follows a gas velocity:
\[ V_{\text{gas}} = \frac{\left( \frac{349}{0.5} \right)}{\left( \frac{0.7 \times 0.35^2 \times 3.14}{4} \right)} = 10364 \text{ m/h} = 2.9 \text{ m/s} \]  
\[ \text{[eq. 8.32]} \]
A gas velocity of 2.9 m/s is reasonable for rotary kilns where gas velocity can reach 5 m/s [22].
The inside lining is made of a high temperature, erosion resistant, castable refractory, which can withstand temperatures up to 1400 K [19]. The castable refractory is mostly made of Zirconium Oxide and stabilizers [23].

The flame is directed down the length of the rotary kiln, typical for calciners [24].

See appendix 8.4 for more calculations.

**8.4 Design air-cooled heat-exchanger E101**

In order to cool gasses from rotary kiln of the membrane process air-cooled heat exchanger will be used:

![Diagram of air-cooled heat exchanger](image)

**Figure 8.4: Air-cooled heat exchanger**

The incoming stream <129> contains gasses from rotary kiln with following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>kg/h</th>
<th>kmol/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>208.47</td>
<td>7.44</td>
</tr>
<tr>
<td>CO₂</td>
<td>40.93</td>
<td>0.93</td>
</tr>
<tr>
<td>H₂O</td>
<td>75.25</td>
<td>4.18</td>
</tr>
<tr>
<td>HF</td>
<td>12.16</td>
<td>0.61</td>
</tr>
<tr>
<td>SO₃</td>
<td>8.03</td>
<td>0.10</td>
</tr>
<tr>
<td>O₂</td>
<td>3.75</td>
<td>0.12</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>348.61</td>
<td>13.38</td>
</tr>
</tbody>
</table>

Table 8.4: The composition of stream <129>
The gasses from rotary kiln have temperature of 520K. It is assumed that they will be cooled to 338K. The required amount of heat to be removed from specified stream will be 69534 J/s, calculated on the basis of heat capacity values of different gas components and evaporation energy of water (see appendix 8.5). The gasses leaving the air-cooled heat exchanger will contain condensed water.

The area of the air-cooled heat exchanger will be calculated with following equation and assumptions:

\[ Q = U * A * dT_m \]  
[eq. 8.33]

where

\[ Q = 69534 \text{ J/s} \]
\[ U = 100 \text{ W/m}^2\text{K} \] [10]

\[ T_{air,in} = 298 \text{ K} \]
\[ T_{air, out} = 323 \text{ K} \]
\[ T_{air, int} = 310.5 \text{ K} \text{ (average of the foregoing temperatures)} \]

\[ T_{l,in} = 520 \text{ K} \]
\[ T_{l, out} = 338 \text{ K} \]
\[ T_{l, avg} = 426.5 \text{ K} \text{ (average of the foregoing temperatures)} \]

It is assumed that the same amount of heat is removed from both parts the tube, see scheme. The logarithmic mean temperature will be calculated for both parts of the tube.

For the upper part of the tube the mean temperature difference is equal to:

\[ dT_{m,2} = \left[ \frac{T_{l,in} + T_{l,avg}}{2} - T_{air,avg,2} \right] \]  
[eq. 8.34]

\[ T_{air,avg,2} = \frac{T_{air, out} + T_{air, int}}{2} \]  
[eq. 8.35]

\[ T_{air,avg}^2 = 316.75 \text{ K} \text{ and } dT_{m,2} = 156.5 \text{ K} \]

The required area for the upper part of the tube will be 2.3m\(^2\).

For the lower part of the tube the logarithmic mean temperature is equal to:

\[ dT_{m,1} = \left[ \frac{(T_{l,avg} + T_{l, out})}{2} - T_{air,avg,1} \right] \]  
[eq. 8.36]

\[ T_{air,avg,1} = \frac{T_{air, in} + T_{air, int}}{2} \]  
[eq. 8.37]
\( T_{\text{air,avg}}^2 = 304.25 \text{ K} \) and \( \Delta T_{\text{ln},i} = 78 \text{ K} \)

The required area for the lower part of the tube will be 4.5\( \text{m}^2 \).

**Tubes upper part:**

If we assume the diameter of the upper tubes to be 0.05m and the length of 1.5m there will be 10 tubes needed to supply the required area of 2.3 \( \text{m}^2 \). Thickness of the tubes is chosen to be 2mm for good heat exchange.

**Tubes lower part:**

If the tubes of the lower part have same diameter and length, there will be 20 tubes needed to supply the required 4.5 \( \text{m}^2 \).

The tubes are closely packed, every tube is 0.01m set apart from the other tubes. Every following row tubes is shifted horizontally in respect to the upper row tubes to maximize the contact between cooling air and the tubes, see figure 2:

![Figure 8.5: Tube arrangement](image)

In order to direct the flow of the air the tubes will be put into a building with following dimensions: 2x2x1 (hxlxw). Fans below the tubes will blow the air [10].

From the above heat to be removed it can be calculated that there will be 5.8E-02 kg/s of cooling air needed Appendix 8.5.

### 8.5 Design of Fluidised Bed FB101

The solid is being cooled from 1300 to 333 K, while the cooling water enters at a temperature of 293 K and leaves the cooler at a maximum temperature of 313 K in order to be able to dump the used water without further cooling. The fluidised bed is designed using the Ergün equation:

\[
\frac{\Delta p}{H_{\text{packed bed}}} = 35,55E6 \cdot U_{mf}^2 + 26,48E5 \cdot U_{mf} \\
\text{[eq. 8.38]}
\]

The minimum fluidisation velocity is then multiplied by 3 yielding the operational fluidisation velocity.
Due to the nature of the process, which is neither a continuous stirred tank reactor (CSTR) nor a plug flow reactor (PFR), the temperature difference between cooling agent and solid is a compromise between the corresponding temperature differences, which equals 515 K for a CSTR and 30 K for a PFR. The average temperature difference is therefore estimated to be 200 K.

**Figure 8.6: Schematic representation of the cooling coils**

**Figure 8.7: Schematic representation of the fluidised bed**
Table 8.5: Detailed design of the fluidised bed

<table>
<thead>
<tr>
<th>Fluidised bed dimensions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>0,30 m</td>
</tr>
<tr>
<td>Diameter</td>
<td>0,78 m</td>
</tr>
<tr>
<td>Volume</td>
<td>0,06 m³</td>
</tr>
<tr>
<td>Residence time</td>
<td>0,80 h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cooling water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoming temperature</td>
<td>293 K</td>
</tr>
<tr>
<td>Outgoing temperature</td>
<td>313 K</td>
</tr>
<tr>
<td>Amount of cooling water</td>
<td>208 m³/h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoming temperature</td>
<td>1300 K</td>
</tr>
<tr>
<td>Outgoing temperature</td>
<td>333 K</td>
</tr>
</tbody>
</table>

For detailed calculations see appendix 8.6.

8.6 Design of Bubble Column M105

The purpose of the bubble column is to strip off the environmentally hazardous components (sulphuric acid, sulphur trioxide, hydrofluoric acid) of the gas stream. The flux of the gas components depends on the solubility of the components in the liquid stream. This solubility is very complex to determine. Therefore a flux is assumed which is constant throughout the column and which is a typical gas-liquid flux. While the flux is (assumed to be) independent of concentration we assume a total removal of the hazardous gases from the gas stream. Hydrofluoric acid is assumed to be the worst soluble gas. This is a justifiable assumption while the amount of hydrofluoric acid is much larger than the amount of sulphuric acid and sulphur trioxide.

When assuming a bubble diameter the flow of hydrofluoric acid to the gas phase can be calculated. Furthermore the concentration, and thereby the amount of hydrofluoric acid per bubble, are known. This results in a residence time, and at a known rising velocity, a column height needed.

Table 8.6: Design of Bubble Column M105

<table>
<thead>
<tr>
<th>Column dimensions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>3,66 m</td>
</tr>
<tr>
<td>Diameter</td>
<td>1,14 m</td>
</tr>
<tr>
<td>Volume</td>
<td>3,75 m³</td>
</tr>
<tr>
<td>Residence time gas</td>
<td>15,9 s</td>
</tr>
</tbody>
</table>

For detailed calculations see appendix 8.7.
8.7 Liquid/ Solid (L/S) Separators

In order to separate liquid and solid phase a variety of techniques are used dependent on the feed solid concentration and the desired separation. Dependent on the stream composition different liquid/solid separators are used.

8.8 Thickener V101

The stream <102> to be treated, leaving the mixer M101 in which MgF$_2$ has precipitated has following composition:

Table 8.7: Composition of stream <102> from the mixer M101

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>Flow (m$^3$/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>3.777E+04</td>
<td>1301*</td>
<td>29.03</td>
<td>98.05</td>
</tr>
<tr>
<td>Solid</td>
<td>7.53E+02</td>
<td>3141**</td>
<td>0.24</td>
<td>1.95</td>
</tr>
</tbody>
</table>

*calculated from stream <101> which has size of 5.7 m$^3$/h
** density of MgF$_2$ as most of the solids is MgF$_2$.

The thickener V101 will be used to concentrate the solids to 25 wt% in the underflow, under this assumption the overflow will be 27.29 m$^3$/h and underflow 1.98 m$^3$/h.

For the estimation of the size of the thickener the following equations are used:

\[ t = \frac{H}{u_t} \]  
[eq. 8.39]
\[ t = \frac{A*H}{Q} \]  
[eq. 8.40]
\[ u_t = \frac{(d_s^2*\Delta\rho*g)}{(18*\mu)} \]  
[eq. 8.41]

The following assumptions have been made:

- the particle size varies from 20 $\mu$m till 400 $\mu$m.
- viscosity is 4 E-03 Pa*s (54).
- the height of the thickener has been set to 2 m.

The dimensions of the thickener will be calculated for settling of particles larger than 20$\mu$m. The terminal settling velocity for particles of 20 $\mu$m is 1.00E-04 m/s. The corresponding residence time is 5.54 hours.
Under these assumptions the area of the thickener will be 81 m$^2$ or a diameter of 10.16 m. The following stream will be leaving the thickener:

Table 8.8: Composition of stream <103>, overflow

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>Flow (m$^3$/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>3.5256E+04</td>
<td>1301</td>
<td>27.29</td>
<td>100</td>
</tr>
<tr>
<td>Solid</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 8.9: Composition of stream <105>, underflow

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>Flow (m$^3$/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>2.259E+03</td>
<td>1301</td>
<td>1.74</td>
<td>75</td>
</tr>
<tr>
<td>Solid</td>
<td>7.53E+02</td>
<td>3141</td>
<td>0.24</td>
<td>25</td>
</tr>
</tbody>
</table>

8.9 Hydrocyclone S101

Stream <105> to be treated, leaving the thickener V101 has the following composition:

Table 8.10: Composition of stream <105> from thickener V101

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>Flow (m$^3$/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>2.259E+03</td>
<td>1301*</td>
<td>1.74</td>
<td>75</td>
</tr>
<tr>
<td>Solid</td>
<td>7.53E+02</td>
<td>3141**</td>
<td>0.24</td>
<td>25</td>
</tr>
</tbody>
</table>

*calculated from stream 101 which has size of 5.7 m$^3$/h
** density of MgF$_2$ as most of the solids is MgF$_2$.

The solids from the stream <105> need to be classified, as small particles are required in the membrane cell to prevent the fouling by scrubbing the membranes with small particles [5]. The best choice for this operation is a hydrocyclone.

The size of the hydrocyclone S101 is based on particle size, which varies from 20 $\mu$m till 400 $\mu$m and where 90% of the incoming solids have diameter smaller than 150 $\mu$m. The total mass of this fraction is 80 wt% of the incoming solid.

The following equation is used [10]:

$$
d_{50} = 4.5 \left( \frac{D_c^3 \mu L}{\eta L^{1.2} (\rho_s - \rho_L)} \right) ^{0.5} \quad [eq. 8.42]
$$

$d_{50}$ - particle diameter for which the cyclone is 50 % efficient ($\mu$m)
$D_c$ - diameter of the cyclone chamber (cm)
$\mu$ - liquid viscosity (Pa*s)
$L$ - feed flow rate (l/min)
$\rho_L$ - liquid density (g/cm$^3$)
$\rho_S$ - solid density (g/cm$^3$)

The following data are used for the calculation of the hydro cyclone:

$L$ – 33 l/min
$\rho_L$ – 1.301 (g/cm$^3$)
$\rho_S$ – 3.141 (g/cm$^3$)
$\mu$ - 4.0E-3 (Pa*s)
The particle diameter for which the cyclone is 50% efficient can be determined from figure 10.22 from Coulson & Richardson’s [10] under assumption that we want to separate 90% of particles with diameter greater than 150 μm. From the figure 10.22 follows a \(d_{50}\) diameter of 100 μm. From the above data and assumptions a diameter of the hydrocyclone can be assessed from figure 10.23 from Coulson & Richardson’s [10] which have a diameter of 30 cm for the specified operation. The stream that contains particles with diameter larger than 150 μm will contain 25 wt% liquid. With the above-specified hydrocyclone the following streams are produced:

Table 8.11: Composition of stream <106>, to membrane cell

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>(\rho) (kg/m(^3))</th>
<th>Flow (m(^3)/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>2.209E+03</td>
<td>1301</td>
<td>1.70</td>
<td>79</td>
</tr>
<tr>
<td>Solid</td>
<td>6.024E+02</td>
<td>3141</td>
<td>0.19</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 8.12: Composition of stream <116>, to mixer M104

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>(\rho) (kg/m(^3))</th>
<th>Flow (m(^3)/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>5.021E+01</td>
<td>1301</td>
<td>0.039</td>
<td>25</td>
</tr>
<tr>
<td>Solid</td>
<td>1.506E+02</td>
<td>3141</td>
<td>0.048</td>
<td>75</td>
</tr>
</tbody>
</table>

8.10 Clarifier V105

Stream <113> to be treated has following composition:

Table 8.13: Composition of stream <113> from mixer M103

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>(\rho) (kg/m(^3))</th>
<th>Flow (m(^3)/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.459E+03</td>
<td>1385*</td>
<td>5.4</td>
<td>100</td>
</tr>
<tr>
<td>Solid</td>
<td>1.10</td>
<td>negligible</td>
<td>negligible</td>
<td>negligible</td>
</tr>
</tbody>
</table>

* calculated from the composition of liquid phase and known densities of different components
** not available

Stream <113> contains very low amount solid \(\text{Al}_2(\text{SiF}_6)_3\), about 0.01 wt%. In order to remove such low percentage solid to produce clear liquid clarifiers are used. Clarification is relatively cheap process compared to other liquid solid separation technology.

The slurry, which is periodically removed from the clarifier, will contain 25 wt% solids. As stream <113> contains very small quantities solid the solids accumulated on the bottom of the clarifier will be removed periodically as the underflow is 2.7 liters/h.

For the estimation of the size of the clarifier the following equations are used:
\[ t = \frac{H}{u_t} \quad \text{[eq. 8.39]} \]
\[ t = \frac{AH}{Q} \quad \text{[eq. 8.40]} \]
\[ u_t = \frac{(d_s^2 - 2\Delta \rho g)}{(18\mu)} \quad \text{[eq. 8.41]} \]

The following assumptions have been made:

- the particle size is very low 20\(\mu\)m.
- viscosity is 4 E-03 Pa*s [10].
- the height of the clarifier has been set to 2 m.
- the density of solid has been set to 3200 kg/m\(^3\)

The dimensions of the clarifier will be calculated for settling of particles larger than 10\(\mu\)m. The terminal settling velocity for particles of 10 \(\mu\)m is 2.47E-05 m/s. The corresponding residence time is 22.46 hours.

Under these assumptions the area of the clarifier will be:

\[ A = \frac{t^*Q}{H} = \frac{22.46*5.4}{2} = 60.64\text{m}^2 \text{ or diameter of } 8.79\text{m} \quad \text{[eq. 8.43]} \]

The required underflow will be 2.73 liter/h, the overflow will be almost equal to the incoming stream <113>.

### 8.11 Sedimentation Centrifuge S102

Stream <117> with precipitated Mg(OH)\(_2\) to be treated has the following composition:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>(\rho) (kg/m(^3))</th>
<th>Flow (m(^3)/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.53E+02</td>
<td>1301*</td>
<td>0.58</td>
<td>84</td>
</tr>
<tr>
<td>Solid</td>
<td>1.39E+02</td>
<td>2370**</td>
<td>0.059</td>
<td>16</td>
</tr>
</tbody>
</table>

*calculated from stream <101> which has size of 5.7 m\(^3\)/h  
** density of Mg(OH)\(_2\)

It is assumed that the solid leaving the L/S separator contains 25wt% liquid and that the particle size varies from 20 \(\mu\)m till 400 \(\mu\)m.

The size of the centrifuge:

For the estimation of the centrifuge the following equations can be used [25]:

\[ t = \frac{V_c}{Q} \quad \text{[eq. 8.44]} \]
\[ \frac{Q}{u_t} = \frac{V_c \omega^2}{g \ln(r_2/r_1)} \quad \text{[eq. 8.45]} \]

Following assumptions are made:
Scroll Discharge is 0.75 m long with 0.26 m diameter or a volume of 0.04 m³ if we assume a cylindrical shape. The pool depth is 0.08 m.

From the above assumption follows a residence time of 6.5 min. Outer radius is 0.26/2 = 0.13 m and the inner radius is 0.26/2 − 0.08 = 0.05 m [10]. Flow rate is 0.37 m³/h. The terminal settling velocity of 20 μm particles is calculated to be 5.282E-05 m/s. From the above made assumptions it can be calculated that the centrifuge should be operated at 1341 rpm.

The stream leaving the centrifuge will have the following composition:

**Table 8.15: Composition of stream <118>, to rotary kiln**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>( \rho ) (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>4.646E+01</td>
<td>1301</td>
<td>0.036</td>
<td>25</td>
</tr>
<tr>
<td>Solid</td>
<td>1.394E+02</td>
<td>2370</td>
<td>0.059</td>
<td>75</td>
</tr>
</tbody>
</table>

**Table 8.16: Composition of stream<119>**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>( \rho ) (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.06E+02</td>
<td>1301</td>
<td>0.54</td>
<td>100</td>
</tr>
<tr>
<td>Solid</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### 8.12 Filtration Centrifuge S103

Stream <134> to be treated has the following composition:

**Table 8.17: Composition of stream <134> from mixer M106**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>( \rho ) (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>7.174E+01</td>
<td>1000*</td>
<td>0.072</td>
<td>40</td>
</tr>
<tr>
<td>Solid</td>
<td>1.067E+02</td>
<td>3600**</td>
<td>0.030</td>
<td>60</td>
</tr>
</tbody>
</table>

* as most of the liquid is water
** as most of the solids is MgO

As the size of the stream is to small (0.102 m³/h), the filtration centrifuge will be operated batch wise. Stream <134> will be collected in the storage tank T106. The simplest machines are basket types, the choice has been made for bottom drive automatic basket, rising knife, which can be designed for variable speed and has automatic discharge, as other basket types are single speed machines [10].

**Dimensions of the batch operating filtration centrifuge:**

The dimensions are based on a batch filtration centrifuge with 1.2 m height and diameter of 0.74 m that has a processing time of 877 s for 140 kg dry solids per cycle with maximum rotation speed of 1050 rpm [25].
A bottom drive automatic basket with comparable dimensions, height of 1m and diameter of 0.6m could be used for the treating of 107 kg dry solids, solids accumulated in one hour, per basket load. The operational time will be approximately 15min. From above dimension and basket load of the batch centrifuge follows a ration between the volume of the batch centrifuge and volume of the slurry treated:

\[
V_{\text{batch}} = \frac{1 \times 3.14 \times 0.6^2}{4} = 0.28 m^3 \quad \text{[eq. 8.46]}
\]

\[
\frac{V_{\text{batch}}}{V_{\text{slurry}}} = \frac{0.28}{0.1} = 2.8 \quad \text{[eq. 8.47]}
\]

The rotation speed could be increased till 1200 rpm in order to obtain dry solids with 5 wt% liquid. Filter media should be chosen which could contain particles larger than 5μm.

### 8.13 Storage tank T101, zinc anode storage

Zinc anodes are supplied in form of plates of 0.95 m wide, 1.95 m and 8 mm thick. The amount of zinc needed equals 132 kg/h. Storage tank T101 should contain a two-week supply of zinc anode cells, which is equal to 44.36 tonne or 6.22 m³. Therefore storage of 420 plates is needed.

If the zinc anode cells are supplied in boxes of 2.1 m length, 2.1 width, 2.1 m height, and one zinc anode cell takes place of 3cm wide, one box contains 70 zinc anode cells. The storage tank should contain 6 boxes. The minimum required size of the storage tank is 55 m³.

### 8.14 Storage tank T102 water storage

As 58.28 kg/h water is required, or 1.4 m³ for one day, the storage tank is designed to contain daily required amount of water or 1.4 m³, with diameter of 1.2 m and height of 1.2 m.

### 8.15 Storage tank T103, dissolved NaOH

Storage tank T103 contains dissolved NaOH. The storage tank will supply the membrane cell with 65.77 kg/h dissolved NaOH or 0.066 m³/h, with 26wt% dissolved NaOH. The storage tank is supplied with dissolved NaOH from stream <137> and stream <125>. The stream <137> contains also 26wt% NaOH in 46.01 kg/h. The stream <125> have same amount dissolved NaOH and is 19.76 kg/h large. As stream <137> is coming from the membrane process and stream <125> outside the battery limits, the storage tank will be designed to contain weekly amount stream <125> or 3.32 m³, with 1.5 m diameter and height of 1.9m.
8.16 Storage tank T104, MgO with dissolved NaOH

Storage tank T104 is used for storage of solid MgO with dissolved NaOH before being processed by filtration centrifuge. The storage should be designed to contain 24 hours production, see also design of filtration centrifuge S103. As stream 134 entering the storage tank contains 178.39 kg/h slurry with density of 1760 kg/m³ (calculated from the composition of stream) the storage tank should be 2.44 m³ to contain 24 hours production or with safety factor to be able to contain two days production the volume will be 5m³, with 2m diameter and height of 1.6m.

8.17 Storage tank T105, storage of MgO

Storage tank T105 is used for storage of solid MgO to be sold. Solid MgO contains 5wt% water. As the production of solid MgO amounts to 112.26 kg/h or 0.031 m³/h, the storage tank is designed to be able to contain production of two weeks of 10.42 m³, with diameter of 3m and height of 1.5m.

8.18 Storage tank T106, waste storage

Storage tank T106 is used for storage of slurry with 25 wt% Al₂(SiF₆)₃, the liquid contains water and dissolved ZnSO₄. As the stream 114 is 4.4 kg/h large with assumed density of 1500 kg/m³, the required volume of the storage tank T106 to store monthly production will be 2.2 m³, with 1.3m diameter and height of 1.7m.

8.19 Fuel supply

Fuel, CH₄, will be delivered by one of the local gas suppliers. The required amount of CH₄ is 14.88 kg/h or 23 m³/h at ambient conditions.

8.20 Hopper V102, Al₂(SO₄)₃ supply

The required amount Al₂(SO₄)₃ is equal to 0.78 kg/h or 3.12E-04 m³/h. The density is assumed to be 2500 kg/m³ (literature values couldn’t be obtained). The hopper will be designed to contain weekly required amount solid Al₂(SO₄)₃, the required volume of the hopper will be 52 liters.

8.21 Hopper V103, SiO₂ supply

The required amount SiO₂ is equal to 0.41 kg/h or 1.5E-04 m³/h. The density is 2700 kg/m³. The hopper will be designed to contain weekly required amount solid SiO₂, the required volume of the hopper will be 28 liters.
8.22 Hopper V104, ZnO supply

The required amount ZnO is equal to 0.15 kg/h or 2.68E-05 m³/h. The hopper will be designed to contain monthly required amount solid ZnO, the required volume of the hopper will be 193 liters.

8.23 Hopper V106, ZnF₂ supply

The required amount of ZnF₂ is 33.56 kg/h. The best way to supply ZnF₂ is by use of a hopper, which can contain 24 hours demanded amount ZnF₂ for the process. The size of the hopper should be 165 liters.
8.24 Pumps, blowers and screws

In this section the places for all pumps and blowers used will be justified and explained. The design specs can be found in the pump data sheets in appendix x. $P_{s,\text{liquid}}$ is the pressure drop for liquids due to shear forces and is assumed to be around 0.5 bar. The pressure drop for gases due to shear is assumed to be $P_{s,\text{gas}} = 0.3$ bar.

**Pump P101**
Pumping capacity $= \phi_V = 5.46 \text{ m}^3/\text{h}$.
In order to pump the purified solution from the main zinc plant to the membrane plant, a centrifugal pump is selected. The only pressure difference required is to compensate for shear, so $\Delta P = P_{s,\text{liquid}} = 0.5$ bar.

**Pump P102**
Pumping capacity $= \phi_V = 27.81 \text{ m}^3/\text{h}$.
A disc pump [26] should be used to pump the liquid flow containing solids from the mixer to the thickener. A disc pump is able to pump a slurry with little trouble and doesn’t show much erosion due to mechanical stress. The only pressure difference required is to compensate for shear, so $\Delta P = P_{s,\text{liquid}} = 0.5$ bar.

**Pumps P103, P104, P105, P106, P107, P109, P114, P117.**
Pumping capacities:

<table>
<thead>
<tr>
<th>Pump</th>
<th>Capacity, $\phi_V$ m$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>P103</td>
<td>25.96</td>
</tr>
<tr>
<td>P104</td>
<td>22.35</td>
</tr>
<tr>
<td>P105</td>
<td>1.87</td>
</tr>
<tr>
<td>P106</td>
<td>1.79</td>
</tr>
<tr>
<td>P107</td>
<td>0.080</td>
</tr>
<tr>
<td>P109</td>
<td>5.45</td>
</tr>
<tr>
<td>P114</td>
<td>0.058</td>
</tr>
<tr>
<td>P117</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Disc pumps [26] should be used here because there are solids in the flows. The only pressure difference required is to compensate for shear, so $\Delta P = P_{s,\text{liquid}} = 0.5$ bar.

**Pump P108**
Pumping capacity $= \phi_V = 5.45 \text{ m}^3/\text{h}$.
When siliciumdioxide is added at M102 the solution is pumped to M103 with a centrifugal pump where precipitation is caused by raising the pH. $\Delta P = P_{s,\text{liquid}} = 0.5$ bar.

**Pump P110**
Pumping capacity $= \phi_V = 0.058 \text{ m}^3/\text{h}$.
This centrifugal pump pumps water to mixer M106. A pumping force of $P_{s,\text{liquid}} = 0.5$ bar is required.
Pump P111
Pumping capacity = $\phi_V = 0.23 \text{ m}^3/h$.
A centrifugal pump is installed to pump liquid from the ampholyte to the catholyte.
$\Delta P = P_{s,\text{liquid}} = 0.5 \text{ bar}$.

Pump P112
Pumping capacity = $\phi_V = 0.054 \text{ m}^3/h$.
Because there are sodium hydroxide losses in the process a centrifugal pump is installed to pump in NaOH from the storage.
A pumping force of $P_{s,\text{liquid}} = 0.5 \text{ bar}$ is required.

Pump P113
Pumping capacity = $\phi_V = 0.26 \text{ m}^3/h$.
A centrifugal pump is used to pump sodium hydroxide from the membrane cell to the mixing unit where MgF$_2$ is converted to Mg(OH)$_2$. A pumping force of $P_{s,\text{liquid}} = 0.5 \text{ bar}$ is required.

Pump P115
Pumping capacity = $\phi_V = 0.28 \text{ m}^3/h$.
A centrifugal pump should be used to pump the clear liquid from the separation step at S201. A pumping force of $P_{s,\text{liquid}} = 0.5 \text{ bar}$ is required.

Pump P116
Pumping capacity = $\phi_V = 5.45 \text{ m}^3/h$.
A centrifugal pump is selected to pump the Purified Solution back to the main zinc plant.
A pumping force of $P_{s,\text{liquid}} = 0.5 \text{ bar}$ is required.

Pump P118
Pumping capacity = $\phi_V = 0.055 \text{ m}^3/h$.
This pump pumps clear NaOH (aq) to it’s storage. A pumping force of $P_{s,\text{liquid}} = 0.5 \text{ bar}$ is required.

Blower K101
Pumping capacity = $\phi_V = 448 \text{ m}^3/h$.
Air has to be transported to the rotary kiln as well. For this purpose a turbo blower is used. It operates at a pressure difference of $\Delta P = P_{s,\text{gas}} = 0.3 \text{ bar}$.

Blower K102
Pumping capacity = $\phi_V = 21 \text{ m}^3/h$.
Here a turbo blower is installed to blow fuel gas to the rotary kiln. Only shear forces have to be compensated here so $\Delta P = P_{s,\text{gas}} = 0.3 \text{ bar}$.

Blower K103
Pumping capacity = $\phi_V = 291 \text{ m}^3/h$.
To pump the hot gases coming from the rotary kiln to the gas stripper M105 a blower should be installed. It operates at a pressure of $\Delta P = P_{s,\text{gas}} = 0.3 \text{ bar}$.
**Blower K104**
Pumping capacity = $\phi_V = 45 \text{ m}^3/\text{h}$. 
A turbo blower is used to transport the hydrogen formed at the electrodialysis cell to the rotary kiln where it can be used as fuel (so less fuel has to be blown by blower K102). This blower only has to compensate for shear so $\Delta P = P_{s,\text{gas}} = 0.3 \text{ bar}$.

**Transporter screw X104**
Pumping capacity = $\phi_V = 0.034 \text{ m}^3/\text{h}$. 
A transporter screw is used to transport the solids coming from the rotary kiln to the fluidized bed for cooling. A screw is selected because it operates as a closed system and so less dust will fly up into the air. This is better for the health of the plants employees.
9 Wastes

In this chapter we will only deal with the direct waste streams. Initially the membrane process produced the following waste streams:

- Off-gases from the rotary kiln, containing SO$_3$<129>,
- Fluoride removal waste stream <114>.

A solution is found to clean the off-gases that leave the rotary kiln. They are led through the process liquid, which enters the membrane reactor <120> in a bubble column (M105). In the bubble column, harmful SO$_3$ present in the off-gases will react with H$_2$O to sulphuric acid. Therefore the off-gas leaving the plant contains CO$_2$ (over 350 t/a) and Nitrogen and oxygen.

The method chosen for the fluoride removal in the stream back to the zinc plant is expensive. Fluoride precipitation, by adding SiO$_2$ and Al$_2$(SO$_4$)$_3$, seems to be the best alternative when all advantages/disadvantages are weighed. The reason for choosing this method can be found in chapter five.

An amount of 9636 kg solid waste is produced per year, which will be brought to the AVR [P9]. The AVR is contacted to obtain information about the processing costs. The costs per tonne are summarized in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Price (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic price (per tonne)</td>
<td>795</td>
</tr>
<tr>
<td>Steel surcharge (per tonne)</td>
<td>225</td>
</tr>
<tr>
<td>Fluoride surcharge (per tonne)</td>
<td>810</td>
</tr>
<tr>
<td>Analysis costs (once per delivery)</td>
<td>95</td>
</tr>
<tr>
<td>Administration costs (only once)</td>
<td>148</td>
</tr>
</tbody>
</table>

Neglecting the administration costs and assuming delivery twice a year, the dumping costs will be 17824 €/year.

Furthermore the membranes, which are replaced every 9 months, will have be disposed of. It is expected that this is not very costly and can be done by the AVR as well. There has been no contact with the AVR on disposal of the membranes. Partly because we don’t think is very costly and partly because we don’t know the exact composition of the membranes as they are removed from the electrolytic cells.
10 Health and Safety

10.1 Health

In order to assess the health aspects of a given chemical process it is sensible to start with identifying all chemicals that exist in the plant. These chemicals are listed in table 10.1. In this table liquid water and steam are listed separately. This is done because there exists an obvious difference in the danger these compounds pose.

For a person to estimate the threats these chemicals pose several data are very useful. We will try to identify the way these chemicals enter the body and toxicity levels (MAC values).

Table 10.1: Chemicals occurring in the plant.

<table>
<thead>
<tr>
<th>Formula:</th>
<th>State:</th>
<th>Name:</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>l</td>
<td>liquid water</td>
</tr>
<tr>
<td>H₂O</td>
<td>g</td>
<td>Steam</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>l/g</td>
<td>sulphuric acid</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>s/aq</td>
<td>zinc sulphate</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>s/aq</td>
<td>magnesium sulphate</td>
</tr>
<tr>
<td>MnSO₄</td>
<td>s/aq</td>
<td>manganese sulphate</td>
</tr>
<tr>
<td>SO₃</td>
<td>g</td>
<td>sulphur trioxide</td>
</tr>
<tr>
<td>O₂</td>
<td>g</td>
<td>oxygen</td>
</tr>
<tr>
<td>ZnO</td>
<td>s</td>
<td>zinc oxide</td>
</tr>
<tr>
<td>ZnS</td>
<td>s</td>
<td>zinc sulphide</td>
</tr>
<tr>
<td>MnO</td>
<td>s</td>
<td>manganese oxide</td>
</tr>
<tr>
<td>MnS</td>
<td>s</td>
<td>manganese sulphide</td>
</tr>
<tr>
<td>CH₄</td>
<td>g</td>
<td>methane</td>
</tr>
<tr>
<td>CO₂</td>
<td>g</td>
<td>carbondioxide</td>
</tr>
<tr>
<td>N₂</td>
<td>g</td>
<td>nitrogen</td>
</tr>
<tr>
<td>ZnF₂</td>
<td>s/aq</td>
<td>zinc fluoride</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula:</th>
<th>State:</th>
<th>Name:</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF₂</td>
<td>s</td>
<td>magnesium fluoride</td>
</tr>
<tr>
<td>NaOH</td>
<td>aq</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>NaF</td>
<td>aq</td>
<td>sodium fluoride</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>s/aq</td>
<td>magnesium hydroxide</td>
</tr>
<tr>
<td>H₂</td>
<td>g</td>
<td>hydrogen</td>
</tr>
<tr>
<td>Zn</td>
<td>s</td>
<td>zinc</td>
</tr>
<tr>
<td>MgO</td>
<td>s</td>
<td>magnesium oxide</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>s/aq</td>
<td>zinc hydroxide</td>
</tr>
<tr>
<td>HF</td>
<td>g</td>
<td>hydrogen fluoride</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>aq</td>
<td>sodium sulphate</td>
</tr>
<tr>
<td>F₂</td>
<td>-</td>
<td>fluor</td>
</tr>
<tr>
<td>Na₂O</td>
<td>s</td>
<td>sodium oxide</td>
</tr>
<tr>
<td>SiO₂</td>
<td>s</td>
<td>siliciumdioxide</td>
</tr>
<tr>
<td>ZnSiF₆</td>
<td>s</td>
<td>zinc silica fluoride</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>s</td>
<td>alumina sulphate</td>
</tr>
<tr>
<td>Al₂(SiF₆)₃</td>
<td>s</td>
<td>alumina silica fluoride</td>
</tr>
</tbody>
</table>
In appendix 10.1 some important properties regarding the used chemicals can be found.

From this table we can very roughly say there are four main health concerns in our plant.
The first problem is the production of HF-gas in the rotary kiln, this is considered dangerous even though the concentration of HF is low. The piping containing HF should be kept as short as possible.
The second potential health hazard is the use of concentrated NaOH coming from the membrane reactor and the NaF to which it is converted. Both substances are dangerous to humans.
The third potential health hazard is the formation of hydrogen at the membrane reactors, which is used again in the rotary kiln as fuel. Good suction hoods have to be installed at the catholyte section, which are airtight so formation of a combustible gas mixture is prevented.
The fourth problem is the dustiness of the solids exiting the rotary kiln. With this in mind, the designers chose to use a transporter screw instead of a transporter belt. This enables the transportation of solids from the rotary kiln (D201) to the mixer (M201) to be operated as a closed system, which will decrease the amount of dust in the air.
It might also be advisable to spray the solids with a slight amount of water right after they exit the rotary kiln (D201) to reduce the amount of dust in the air.
10.2 Safety

10.2.1 Safety analysis using HAZOP

Before a Hazard and Operability Studies (HAZOP, [27]) is started we first decide which process parts we will analyze. The plant has only one part that operates at dangerous levels. This is the rotary kiln. So there will only be a HAZOP-analysis for the rotary kiln. This analysis can be found in appendix 10.2.

Several things can be concluded from the HAZOP table (appendix 10.2). One is that there seems to be little danger of a completely uncontrollable situation. Most problems seem controllable.

A list of things that might be desirable to incorporate in the design can now be made.

- For pumps and blowers spares should be installed.
- Pressure relief valves should be installed.
- Install ratio controls. Especially for the ratios between a feed and fuel flow.
- Install temperature control.
- Measure methane flow at the beginning of the plant and just before the rotary kiln.
- Patrolling the site can be considered.
- Building a storage vessel just before the rotary kiln.
- Keep the pipe for the exiting gas flow as short as possible.
- Install a vent in rotary kiln.

The spare pumps and blowers will be installed (see equipment sheets).
Pressure relief valves, ratio controls and flow controls will be implemented (chapter 6, Process Control).
The storage vessel’s importance just before the rotary kiln is disputable. A good flow ratio controller between the feed / fuel ratio might be enough to avoid any problems. Therefore it will not be taken up in the design.

If there’s a problem with the rotary kiln section, shutdown the methane flows first because this takes away a large part of the danger.
10.2.2 Fire and Explosion analysis.

In order to say something about the safety of the process an analysis based on the Dow Fire and Explosion Index can be made (FEI, [27]). First we identify the dangerous sections in the process. A FEI will be calculated for only one section. The rotary kiln section because high temperatures and methane are used here. The conversion from MgF₂ to Mg(OH)₂ and the membrane reactors are considered to be a lot less hazardous.

This actual analysis consists of two parts. The first part says something about the danger coming from the used chemicals expressed in Material Factors. These factors say something about the reactivity (adiabatic decomposition temperature) and flammability (flash point, heat of combustion and volatility). For further explanation of the FEI method see [27], [10].

Material Factors can be determined using table 10.2:

**Table 10.2: Determining a Material Factor.**

<table>
<thead>
<tr>
<th>Flash point °C</th>
<th>Tₐ (K)</th>
<th>Flammability</th>
<th>Material Factor (MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>&lt;830</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>&gt;100</td>
<td>830 - 935</td>
<td>1</td>
<td>24</td>
</tr>
<tr>
<td>40 - 100</td>
<td>935 - 1010</td>
<td>4</td>
<td>29</td>
</tr>
<tr>
<td>-20 - 40</td>
<td>1010 - 1080</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>&gt;-20</td>
<td>&gt;108</td>
<td>4</td>
<td>21</td>
</tr>
</tbody>
</table>

Flammability:
- Flammability: 0 - 40
- Flammability: 40 - 60
- Flammability: >60

Material Factors:
- Material Factor: 0 - 2
- Material Factor: 2 - 4
- Material Factor: >4

This leads to the following material factors:

**Table 10.3: Material Factors for given compounds.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactivity</th>
<th>Flammability</th>
<th>Material Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>2</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>HF</td>
<td>1</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>NaOH</td>
<td>1</td>
<td>0</td>
<td>14</td>
</tr>
</tbody>
</table>
The second part of a FEI analysis consists of identifying and quantifying process hazards. For these hazards a penalty will be given. It must be said that there are two problems with FEI. First of all the actual plant layout (including equipment placing and piping layout) is not known yet. Second the authors are inexperienced with making a FEI, so the penalties given may deviate from the penalties a more experienced annalist would give.

The following penalties are given for general process hazards:

**Table 10.4: General Process Hazards Factor, rotary kiln section.**

<table>
<thead>
<tr>
<th>Base factor</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Exothermic chemical reactions</td>
<td>-</td>
</tr>
<tr>
<td>B: Endothermic processes (+ burning of CH₄)</td>
<td>0.40</td>
</tr>
<tr>
<td>C: Material handling and transfer.</td>
<td>-</td>
</tr>
<tr>
<td>D: Enclosed or indoor process units (dust)</td>
<td>-</td>
</tr>
<tr>
<td>E: Access¹</td>
<td>-</td>
</tr>
<tr>
<td>F: Drainage and spill control.</td>
<td>-</td>
</tr>
<tr>
<td><strong>General Process Hazards Factor (Fₗ)</strong></td>
<td>1.40</td>
</tr>
<tr>
<td>¹: unknown yet, so assumed zero.</td>
<td></td>
</tr>
</tbody>
</table>

For special process hazards the following penalties are given:

**Table 10.5: Special Process Hazards Factor, rotary kiln section.**

<table>
<thead>
<tr>
<th>Base factor</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Toxic materials</td>
<td>0.70</td>
</tr>
<tr>
<td>B: Sub-atmospheric pressure</td>
<td>-</td>
</tr>
<tr>
<td>C: Operation in or near flammable range</td>
<td></td>
</tr>
<tr>
<td>1. Tank farms storage flammable liquids</td>
<td>-</td>
</tr>
<tr>
<td>2. Process upset or purge failure</td>
<td>-</td>
</tr>
<tr>
<td>3. Always in flammable range</td>
<td>-</td>
</tr>
<tr>
<td>D: Dust explosion</td>
<td>-</td>
</tr>
<tr>
<td>E: Pressure</td>
<td>-</td>
</tr>
<tr>
<td>F: Low temperature</td>
<td>-</td>
</tr>
<tr>
<td>G: Quantity of flammable/unstable material</td>
<td></td>
</tr>
<tr>
<td>1. Liquids, gases and reactive materials in process</td>
<td>0.60</td>
</tr>
<tr>
<td>2. Liquids or gases in storage</td>
<td>-</td>
</tr>
<tr>
<td>3. Combustible solids in storage dust in process</td>
<td>-</td>
</tr>
<tr>
<td>H: Corrosion and erosion</td>
<td>0.30</td>
</tr>
<tr>
<td>I: Leakage joints and packing</td>
<td>-</td>
</tr>
<tr>
<td>J: Use of fired heaters</td>
<td>0.30</td>
</tr>
<tr>
<td>K: Hot oil heat exchange system</td>
<td>-</td>
</tr>
<tr>
<td>L: Rotating equipment</td>
<td>0.50</td>
</tr>
<tr>
<td><strong>Special hazards factor</strong></td>
<td>3.40</td>
</tr>
</tbody>
</table>

To calculate the final index number, the material factor for CH₄ or H₂ (= 21 = the highest material factors here) is multiplied with 1.40 and 3.40, which leads to a number of 99.96.

This process section can now be classified as having a intermediate degree of hazard [10]. This is a conclusion, which is considered acceptable by the authors. However this conclusion should in no way keep anybody (designers, operators, or anybody else) from suggesting safety measures, which could make the process safer.
11 Economy

In order to make an estimation of the costs of the project the factorial method, also known as the Lang method [10], is used. This method is based on an estimation of the costs of major equipment after which all other fixed capital costs, i.e. buildings, storages, piping, are defined as a factor of these major equipment costs. The costs of major equipment are widely available in literature [10,28] and internet [29]. As the fixed capital costs are known the working capital, all costs, which are made before any profit is made, are estimated by a fraction of the fixed capital costs. The sum of these costs equal the total investment needed for the process. The annual production costs can now be calculated by summing up all costs, which are made each year. The production costs can be defined into variable costs, costs that vary with the amount of production, and costs that are fixed now matter what the amount of production is.

As the total process is defined to remove twice as much magnesium as needed we have to make a correction for this. The capacity of the units is therefore also two times too high. The costs of the equipment can however not be divided by two. This would be an underestimation. Using the step counting method [10] we are able to make a more accurate estimation. When doubling the capacity (at a conversion rate of 1) the capital costs are a factor 1,23 higher. The total investment needed is therefore divided by this factor. The costs of chemicals, membrane, wastes and utilities can be divided by two, as these are directly proportional to the amount of production. The fixed production costs are either depending on the capital costs and are therefore already corrected or are indeed fixed.

Normally, when knowing the annual production costs, the amount of product and product price, we can calculate economic performance criteria like the pay-back time, break-even point and discounted cash-flow rate of return. In this type of process, which is a purification part of another process, we are not able to calculate such criteria. From the existing magnesium removal process and a comparison with the evaporation process we can however judge the economic performance of the process. The costs per kilogram magnesium that is removed will serve as the performance indicator.

Table 11.1 Economic Criteria of the Evaporation Process

<table>
<thead>
<tr>
<th>Costs</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment costs</td>
<td>3523 k euro</td>
</tr>
<tr>
<td>Operational costs</td>
<td>3753 k euro</td>
</tr>
<tr>
<td>Magnesium removal costs</td>
<td>14,6 euro/kg</td>
</tr>
</tbody>
</table>

The costs per kilogram magnesium using the membrane process equals 14,6 euro. The error in this value may be estimated to be 10%. These costs are too high for this process to be competitive with the existing magnesium removal process.

In appendix 11.1 a detailed calculation of the purchase costs of the major equipment can be found. The economic performance is available in appendix 11.2.
Evaporation Process
12 Process Structure and Description

12.1 Criteria and Selections

12.1.1 Evaporation

Choice for type of evaporator

Because a lot of water has to be removed, it is economically not favourable to do the evaporation in one single step. Because there is 6 bar steam present, it will be very energy-efficient to make use of the multi-stage evaporation principle. This implies that a cascade of evaporators should be designed. The steam that will be produced in one evaporator will be used in the next one. A driving force is maintained by lowering the pressure from unit to unit, which causes a drop in the liquid boiling temperature. In the next paragraph, a calculation will be made to make a reasonable estimation for the number of units required.

According to the model used, the first 70 % of the evaporation there is no solid to deal with. The most commonly used evaporator for non-viscous liquids is the falling film evaporator. This is a relative cheap, energy-efficient evaporator in which the liquid falls through a vertical heat exchanger. A distributor on top of the column makes the water falling in a film along the tube walls. Subsequently, the heated liquid will enter an expansion vessel in which the formed vapour will be separated from the liquid.

During the last 30 % of the evaporation, slurry will be formed. Due to this, a falling film evaporator will not be useful anymore. A reactor has to be used in which water will be evaporated, slurry will sedimentate and part of the liquid has to be fed to the next unit. A reactor suitable to do this is a forced circulation evaporator. A picture of this type of evaporator is shown in figure 12.1. However, the vapour condensing section is not included in the type of evaporator used in our process.
Figure 12.1: schematic representation of a falling film evaporator [30]

Estimation of costs and optimum number of evaporator units for the evaporation process

Co-current flow

In appendix [12.2], a Matlab script is used to calculate the optimum number of stages for the evaporation process. Assumptions and calculations are given in appendix [12.1] as well.

The following (simplified) block scheme is used for modelling:
Figure 12.2: block scheme used for calculating optimum number of stages (2 units)

The following equations have been used for each unit:

\[ T_{i+1} = T_{i+1} \]  \[ \text{[eq. 12.1]} \]

\[ C_p \cdot L_i \cdot T_{i+1} - C_p \cdot L_i \cdot T_{i+1} + U \cdot A \cdot (T_{i+1} - T_{i+1}) = V_{i+1} \cdot \Delta H_{vap} \]  \[ \text{[eq. 12.2]} \]

\[ L_i = L_i + V_{i+1} \]  \[ \text{[eq. 12.3]} \]

\[ V_{i+1} \cdot \Delta H_{vap} = U \cdot A_i \cdot (T_{i+1} - T_{i+1}) / \eta \]  \[ \text{[eq. 12.4]} \]

Using a general formula given in [10], the total costs for a multistage evaporator can be estimated, which consists of equipment costs and steam costs.

The formula for the cost of evaporators is as follows [10]:

\[ Cost = \sum_i f \cdot c \cdot A_i^n \]  \[ \text{[eq. 12.6]} \]

Values for the different constant can be found in [10].

As calculated earlier, when 68.7% of the water has been evaporated, ZnSO$_4$ will begin to precipitate. Therefore, it is important to know after which stage ZnSO4 will begin to precipitate. All previous units will be falling film evaporators; all other units will be forced recirculation evaporators. This has to be taken into account when calculating the total cost. For falling film evaporators, the costs can be modelled using equation [12.7].

\[ unitcost_{ff} = \sum_{i=1}^{n_{fall}} 1.6 \cdot 11000 \cdot area(i)^{0.52} \]  \[ \text{[eq. 12.7]} \]

Equipment costs for forced recirculation evaporators can be modelled using equation [12.8]:

\[ unitcost_{fre} = \sum_{i=1}^{n_{fre}} 1.6 \cdot 1.56 \cdot (4100 + 11000 \cdot area(i)^{0.52} + 2 \cdot 1500 \cdot \left( \frac{2}{i} \right)^{0.6} \]  \[ \text{[eq. 12.8]} \]

The total equipment costs are calculated using equation [12.9], taking depreciation into account:

\[ equipcost = \frac{unitcost_{ff} + unitcost_{fre}}{15 \cdot 365 \cdot 24} \]  \[ \text{[eq. 12.9]} \]

Steam costs are modelled using the equation below:

\[ steamcost = \frac{steamreq \cdot 11.2}{1000} \]  \[ \text{[eq. 12.10]} \]

All costs are in €/hr.

For simplicity, it is assumed that all evaporator costs can be modelled by equation [12.7] (falling film evaporators).

In the following tables the results for co-current flow are shown.
Table 12.1: estimation of total costs for multistage evaporator if 98% water is evaporated

<table>
<thead>
<tr>
<th>Number of evaporators [-]</th>
<th>Steam consumption [kg/h]:</th>
<th>Heat exchange area [m²]:</th>
<th>Equipment Cost [€/h]:</th>
<th>Steam Cost [€/h]:</th>
<th>Total Cost [€/h]:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4016</td>
<td>101</td>
<td>1.48</td>
<td>44.97</td>
<td>46.45</td>
</tr>
<tr>
<td>2</td>
<td>2098</td>
<td>105; 84</td>
<td>2.85</td>
<td>23.50</td>
<td>26.36</td>
</tr>
<tr>
<td>3</td>
<td>1456</td>
<td>110; 88; 81</td>
<td>4.23</td>
<td>16.31</td>
<td>20.54</td>
</tr>
<tr>
<td>4</td>
<td>1137</td>
<td>114; 91; 85; 77</td>
<td>5.61</td>
<td>12.74</td>
<td>18.35</td>
</tr>
<tr>
<td>5</td>
<td>949</td>
<td>119; 95; 89; 81; 73</td>
<td>6.99</td>
<td>10.63</td>
<td>17.62</td>
</tr>
<tr>
<td>6</td>
<td>826</td>
<td>125; 100; 92; 85; 77; 69</td>
<td>8.36</td>
<td>9.26</td>
<td>17.68</td>
</tr>
<tr>
<td>7</td>
<td>741</td>
<td>130; 104; 96; 88; 80; 73; 65</td>
<td>9.73</td>
<td>8.30</td>
<td>18.04</td>
</tr>
</tbody>
</table>

The total cost can be found in the last column. The optimum number of stages is assumed to be 5. The total costs are minimized to € 17.62 per hour.

The temperatures for the outgoing liquid flows chosen for the 5-stage evaporation process are shown in table 12.2.

Table 12.2: chosen liquid temperatures for a 5-stage evaporation process

<table>
<thead>
<tr>
<th>Stage number [-]</th>
<th>Liquid feed temperature [K]</th>
<th>Outgoing liquid temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>413.15</td>
<td>413.15</td>
</tr>
<tr>
<td>2</td>
<td>413.15</td>
<td>393.15</td>
</tr>
<tr>
<td>3</td>
<td>393.15</td>
<td>373.15</td>
</tr>
<tr>
<td>4</td>
<td>373.15</td>
<td>353.15</td>
</tr>
<tr>
<td>5</td>
<td>353.15</td>
<td>333.15</td>
</tr>
</tbody>
</table>

The resulting vapour flows temperatures and corresponding pressures are shown in the below. The corresponding pressures are taken from the vaporization curve of water.

Table 5.3: calculated vapour flow temperatures and corresponding pressures for a 5-stage evaporation process

<table>
<thead>
<tr>
<th>Stage number [-]</th>
<th>Inlet steam temperature [K]</th>
<th>Inlet steam pressure [bar]</th>
<th>Outlet steam temperature [K]</th>
<th>Outlet steam pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>433.15</td>
<td>6.100</td>
<td>413.15</td>
<td>3.590</td>
</tr>
<tr>
<td>2</td>
<td>413.15</td>
<td>3.590</td>
<td>393.15</td>
<td>1.960</td>
</tr>
<tr>
<td>3</td>
<td>393.15</td>
<td>1.960</td>
<td>373.15</td>
<td>1.013</td>
</tr>
<tr>
<td>4</td>
<td>373.15</td>
<td>1.013</td>
<td>353.15</td>
<td>0.465</td>
</tr>
<tr>
<td>5</td>
<td>353.15</td>
<td>0.465</td>
<td>333.15</td>
<td>0.200</td>
</tr>
</tbody>
</table>

The resulting liquid and steam flows can be found in table 12.3 below:
Table 64: calculated flows for falling film evaporators for evaporation of the first 70 % of the water

<table>
<thead>
<tr>
<th>Stage number [-]</th>
<th>Incoming liquid flow [kg/h]:</th>
<th>Incoming steam flow [kg/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4778</td>
<td>949</td>
</tr>
<tr>
<td>2</td>
<td>4019</td>
<td>759</td>
</tr>
<tr>
<td>3</td>
<td>3313</td>
<td>706</td>
</tr>
<tr>
<td>4</td>
<td>2666</td>
<td>647</td>
</tr>
<tr>
<td>5</td>
<td>2084</td>
<td>583</td>
</tr>
<tr>
<td>exit</td>
<td>1566</td>
<td>518</td>
</tr>
</tbody>
</table>

\(^1\) sum of liquid and solid stream leaving this unit

\(^2\) sum of liquid and solid streams leaving last 2 units

As calculated earlier, when 68.7% of the water has been evaporated, ZnSO\(_4\) will begin to precipitate. This equals a liquid flow of 2467.17 kg/h. Therefore the first 3 units will be falling film evaporators, because no salts will precipitate in the first 3 stages.

Also calculated earlier, when 75.2% of the water has been evaporated, MgSO\(_4\) will begin to precipitate. Because the amount of water evaporated after the first forced circulation evaporator is higher than 75.2%, the solid stream leaving the first forced circulation evaporator will already contain some MgSO\(_4\) and MnSO\(_4\).

Because we don’t exactly evaporate 98% of the water, an error will be made when calculating the amount of metal sulphate that will precipitate. By iteration this error could be minimized.

**Counter-current flow**

The following (simplified) flow scheme is used for modelling:

![Figure 12.3: block scheme used for calculating optimum number of stages (2 units)](image)

The following equations hold for each unit:

\[
L_{n+1} = L_{n+2} - V_{n+1} \\
V_i \cdot \Delta H_{vap} = U \cdot A_{n+1-i}(T_{V,j} - T_{V,j+1}) / \eta \\
C_p \cdot L_{n+1} \cdot T_{L,n+1-i} - C_p \cdot L_{n+1} \cdot T_{V,j+1} + U \cdot A_{n+1-i}(T_{V,j} - T_{V,j+1}) = V_{j+1} \cdot \Delta H_{vap} \\
T_{L,n+2-i} = T_{V,j+1}
\]
Taking a closer look at the above equations, it follows that the only difference between the co-current and counter-current process is the fact that in the co-current process the feed is preheated before it enters the first stage, while for the counter-current process the feed is heated up with each step. Either way, the temperature difference at each step and therefore the heat exchange area required, will be the same for both processes. We have chosen to use co-current streams, because this is the most common configuration in the industry.

Pressure valves

To lower the pressure (and thereby the temperature) of the liquid stream between two stages, control valves need to be installed; pressure control has to be used to ensure the right pressure drop is applied.

12.1.2 Solid/liquid-separation

Choice for type of filter

Filter S201

Stream <246> to be treated leaving the crystalliser E208 has following composition:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow [kg/h]</th>
<th>ρ [kg/m³]</th>
<th>Flow [m³/h]</th>
<th>Weight perc. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>9.08E+02</td>
<td>1800</td>
<td>0.50</td>
<td>66.7</td>
</tr>
<tr>
<td>Solid</td>
<td>4.54E+02</td>
<td>3265**</td>
<td>0.14</td>
<td>33.3</td>
</tr>
</tbody>
</table>

* assumption, as most of the liquid is sulphuric acid 75 wt%

** assumption, calculated from the composition of solid phase and known densities of different components

For this amount solid, 33.3 wt%, present in the feed the choice can be made between filters and centrifuges [10]. The liquid consists mostly out of sulphuric acid. The continuous operating centrifuge that is able to process the amount of solid mentioned above, is a scroll discharge decanter, a sedimentation centrifuge. From continuous operating filters, rotary drum filter, is the most commonly used liquid solid separator in the industry and the energy consumption is much lower than for a centrifuge; for that reason a rotary drum filter has been chosen. The particle size is assumed to be 200 μm, it is assumed that there are no fine particles, which need to be separated at the large rotational speed used by centrifuges.

Filter S202

Stream <255> to be treated, leaving mixer M201 used for dissolving MgSO₄, has the following composition:
Table 12.6: Composition of stream <255> leaving mixer M201

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>(\rho) (kg/m(^3))</th>
<th>Flow (m(^3)/h)</th>
<th>Weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>1.455E+03</td>
<td>1000(^*)</td>
<td>1.455</td>
<td>89</td>
</tr>
<tr>
<td>Solid</td>
<td>1.70E+02</td>
<td>2881(^**)</td>
<td>0.059</td>
<td>11</td>
</tr>
</tbody>
</table>

\(^*\) as most of the liquid is water 88 wt%  
\(^**\) calculated from the composition of solid phase and known densities of different components

As stream <255> contains 11wt% solids, filters and centrifuges are the best liquid/solid separators for mentioned solid concentration and able to remove large quantity liquid [10]. As stream doesn’t contain fine particles and solids don’t need to be very dry the best choice is to use continuous operating rotary drum filter instead of a centrifuge that uses more energy. The solids from the rotary drum filter will be returned to the roasting unit in the zinc plant. The more liquid is removed from solids the larger is the stream to be processed by the following evaporator, the higher is energy consumption.

12.1.3 MgSO\(_4\) purification

After the solid/liquid separation, slurry is obtained that consists of zinc sulphate, magnesium sulphate and manganese sulphate. In order to separate these components, we can make use of the difference in decomposition temperature.

At 1173 K, zinc sulphate and manganese sulphate are already decomposed into sulphides and oxides. This makes separation possible, because ZnS, ZnO, MnS and MnO are insoluble in water and MgSO\(_4\) is very soluble. After a new liquid/solid separation a final evaporation step will give pure magnesium sulphate. This process is summarized in the following figure:

![Figure 12.4: block diagram for purification of MgSO\(_4\)](image-url)
Choice for equipment to purify MgSO₄

Decomposition reactor

In order to calcinate the solids, process of heating solid material to drive out the volatile chemically combined component, high temperatures are required. The best-known furnaces for this kind of operation used to be the Herreshoff furnaces; nowadays they have made room for rotary kiln furnaces with much better energy saving. Rotary kiln furnaces are more flexible, which can be changed to process different feeds, such as the inclination of the furnace and the rotational speed. However the residence time for different particle sizes in the Herreshoff furnace is the same as the furnace is operated vertically, in contrast to the rotary kiln, which is operated under inclination and where the larger particles will roll faster down the reactor. Rotary kilns are easier to design for processing smaller feeds, and will be used in our process.

Cooling

For the cooling of the solid particles the same solution as in the membrane process is used, namely a fluidised bed. In this fluidised bed a coil with cooling water is used. To cool and strip the gas flow leaving the rotary kiln, a bubble column will be used. This is an easy way to remove both unwanted components like SO₃ from the gas stream and to cool the gas flow at the same time.

Solid/liquid-separation

The solid/liquid separation is already described in the previous paragraph (12.1.2).

Evaporation

For the evaporation again a forced circulation evaporator is chosen. The only difference with the preceding ones is the absence of a cyclone to remove part of the liquid.
12.2 Process Flow Scheme

On the following pages the flow scheme of the evaporation process can be found, with units mentioned in the preceding chapter 5.1 and designed in chapter 15, Process and Equipment Design.
12.3 Process Stream Summary

The complete process stream summary is given in appendix 12.3.

12.4 Description and assumptions regarding the PFS

Each unit in the following process flow scheme will be described and designed in the chapter Process and Equipment design (chapter 15).

The assumptions made are listed below.

- For the slurry, a total solid/liquid mass ratio of 1:2 is assumed; furthermore, it is assumed that because of this, about 98% of the total amount of water will be evaporated in the end; the remaining 2 percent will be divided over the remaining liquid stream leaving the final stage and over all solid streams leaving each forced circulation evaporator unit.
- For calculations, it is estimated that 70% of the magnesium will be removed.
- 5 wt% of the solids precipitated in each forced circulation evaporator will go with the liquid flow leaving that reactor.
- Air and fuel gas (CH₄) will be added in stoichiometric amounts.
- Other assumptions for each unit are given in various appendices, in their detailed design, and in chapter 12.1.
12.5 Utilities

The utilities required in the evaporation process are summarized in table 12.7. Fuel and steam are not included in the utilities because they are already mentioned in the stream summary.

Table 12.7: utilities required for the evaporation process, except fuel and steam

<table>
<thead>
<tr>
<th>Utility</th>
<th>Process Unit(s)</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>M201-202</td>
<td>0.95 kW</td>
</tr>
<tr>
<td></td>
<td>P201-214</td>
<td>12.85 kW</td>
</tr>
<tr>
<td>Cooling water</td>
<td>FB201</td>
<td>76.4 m³/h</td>
</tr>
<tr>
<td>Air</td>
<td>E205-206, E209, E211-212</td>
<td>1022 m³/h</td>
</tr>
</tbody>
</table>

Electricity is needed for the mixers and the pumps. Furthermore, cooling water is used in the fluidised bed, in order to cool the hot solid particles leaving the rotary kiln.

The last utility needed is air. Air is used to cool hot liquid and gas streams when necessary and is also used as oxygen supply with the fuel streams.

A complete summary of the utilities is given in appendix 12.4.
12.6 Process Yields

A quick overview of the overall process performance, in terms of process yields, is given in appendix 12.5.

There is one existing process that removes magnesium out of the purified solution, being the biological USB process [4]. In chapter 20, the evaporation process will be compared to the biological process, and to the membrane process as well.

The object of the evaporation process is to remove 28.5 kg Mg/h or 1186.79 t MgSO₄/a (basic assumptions). The amount of MgSO₄ removed in this process is $158.05/1000 \times 8410 = 1329.20$ t/a. Therefore the specifications are met.

In evaporation process there is no zinc loss.
13 Process Control

In general, the evaporation process is quite a robust process, because no additional chemicals are added to produce magnesium sulphate. For this reason, fluctuations in flows (amount), composition, pressure or temperature anywhere in the process will not cause by-products to be formed, or runaway reactions to occur (the only exothermal reaction is the fuel burning for preheating the feed flow and for the rotary kiln, D201).

Still the process should be controlled, for several reasons. Of course, product quality must be maintained, but this quality depends mainly on the effectiveness of the solid/liquid separation in unit S202, because this is the unit where zinc and manganese salts are separated from magnesium sulphate. However, the total costs of the evaporation process depend mainly on the amount of magnesium sulphate produced per m³ incoming solution from the zinc plant. It is of great importance that as little as possible magnesium is lost. For this reason, several process units should be controlled to reduce magnesium loss.

Fluctuations in performance of equipment occur in any chemical process. Process control is necessary in order to know when a particular reactor, pump or heater is not operating as assumed.

In the following table, a summary of the controllers used is given.

Table 7.1: Type of controllers used in the evaporation process

<table>
<thead>
<tr>
<th>Controller</th>
<th>Symbol</th>
<th>Controlled variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow controller</td>
<td>FC</td>
<td>Mass flow of process stream (can also be used to measure density)</td>
</tr>
<tr>
<td>Pressure controller</td>
<td>PC</td>
<td>Pressure of process stream or unit</td>
</tr>
<tr>
<td>Temperature controller</td>
<td>TC</td>
<td>Temperature of process stream or unit</td>
</tr>
<tr>
<td>Level controller</td>
<td>LC</td>
<td>Height of liquid-gas interface in certain unit</td>
</tr>
<tr>
<td>Ratio controller</td>
<td>RC</td>
<td>Ratio of two mass flows</td>
</tr>
</tbody>
</table>

A description of all controllers can be found in [13].

All controllers are included in the flowsheet of the evaporation process. In the following chapters, for all units the control system (if needed) will be described and explained briefly.

13.1 Feed stream

The feed stream entering the first step of the evaporation process should be kept constant, because later in the process, there are 3 falling film evaporators present. As will be explained later, it is of great importance that the feed stream entering a falling film evaporator is kept constant. For this reason, a flow controller is placed after pump P201.
13.2 Falling film evaporators (E202, E203, E204)

Falling film evaporators are highly responsive to alterations of parameters such as energy supply, vacuum, feed rate, concentrations, etc. When equipped with a well-designed automatic control system they can produce a product with very consistent composition. As stated before, it is of great importance to keep the feed flow entering a falling film evaporator at a constant value. This is because sufficient wetting of the heating surface by liquid is extremely important for trouble-free operation of the evaporator unit. If the heating surfaces are not wetted sufficiently, dry patches and incrustations will occur; at worst, the heating tubes will be completely clogged, not to mention the fact that the dissolved salts will precipitate within the tubes if they are insufficiently wetted [31]. For this reason, it is important that the feed splitter is well designed, to ensure sufficient wetting of all tubes. For the first falling film evaporator (E 202), a flow controller, both for the steam feed and the liquid feed, must be installed. For the same reason, a temperature (or pressure) controller should be installed, also correcting the steam feed flow, as a change in the temperature of the liquid feed may cause fluctuations in the amount of heat transferred.

For the next stages, the temperature of the liquid-gas separation section could be used to control the steam flow or steam pressure, to make sure the right amount of heat is transferred at any time. Because the steam flow leaving any stage will be used as feed for the next stage, two options are possible: to adapt the steam flow to changes within a particular stage or to adapt the steam pressure; this can be done because the amount of latent heat that can be obtained from condensing steam changes with steam pressure. Increasing the steam pressure decreases the amount of heat that can be obtained, and vice versa [32]. In both cases, an extra steam inlet is needed if an increase is needed. For this process, pressure control is chosen. A temperature controller that adapts the incoming steam pressure to temperature changes in the separating section should thus be installed. The set points differ for each stage, decreasing from 3.5 bar for the first stage to 1 bar for the last stage.

Between two stages, the liquid flow leaving the former stage will be injected into the latter. To create a temperature difference in the latter stage, the pressure and thereby the temperature of the liquid flow is decreased (causing some liquid to evaporate right away). However, a pressure control is needed to prevent deviations in the next stage. For each unit (except the final stage), a pressure controller must be installed. The set points differ for each stage.

13.3 Forced circulation evaporators (E207, E208)

For forced circulation evaporators, in general there are 2 basic control objectives:

- Concentrate the liquid to a predefined solids content
- Keep a constant predefined solid flow leaving the evaporator.

Most control systems in industry are based on these 2 objectives.

In our evaporation process, the following control loops will be placed, to meet the objectives mentioned above:
To keep a constant solids concentration, a mass flow meter for density measurement should be placed at the solids outlet (this is the most common method used in industry) [33]. The density measurement, which is easily converted to a solids content, can then be used to control either product removal rate from the evaporator, steam flow, or feed flow. In this process, for evaporators E207 and E208, the incoming steam pressure will be adapted to changes in the solids content of the slurry leaving each forced circulation evaporator, analogous to the system described for falling film evaporators. For evaporator E211, the boiler power will be adapted by changing the fuel flow rate. Again, a ratio control loop is used to keep a fixed fuel-air ratio.

For evaporators E207 and E208, sufficient wetting of the tubes in the heat changer section is not as much an issue here as it was for falling film evaporators, as it is assumed that the wetted surface equals the cross sectional area of the tubes. However, clogging of the tubes should still be kept to a minimum; a well-designed feed splitter is required.

Also, for evaporator E207 it is important to keep the total liquid flow (as well as the composition) leaving the evaporator via the cyclone at a constant value, because this is the feed flow for E208. A flow controller should be placed at the cyclone outlet to keep constant flow.

Summarizing, the procedure here to combine concentration and level control is to set the incoming steam pressure at the design value, remove product based on density in the recirculation loop, and adjust the feed flow to maintain liquid levels in the evaporator. When a higher throughput is required, then the steam pressure is lowered (in this way more latent heat can be obtained). This technique provides good control of the product concentration with conventional analog controllers.

13.4 Boiler furnace (F201, F202)

The stream leaving furnace F201 will enter the first falling film evaporator; to keep this flow at a constant temperature, a temperature controller must be installed that adapts furnace power, if the temperature of the stream entering the furnace deviates from its regular value. The set point for the outgoing flow is 413 K. F202 is used to evaporate water to concentrate the magnesium sulphate solution; because the concentrated MgSO₄ will be stored in a tank to dry, it doesn’t matter that much how much water is evaporated exactly, so a control system will not be necessary here.

13.5 Fluidised bed (FB201)

This unit is needed to cool the solid dust particles leaving the rotary kiln. The amount of solid in the bed doesn’t have to be controlled, because it will just flow over the edge, into the hopper section (see fig.8.7). To control the temperature of the bed and the cooling water, a cascade control will be installed. If the outgoing cooling water temperature deviates from its regular value,
the coolant flow is adjusted. If the bed temperature deviates from its regular value, the cooling water flow is also adjusted, overruling the former adjustments if necessary.

### 13.6 Air-cooled heat exchangers (E205, E206, E 212)

These are used to cool the condensed vapour flows leaving each falling film evaporator. Detailed control of exchanger E212 is not of great importance, as the cooled condensed vapour will not be used in a following process step. However, the streams cooled by exchangers E 025 and E 206 will be used in mixer M201 later. Because the temperature of this flow determines the amount of magnesium that will dissolve in the mixer, temperature controllers should be installed, to prevent loss of not dissolved magnesium. There are two ways to control the liquid outgoing stream temperature in an air-cooled heat exchanger:

- Vapour (air) flow recompression (VPR)
- Air flow adjustment

In the evaporation process, airflow adjustment will be used, as this is the most common method in industry [34]. A few methods mentioned here to change the airflow are usage of an adjustable power engine, fan shut-off in sequence, or usage of adjustable louvers. Fan shut-off is most commonly used for simple systems because energy is saved when the airflow reduces, and it will be sufficient for our process as well.

### 13.7 Mixer (M201)

This unit is used to dissolve all magnesium sulphate, while zinc and manganese salts do not dissolve at all. To make sure sufficient water is added, one must control the incoming water flow (essentially the split fraction of splitter Y202), using a solid mass flow meter to measure the total mass flow of stream <250>. To keep the liquid level at a constant value, a level controller is placed to control the incoming water flow.

### 13.8 Rotary kiln (D201)

This is the only unit where chemical reactions take place. To ensure full conversion, and to minimise energy costs, a good control system is essential. The following parameters should be controlled: airflow, fuel flow, reactor temperature, exit vapour composition, and dust control.

To react to changes in the slurry mass flow, a flow controller should be installed to adapt the fuel flow; a ratio controller could then be installed to ensure a fixed ratio between the air inflow and the fuel flow. Also, cascade control loop should be designed: a temperature controller, placed at the reactor gas flow exit, could control the fuel feed flow. The ratio controller then adjusts the air inflow. The same system could be used to control the exiting gas flow composition.
If the airflow becomes too high, an increasing number of small dust particles leave the reactor. To prevent this, a maximum value should be assigned for the incoming gas flows.

13.9 Bubble column (M202)

This column is used to strip the gas flow leaving unit D201. To make sure all SO₃ is converted to H₂SO₄, a simple control system is required. The flue gas should be analysed by a composition analyser; if there is too much SO₃ present, then the stirrer power is increased to improve gas-liquid transfer. A second control loop is used to increase the liquid level if faster stirring is insufficient, thereby increasing the residence time of the gas. This can be done by adjusting the liquid feed flow. To keep the temperature within the mixer constant, the cooling water flow can be adjusted by a temperature controller.

13.10 Rotary filters (R201, R202)

After both filters, a mass flow meter for density measurement of streams <248> and <264> should be installed, to adapt pump rates for pumps 210 and 212, respectively. A higher flow rate generates a higher pressure difference, and thereby generating a higher solid /liquid separation efficiency.

13.11 Pressure valves and non return valves

Streams <214> and <216> leaving the second and third falling film evaporator respectively, will be mixed to add to the mixer M201. To prevent the flow leaving E203 going back into E204 (because the pressure of stream <216> is much higher), both streams are expanded to 1 bar. To cope for deviations, two non-return valves will be placed before the mixing points, and the pressure of both streams will be controlled by a PC.

As stated before, pressure valves will be placed to control the pressure of the incoming stream (both vapour and liquid streams) between two falling film evaporators.

13.12 Blowers (K201, K202, K203)

A flow controller is placed after every blower to ensure a constant gas flow.
14 Mass and Heat balances

The streamsummary for the evaporation process is given appendix 12.3. Also included here are:
- A total mass balance over the battery limit.
- A total enthalpy balance over the battery limit.
- A total element balance over the battery limit.
- Mass balances over three sections. These sections are
  1. Falling film evaporation section. This corresponds to the first A3 paper sheet of the process flow scheme of the evaporation process.
  2. Forced circulation evaporation section. This section corresponds to the second A3 paper sheet of the process flow scheme of the evaporation process.
  3. Rotary kiln & Final forced circulation evaporation section. This section corresponds to the second A3 paper sheet of the process flow scheme of the evaporation process.
- Mass and enthalpy balances over some important pieces of equipment. (E202, E203, E204, E207, E208, E210+F202, D201, F201)

The total mass balance gives a satisfactory result. The difference between incoming and outgoing flows is only (7851.04-7850.95)/7851.04 · 100 % = 0.0011 %.

The total element balance is satisfactory as well. No faults are observed here at all.

The mass balances over the three sections are also satisfactory.
Section 1, outgoing – incoming flows: -0.02 kg/h.
Section 2, outgoing – incoming flows: 0 kg/h.
Section 3, outgoing – incoming flows: 0.11 kg/h.

The mass balances over the separate pieces of equipment are all right as well.

However there is one problem. The total enthalpy balance has a large fault. This fault can partly be attributed to heat losses, which are assumed at units containing heat transfer. But even when this is taken into account, the enthalpy balances will not close.

The explanation for this is as follows: When defining the way to calculate enthalpies (see chapter 4.3), the enthalpy of hydration is assumed approximately equal to the lattice energy for solids. Both are therefore ignored. Although this is approximately true for some salts, a deeper inspection of enthalpy tables shows this assumption is very wrong.

If this is indeed the reason for the differences in the enthalpy balance one would expect that there is a certain correlation between the differences from what is expected because the concentration of salts increase at each evaporation step. Some calculations show that such a correlation indeed exists.
15 Process and Equipment Design

15.1 Furnace design (F201)

The furnace, used for preheating, will be fed with natural gas, which is assumed to consist of pure methane. The following reaction will occur.

\[
\text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad [\text{eq. 15.1}]
\]

\[
\Delta H_r = -5.55 \times 10^7 \text{ J/kg} \quad [3]
\]

The heat duty required is calculated in order to decide the amount of natural gas needed.

\[
Q = \Phi_{m,\text{liquid}} c_p (T_{\text{out}} - T_{\text{in}}) \quad [\text{eq. 15.2}]
\]

\[
\Phi_{m,\text{CH}_4} = \frac{Q}{\Delta H_r} \quad [\text{eq. 15.3}]
\]

with: \( \Phi_{m,\text{liquid}} = 4779 \text{ kg/h} \)

\( c_p = 4.18 \times 10^3 \text{ J/(kgK)} \quad [3] \)

This gives a heat duty of 544 kW that requires a mass flow rate of 35.3 kg/h CH\(_4\). Air is added at a 2:1 molar ratio (O\(_2\):CH\(_4\)); this is assumed to be needed in the furnace. This equals an amount of 634.9 kg/h air.

A value for the heat transfer coefficient of 200 W/(m\(^2\)K) is assumed. The combustion temperature of methane is assumed to be 700 K. The following equations are used to calculate the heat transfer surface required.

\[
Q = UA \text{ LMTD} \quad [\text{eq. 15.4}]
\]

\[
\text{LMTD} = \frac{(T_{\text{comb}} - T_{\text{out}}) - (T_{\text{comb}} - T_{\text{in}})}{\ln \left( \frac{T_{\text{comb}} - T_{\text{out}}}{T_{\text{comb}} - T_{\text{in}}} \right)} \quad [\text{eq. 15.5}]
\]

This equation yields a LMTD of 333 K and a heat transfer surface of 8.2 m\(^2\).

U-tubes are used to heat the incoming liquid. The diameter of the tubes is decided to be 20 mm o.d. (16 mm i.d.) and the total length will be 4 m. The amount of tubes needed, the dimensions of the furnace and the velocity of the liquid in the tubes is calculated analogous to paragraph 15.2 (design forced circulation evaporators). The results are summarized in table 15.1.
**15.2 Design falling film evaporators**

In the process we make use of 3 falling film evaporators (E202-E204). Falling film evaporators can be separated into a heating section and an expansion section. First, the heating section will be discussed; subsequently the expansion section will be worked out in detail.

**15.2.1 Design of the heating section**

The heating section consists of a bundle of tubes in which a liquid film falls down. This liquid film exchanges heat with steam on the outside of the tubes. We have made some assumptions with respect to the heating section:

- Length of tubes: 10 m
- Inner diameter of tubes: 0.04 m
- Water film thickness: 0.002 m
- Thickness of tubes: 0.003 m
- Thickness of outside wall: 0.05 m
- Pressure drop over the tubes is ignored
- The value for the specific heat, liquid density and liquid viscosity vary in each step. For the calculation of these quantities the weighted average is taken of the values of pure water and sulphuric acid, depending on the ratio in which they occur.

The number of tubes needed at each stage is calculated using the following equations:

\[ A_{\text{tube}} = \pi D_{\text{tube}} L_{\text{tube}} \]  
\[ n_{\text{tube}} = \frac{A_{\text{needed}}}{A_{\text{tube}}} \]  

The results for all stages are given in the following table:

**Table 15.2: calculated heat exchanger areas and number of tubes**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Heat exchange area needed [m²]</th>
<th>Number of tubes (n_{\text{tube}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>E202</td>
<td>119</td>
<td>95</td>
</tr>
<tr>
<td>E203</td>
<td>95</td>
<td>76</td>
</tr>
<tr>
<td>E204</td>
<td>89</td>
<td>71</td>
</tr>
</tbody>
</table>

The tubes will be placed in a configuration as shown in figure 15.1.
From the chosen tube configuration, the total diameter of heating section can be estimated. The cross-section surface of the heating section due to \( n \) tubes can be approximated using the following equation:

\[
A_{\text{tot}}^{\text{est}} = 2(D_{\text{tube}} + 2\delta_{\text{tube-wall}})^2 n_{\text{tube}} \quad \text{[eq. 15.8]}
\]

\[
D_{\text{tot}}^{\text{est}} = \left( \frac{4A_{\text{cross-tot}}^{\text{est}}}{\pi} \right) \quad \text{[eq. 15.9]}
\]

\[
D_{\text{tot}} = D_{\text{xo}}^{\text{est}} + x + 2\delta_{\text{outside}} \quad \text{[eq. 15.10]}
\]

\[
A_{\text{cross-tot}} = \frac{\pi}{4} D_{\text{tot}}^2 \quad \text{[eq. 15.11]}
\]

To compensate for some extra surface on the edge of the bundle, the surface is extended with a shell with a thickness of \( x/2 \) m. For \( x \), a value of 0.05 m is assumed. The dimensions of the heating sections for every stage are given in the following table.

**Table 15.3: Dimensions heating section falling film evaporators**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Diameter heating section [m]</th>
<th>Height heating section [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E202</td>
<td>0.86</td>
<td>10</td>
</tr>
<tr>
<td>E203</td>
<td>0.79</td>
<td>10</td>
</tr>
<tr>
<td>E204</td>
<td>0.77</td>
<td>10</td>
</tr>
</tbody>
</table>
The velocities of liquid and steam inside and outside the tubes are calculated using the equations 15.12-15.14.

\[ v_{\text{liq}} = \frac{\varphi_{n,\text{liq}}}{\rho_{\text{liq}}} \left( \frac{1}{\frac{1}{2}D_{\text{tube}}^2 - \frac{1}{2}(D_{\text{tube}} - 2D_{\text{film}})^2} \right) n_{\text{tube}} \]  
[eq. 15.12]

\[ v_{\text{vap, in}} = \frac{\varphi_{n,\text{vap}}}{\rho_{\text{vap}}} \left( \frac{1}{\frac{1}{2}(D_{\text{tube}} - 2\delta_{\text{film}})^2} \right) n_{\text{tube}} \]  
[eq. 15.13]

\[ v_{\text{vap, out}} = \frac{\varphi_{n,\text{vap}}}{\rho_{\text{vap}}} \left( \frac{1}{\frac{1}{2}(D_{\text{tube}} - 2\delta_{\text{out}})^2} - n_{\text{tube}} \frac{1}{\frac{1}{2}(D_{\text{steam}} + 2\delta_{\text{tube}})^2} \right) \]  
[eq. 15.14]

The results are summarized in table 15.4:

**Table 15.4: velocities of liquids and gases in heating section falling film evaporators**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Initial liquid velocity [m/s]</th>
<th>Outgoing vapour velocity (inside tubes) [m/s]</th>
<th>Ingoing vapour velocity (outside tubes) [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E202</td>
<td>0.057</td>
<td>1.11</td>
<td>0.27</td>
</tr>
<tr>
<td>E203</td>
<td>0.053</td>
<td>2.26</td>
<td>0.43</td>
</tr>
<tr>
<td>E204</td>
<td>0.038</td>
<td>4.18</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The results for the velocities look quite reasonable. This is a first check for the adequacy of the made assumptions. Recalculating the overall heat transfer coefficient will do a second check.

The heat transfer coefficient initially was estimated to be 200 W/m²/K. The following equations are used to recalculate this parameter.

\[ \frac{1}{U} = \frac{1}{h_{\text{inside}}} + \delta_{\text{tube}} + \frac{1}{h_{\text{outside}}} \]  
[eq. 15.15]

where:  
\[ h_{\text{inside}} = \frac{Nu_{\text{inside}} \lambda_{L}}{L_{\text{tube}}} \]  
[eq. 15.16]

\[ Nu_{\text{inside}} = (1.3 + bD_{\text{tube}})Pr_{L}^{0.9} Re_{L}^{0.23} R_{L}^{0.34} (\frac{P_{L}}{\rho_{\text{steam}}})^{0.25} \eta_{L} \]  
[eq. 15.17]

\[ Pr_{L} = \frac{C_{P,L} \eta_{L}}{\lambda_{L}} \]  
[eq. 15.18]

\[ Re_{L} = \frac{\rho_{L} v_{\text{liq}} D_{L}}{\eta_{L}} \]  
[eq. 15.19]

\[ Re_{L} = \frac{\rho_{\text{steam}} v_{\text{vap, in}} (D_{\text{tube}} - 2\delta_{\text{film}})}{\eta_{\text{steam}}} \]  
[eq. 15.20]
\[ h_{outside} = 5700 \quad [30] \quad \text{[eq. 15.21]} \]

All values used for the given constants are summarized in appendix 15.1.

**Table 15.4: Recalculated heat transfer coefficients falling film evaporators**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Heat transfer coefficient U (recalculated) [W/m²/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E202</td>
<td>4673</td>
</tr>
<tr>
<td>E203</td>
<td>4686</td>
</tr>
<tr>
<td>E204</td>
<td>4693</td>
</tr>
</tbody>
</table>

As the heat transfer coefficients are much bigger than the estimated value of 200 W/m²/K, the calculation of the number of units necessary is not correct. We have assumed an optimal cascade of three falling film evaporators and two forced circulation evaporators. The optimal configuration with the new heat transfer coefficient is 6 falling film evaporators and 5 forced circulation evaporators.

With this new coefficient the estimated costs are 9.34 €/hr, while the estimated costs for the first estimation 17.62 €/hr. For the economy of the evaporation we will divide the calculated costs by a factor of 17.62/9.34≈1.89. This factor will be referred to as duty correction factor.

All calculations for the heating section of the falling film evaporator design are done using the matlab script in appendix 15.2.

**15.2.2 Expansion section**

The expansion section is a vessel in which the formed liquid/vapour mixture is collected. A schematic representation of the expansion vessel is shown in figure 15.2.

![Figure 15.2 expansion section falling film evaporator](image)

A relative short residence time is commendable, because every second the mixture is in the vessel will give bigger heat losses. However, the residence time cannot be too short, because a good separation of solid and liquid has to be achieved.
The expansion sections have the following incoming streams.

### Table 15.5: incoming streams in the expansion vessel

<table>
<thead>
<tr>
<th>Stage</th>
<th>Mass flow [kg/h]</th>
<th>Density [kg/m³]</th>
<th>Volume flow [m³/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>liquid</td>
<td>vapour</td>
<td>liquid</td>
</tr>
<tr>
<td>E202</td>
<td>4019</td>
<td>759</td>
<td>1343</td>
</tr>
<tr>
<td>E203</td>
<td>3313</td>
<td>706</td>
<td>1417</td>
</tr>
<tr>
<td>E204</td>
<td>2666</td>
<td>647</td>
<td>1495</td>
</tr>
</tbody>
</table>

1 Density estimated as described in chapter 4.4: Thermodynamic Properties

The needed residence time for liquid in the expansion section is assumed to be 60 s to make the liquid volume big enough to control the liquid level in the vessel. The residence time of the vapour needed to get in equilibrium is chosen to be 10 s. The volume needed is equal to the volume flow multiplied by the residence time. The results for the volumes are given in table 15.6.

### Table 15.6: volumes expansion section falling film evaporators

<table>
<thead>
<tr>
<th>Stage</th>
<th>Volume liquid [m³]</th>
<th>Volume solid [m³]</th>
<th>Total volume [m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E202</td>
<td>0.050</td>
<td>1.07</td>
<td>1.12</td>
</tr>
<tr>
<td>E203</td>
<td>0.039</td>
<td>1.75</td>
<td>1.79</td>
</tr>
<tr>
<td>E204</td>
<td>0.030</td>
<td>3.00</td>
<td>3.03</td>
</tr>
</tbody>
</table>

To determine the height and the diameter of the expansion vessel the H/D ratio is set equal to 3. Calculation of the needed volumes and diameters provide the following dimensions.

### Table 15.7: Dimensions expansion section falling film evaporators

<table>
<thead>
<tr>
<th>Stage</th>
<th>Height [m]</th>
<th>Diameter [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E202</td>
<td>2.34</td>
<td>0.78</td>
</tr>
<tr>
<td>E203</td>
<td>2.74</td>
<td>0.91</td>
</tr>
<tr>
<td>E204</td>
<td>3.26</td>
<td>1.09</td>
</tr>
</tbody>
</table>
15.3 Design Forced circulation evaporators

In our process we use three forced circulation evaporators. Two of them are used in the multi-effect evaporation part. The last one is needed to obtain the solid magnesium sulphate. A schematic figure of a forced circulation evaporator is shown below.

![Schematic picture forced circulation evaporator](image)

In a forced circulation evaporator the process stream enters the evaporation section. On top of this cyclone-like unit the steam is going out and in the bottom the slurry is removed. Part of the liquid is pumped around to the heating section using an axial-flow pump. A rather huge flow is needed to get an effective heat exchange. In the 2 forced circulation evaporators in the multi-effect part also a cyclone is added to remove a liquid stream.

Assumed is the presence of 10% solids in the liquid, which is circulated in evaporator E208. In E209 this amount is assumed to be 20%.

15.3.1 Boiler design (F202/E210)

The used furnace will be fed with natural gas, which is assumed to consist of pure methane. The following reaction will occur.

\[
\text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \\
\Delta H_r = -5.55 \times 10^7 \text{ J/kg} \quad [3]
\]

To decide the mass flow of natural gas needed, the following equation is used:

\[
\Phi_{m, \text{CH}_4} \Delta H_r = -\Phi_{m, \text{prod. steam}} \Delta H_{\text{vap. H}_2\text{O}}
\]

[eq. 15.23]
with: \( \Phi_{\text{m,prod,steam}} = 1000 \text{ kg/h} \)
\( \Delta H_{\text{vap,H}_2\text{O}} = 2.26 \times 10^6 \text{ J/kg} \) [3]

This gives a mass flow rate of 40.7 kg/h CH\(_4\).

A value of the heat transfer coefficient of 200 W/(m\(^2\)K) is assumed. The combustion temperature of methane is assumed to be 700 K, while the boiling temperature of the liquid is 373.15 K at 1 bar. The following equation is used to calculate the heat transfer surface required.

\[ UA(T_r - T_i) = -\Phi_{m,\text{CH}_4} \Delta H_r \]  
\[ \text{[eq. 15.24]} \]

This equation yields a surface needed of 9.60 m\(^2\).

**15.3.2 Design of the heating section**

Analogous to the falling film evaporators, the starting point of our design will be the heating section. For this type evaporator the following assumptions are made:

- Length of tubes: 5 m
- Inner diameter of tubes: 0.08 m
- Thickness of tubes: 0.006 m
- Thickness of outside wall: 0.05 m
- Pressure drop over the tubes is ignored
- For each step, because the ratio of the 2 main components (water and sulphuric acid), the average value of the specific heat and the liquid viscosity has been used, depending on the ratio of water and sulphuric acid.

All calculations in the heating section are made in the Matlab script given in appendix 15.3.

The number of tubes needed at each stage is calculated using equations 15.6 and 15.7.

The results for both stages are given in the following table:

**Table 15.8: calculated heat exchanger areas and number of tubes**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Heat exchange area needed [m(^2)]</th>
<th>Number of tubes ((n_{\text{tube}})) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E207</td>
<td>81</td>
<td>65</td>
</tr>
<tr>
<td>E208</td>
<td>73</td>
<td>59</td>
</tr>
<tr>
<td>E210</td>
<td>14</td>
<td>18</td>
</tr>
</tbody>
</table>

The total diameter of the heating section follows from equations 15.8-15.11. The results are shown in table 15.9.
Table 15.9: Dimensions heating section Forced circulation evaporators

<table>
<thead>
<tr>
<th>Stage</th>
<th>Diameter heating section [m]</th>
<th>Height heating section [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E207</td>
<td>1.33</td>
<td>5</td>
</tr>
<tr>
<td>E208</td>
<td>1.27</td>
<td>5</td>
</tr>
<tr>
<td>E210</td>
<td>0.78</td>
<td>3</td>
</tr>
</tbody>
</table>

We can choose some reasonable incoming liquid velocities for the heating section. The vapour velocities can be calculated using equations 15.25-15.27:

\[
v_{\text{liq}} = \frac{\frac{\Phi_{\text{in}}}{\rho_{\text{liq}}}}{\frac{\frac{\pi}{4} D_{\text{tube}}^2}{n_{\text{tube}}}} \frac{1}{n_{\text{tub}}} \]

[eq. 15.25]

\[
v_{\text{vap, in}} = \frac{\frac{\phi_{\text{vap, in}}}{\rho_{\text{vap}}}}{\frac{\frac{\pi}{4} D_{\text{vap}}^2}{n_{\text{tube}}}} \frac{1}{n_{\text{tub}}} \]

[eq. 15.26]

\[
v_{\text{vap, out}} = \frac{\frac{\phi_{\text{vap, out}}}{\rho_{\text{vap}}}}{\frac{\frac{\pi}{4} (D_{\text{tot}} - 2\delta_{\text{out}})^2}{n_{\text{tube}}} - \frac{\pi}{4} (D_{\text{tot}} + 2\delta_{\text{tube}})^2} \]

[eq. 15.27]

Table 15.10: Velocities of liquids and gases in heating section forced circulation evaporators

<table>
<thead>
<tr>
<th>Stage</th>
<th>Initial liquid velocity [m/s]</th>
<th>Outgoing vapour velocity (inside tubes) [m/s]</th>
<th>Ingoing vapour velocity (outside tubes) [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E207</td>
<td>0.25</td>
<td>1.70</td>
<td>0.40</td>
</tr>
<tr>
<td>E208</td>
<td>0.25</td>
<td>3.77</td>
<td>0.80</td>
</tr>
<tr>
<td>E210</td>
<td>0.25</td>
<td>10.3</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

Analogous to the falling film evaporators the heat exchange coefficients (first estimate: 200 W/(m²K)) are recalculated for evaporators E207 and E208. The results are given in table 15.11:

Table 15.11: Recalculated heat transfer coefficients forced circulation evaporators

<table>
<thead>
<tr>
<th>Stage</th>
<th>Heat transfer coefficient (recalculated) [W/m²/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E207</td>
<td>3998</td>
</tr>
<tr>
<td>E208</td>
<td>3999</td>
</tr>
</tbody>
</table>

Here also, the initial estimates of the heat transfer coefficients are far too low. The duty correction factor, introduced in the paragraph 15.2.1, will also hold for the forced circulation evaporators.

15.3.3 Cyclone design

The hydro cyclones will be designed according to a method described in Coulson and Richardson [10]. This method is described shortly in during the design of the hydro cyclones in the membrane process [chapter 8.9].
To design a hydro cyclone, a particle size distribution has to be assumed. We assume a distribution of 50-500 µm. A cyclone will be designed which separates 90% of the particles with a diameter greater than 100 µm of the dilute slurry. This gives a \(d_{50}\) value of 70 micron.

Furthermore the following assumptions have been made:
\[
\begin{align*}
\rho_L &= 1 \text{ g/cm}^3 \\
\rho_S &= 3.5 \text{ g/cm}^3 \\
\mu &= 2.10^{-3} \text{ Pa} \cdot \text{s}
\end{align*}
\]

The incoming liquid flow is assumed to be 1.5 times the amount of liquid, which has to be removed.

**Table 15.12: incoming flow rate and diameter of the cyclone**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Incoming flow rate [m³/h]</th>
<th>Dc [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.50</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>12</td>
</tr>
</tbody>
</table>

All incoming and outgoing flow rates are summarized in table 15.13:

**Table 15.13: incoming and outgoing streams of the cyclone**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Incoming stream L [kg/h]</th>
<th>Outgoing “liquid” L [kg/h]</th>
<th>Outgoing “slurry” S [kg/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1970</td>
<td>1448</td>
<td>522</td>
</tr>
<tr>
<td>2</td>
<td>244</td>
<td>187</td>
<td>57</td>
</tr>
</tbody>
</table>

The angle of the cyclone wall is chosen at the typical value of 10°.

**15.3.4 Pump design**

In each forced circulation evaporator a pump is needed to circulate the liquid from the evaporation section to the heating section and eventually to the cyclone. An axial-flow circulating pump is used to do this. The volume flows to be transported by the pumps are given in table 15.14.

**Table 15.14: incoming and outgoing streams of the cyclone**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Volume flow heating section [m³/hr]</th>
<th>Volume flow cyclone [m³/hr]</th>
<th>Total volume flow pump [m³/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>294.1</td>
<td>1.50</td>
<td>295.6</td>
</tr>
<tr>
<td>2</td>
<td>266.9</td>
<td>0.25</td>
<td>267.2</td>
</tr>
<tr>
<td>3</td>
<td>135.7</td>
<td>0</td>
<td>135.7</td>
</tr>
</tbody>
</table>
15.3.5 Expansion section design

A schematic representation of the expansion section is shown in figure 15.4. The middle section consists of a cyclone in which the liquid is mixed. The vapour, which is formed in the heating section, will leave the vessel at the top. The bigger solid particles will go down in an elutriating leg. To get relative thick slurry a Swenson patented slurry inlet device can be used [35].

The volume of the liquid in the expansion section is estimated by choosing a residence time. The total volume of the vessel is assumed to be twice the liquid volume. For the dimensions a H/D ratio of 2 is used.

![Figure 15.4: expansion section](image)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Residence time [s]</th>
<th>Liquid Volume [m³]</th>
<th>Vessel volume [m³]</th>
<th>Height [m]</th>
<th>Diameter [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1800</td>
<td>0.879</td>
<td>1.76</td>
<td>2.08</td>
<td>1.04</td>
</tr>
<tr>
<td>2</td>
<td>1800</td>
<td>0.499</td>
<td>1.00</td>
<td>1.72</td>
<td>0.86</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>0.258</td>
<td>0.52</td>
<td>1.38</td>
<td>0.69</td>
</tr>
</tbody>
</table>

15.3.6 Discussion third evaporator

In the process flow sheet, a boiler heats the third evaporator. Calculations have shown relative high costs for this unit. To save costs, the last forced circulation evaporator can be included as one or two extra effects in the multi-effect stage. This will increase the heat integration throughout the process. As a result, less energy is needed.
15.4 Design air cooled exchanger:

15.4.1 Choice of equipment

Streams <209> and <213> need to be cooled down, as they will be used in another unit later, which doesn’t allow high temperatures or high pressures. As pointed out by [10], air cooled condensers are more energy efficient when the temperature of the process stream that needs to be cooled is above 338 K. Because the temperature of streams <209>, <213> are all above this temperature (respectively 413 K, 393 K and 433 K), an air-cooled exchanger is used to cool the water.

15.4.2 Description and design

In the evaporation process, there are 3 air-cooled exchangers present (E205, E206 and E212). All three are used to cool a condensed steam flow leaving any of the falling film evaporators. The chosen air-cooled exchanger consists of banks of finned tubes over which air is blown by fans mounted below the tube (or tube bundle if a relatively large heat exchange area is needed). To distribute the airflow equally, a propeller is used. A schematic illustration of the exchanger chosen can be found in [10].

For the design, the following (simplified) block scheme is used:

![Figure 15.5: Block scheme used to calculate dimensions of an air cooled heat exchanger](image)

It is assumed that there is no horizontal air temperature gradient. As a result, the air temperature over the entire tube length for both directions used in the equations is assumed to be constant. The air temperature only changes with height. Also, the vertical part of the tube will be ignored for calculations. The flow rate of water entering the air-cooled exchangers can be found in table 15.16.
Table 15.16: flow rate of incoming water

<table>
<thead>
<tr>
<th>Stream number</th>
<th>Heat exchanger</th>
<th>Mass flow rate of incoming water [kg/h]</th>
<th>Liquid temperature decrease needed [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>209</td>
<td>E205</td>
<td>759.27</td>
<td>40</td>
</tr>
<tr>
<td>213</td>
<td>E206</td>
<td>706.30</td>
<td>20</td>
</tr>
<tr>
<td>266</td>
<td>E212</td>
<td>949.09</td>
<td>113</td>
</tr>
</tbody>
</table>

The required heat exchange area and the airflow needed are calculated using the following set of equations:

\[
\phi_L \cdot C_{p, L} \cdot (T_{L, in} - T_{L, avg}) = U \cdot A_1 \cdot \left[ \frac{T_{L, in} + T_{L, avg}}{2} - T_{air, avg, 1} \right] \tag{eq. 15.28}
\]

\[
\phi_L \cdot C_{p, L} \cdot (T_{L, avg} - T_{L, out}) = U \cdot A_2 \cdot \left[ \frac{T_{L, in} + T_{L, avg}}{2} - T_{air, avg, 2} \right] \tag{eq. 15.29}
\]

\[
T_{air, avg, 1} := \frac{T_{air, out} + T_{air, int}}{2} \tag{eq. 15.30}
\]

\[
T_{air, avg, 2} := \frac{T_{air, in} + T_{air, int}}{2} \tag{eq. 15.31}
\]

\[
\phi_{v, air} := \frac{\phi_L \cdot C_{p, L} \cdot (T_{L, in} - T_{L, out})}{C_{p, air} \cdot (T_{air, out} - T_{air, in})} \cdot \frac{3600}{\rho_{air}} \tag{eq. 15.32}
\]

The detailed calculations are given in Appendix 15.4.

The resulting heat exchange area and gas flow for each unit is given in table 15.17.

Table 15.17: heat exchange area and gas flow per unit

<table>
<thead>
<tr>
<th>Heat exchanger</th>
<th>Heat exchange area upper section (A₁) [m²]</th>
<th>Heat exchange area lower section (A₂) [m²]</th>
<th>Gas flow [m³/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E205</td>
<td>0.78</td>
<td>0.61</td>
<td>2455</td>
</tr>
<tr>
<td>E206</td>
<td>0.45</td>
<td>0.34</td>
<td>1142</td>
</tr>
<tr>
<td>E212</td>
<td>3.41</td>
<td>2.67</td>
<td>10210</td>
</tr>
</tbody>
</table>

For exchangers E205 and E206, because the required areas are relatively small, a few tubes will be enough to cool the incoming water, while the length of the tube will still be reasonable.

For E 212 though, a larger area is needed; therefore, a set of tubes is needed to reduce the tube length. Results are given in table 15.18.
Table 15.18: Heat exchanger dimensions

<table>
<thead>
<tr>
<th>Heat exchanger</th>
<th>Tube diameter upper section [m]</th>
<th>Tube diameter lower section [m]</th>
<th>Tube length [m]</th>
<th>Number of tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>E205</td>
<td>0.031</td>
<td>0.025</td>
<td>2.0</td>
<td>4</td>
</tr>
<tr>
<td>E206</td>
<td>0.024</td>
<td>0.018</td>
<td>2.0</td>
<td>3</td>
</tr>
<tr>
<td>E212</td>
<td>0.054</td>
<td>0.042</td>
<td>2.0</td>
<td>10</td>
</tr>
</tbody>
</table>

Also, the dimensions of the surrounding buildings are given in App. 15.4.

The tubes are closely packed; every tube is set apart 0.01m set apart from the other tubes. Every following row tubes is shifted horizontally in respect to the upper row tubes to maximize the contact between cooling air and the tubes, see figure 2:

Figure 15.6: Tube arrangement

In order to direct the flow of the air the tubes will be put into a building with following dimensions: 2×2×1 (h×l×w). Fans below the tubes will blow the air [10].

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15.5 Design air cooled condensers

15.5.1 Choice of equipment

The vapour flows leaving units E208 and E210 need to be condensed before sending them back to the plant. As pointed out earlier, air-cooled heat exchangers are more efficient if the temperature of the stream to be cooled is above 65 °C. Water coolers are more efficient if the temperature becomes lower than 50 °C. Because the temperature of stream 230 is 60 °C (which is closer to 65 °C), it is assumed that an air-cooled heat exchanger will be more energy efficient. The temperature of stream leaving E210 is 100 °C, so it’s clear that in this case an air-cooled heat exchanger will be the best option here. According to [10], an air-cooled heat exchanger can also be used as an air-cooled condenser; for this reason, an air-cooled heat exchanger is used to condensate the gas flows.

15.5.2 Description and design

In the evaporation process, there are 2 air-cooled exchangers present (E209 and E211). Both of them are used to condensate vapour flows leaving a forced crystallization evaporator. Further specifications are given in the description and design for the air-cooled heat exchanger.

For the design, the same block scheme is used (see figure 15.5).

The same assumptions as made for the air-cooled heat exchanger have been made here again. Also, it is assumed that half the water is condensed at the upper section, the other half at the lower section.

The same equations are used here as for the air-cooled heat exchanger, except eq. 28, 29 and 32, which are replaced by the following 3 equations:

\[
\frac{1}{\eta} - 0.5 \phi_{L} \Delta H_{vap} = U \cdot A_{1} \left( T_{L, in} - T_{air, avg, 1} \right) \quad \text{[eq.15.33]}
\]

\[
\frac{1}{\eta} - 0.5 \phi_{L} \Delta H_{vap} = U \cdot A_{2} \left( T_{L, in} - T_{air, avg, 2} \right) \quad \text{[eq.15.34]}
\]

\[
\phi_{V, air} = \frac{\phi_{L} \Delta H_{vap}}{C_{P, air} \left( T_{air, out} - T_{air, in} \right)} \frac{3600}{\rho_{air}} \quad \text{[eq.15.35]}
\]

Calculations are given in Appendix 15.5. The results are summarized in table 15.19.

<table>
<thead>
<tr>
<th>Heat exchanger</th>
<th>Heat exchange area upper section (A1) [m²]</th>
<th>Heat exchange area lower section (A2) [m²]</th>
<th>Gas flow [m³/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E209</td>
<td>43.3</td>
<td>19.7</td>
<td>3.02 \cdot 10^4</td>
</tr>
<tr>
<td>E211</td>
<td>19.9</td>
<td>15.5</td>
<td>5.82 \cdot 10^4</td>
</tr>
</tbody>
</table>
For both exchangers, multiple tubes are needed to reduce the tube length. The results are summarized in the table below:

**Tabel 15.20: tube dimensions for heat exchangers E 209 and E 211**

<table>
<thead>
<tr>
<th>Heat exchanger</th>
<th>Tube diameter upper section [m]</th>
<th>Tube diameter lower section [m]</th>
<th>Tube length [m]</th>
<th>Number of tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>E209</td>
<td>0.034</td>
<td>0.016</td>
<td>2.0</td>
<td>200</td>
</tr>
<tr>
<td>E211</td>
<td>0.052</td>
<td>0.049</td>
<td>2.0</td>
<td>100</td>
</tr>
</tbody>
</table>

Also, the dimensions of the surrounding building are given in App. 15.5.
15.6 Design of Rotary kiln furnace (D201)

Stream <248> to be treated by Rotary kiln contains MgSO₄, ZnSO₄ and MnSO₄.
Stream <248> is 756 kg/h large with 40 wt% liquid. With assumption that the density of liquid is 1000 kg/m³ and that of the solid is equal to the density of Mg(OH)₂ 2370 kg/m³, the density of the total stream is calculated:

\[ \rho = \frac{756}{0.6 \times 756 + 0.4 \times 756} = 1531 (\text{kg/m}^3) \]  

[eq 15.36]

For the determination of the size of Rotary kiln a residence time has been set to 1 hour. The required volume is determined by:

\[ t = \frac{V}{\phi_v} \]  

[eq 15.37]

\[ \phi_v = \frac{756}{1531} = 0.49 (\text{m}^3/\text{h}) \]  

[eq 15.38]

From the above data follows a required volume of 0.49 m³.

However the incoming feed doesn’t occupy the entire volume of Rotary kiln, only 30 %, in order to have enough exchange area between the outgoing gasses and incoming solids.

The real volume of the required Rotary kiln is:

\[ V_{\text{tot}} = \frac{V}{0.3} = 1.63 \text{m}^3 \]  

[eq 15.39]

The ration between length and diameter of a Rotary kiln is assumed to be equal to 10 [18]. Under this assumption the Rotary kiln has the following dimensions:

L=5.9m
D=0.59m

As the thickness of the wall is approximately 0.25m [19] the outer diameter is 1.09m.

The rotary kiln is operated under inclination of 3% as most of the rotary kilns are operated between 1% and 6% [20]. Three percent inclination is equal to a triangle with horizontal side of 100 and vertical side of 3 that corresponds with 1.72°.

Rotary kilns, which operate feeds between 20kg/h and 200 kg/h, are rotated at speeds between 3 and 6 rpm [19]. Under these typical values the rotary kiln with stream size of 756 kg/h is rotated at 10 rpm.

The gas velocity through the rotary kiln is calculated on the basis of gas production from the rotary kiln, 1095.27 kg/h, density of air at 700°C of 0.5 kg/m³ [21] (as gas leaving the rotary kiln is mostly composed of N₂ at 793°C) and the area trough which the gas passes, which is equal to 70 % of the cross section of the rotary kiln.
From the above data follows a gas velocity:

\[ v_{\text{gas}} = \frac{\left( \frac{1095.27}{0.5} \right)}{\frac{0.7 \times 0.59^2 \times 3.14}{4}} = 11446 \text{ m/h} = 3.18 \text{ m/s} \quad \text{[eq 15.40]} \]

A gas velocity of 3.18 m/s is reasonable for rotary kilns where gas velocity can reach 5 m/s [22]. The inside lining is made of a high temperature, erosion resistant, castable refractory, which can withstand temperatures up to 1400 [19] K. The castable refractory is mostly made of Zirconium Oxide and stabilizers [23].

The flame is directed down the length of the rotary kiln, typical for calciners [24].

### 15.7 Design of Fluidized Bed

The same type of fluidised bed is used as described in chapter 8.5. The bed is designed in exactly the same way. For detailed calculations see appendix 15.6. The most important results are listed in table 15.21.

<table>
<thead>
<tr>
<th>Table 15.21: Results regarding fluidised bed FB201</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume V</td>
</tr>
<tr>
<td>Height H</td>
</tr>
<tr>
<td>Diameter D</td>
</tr>
<tr>
<td>Mass Flow Solid $\Phi_{\text{m,solid}}$</td>
</tr>
<tr>
<td>Mass Flow Gas $\Phi_{\text{m,gas}}$</td>
</tr>
<tr>
<td>Mass Flow Cooling Water $\Phi_{\text{m,cw}}$</td>
</tr>
<tr>
<td>Superficial Velocity Gas $v_{\text{gas}}$</td>
</tr>
<tr>
<td>Residence Time Liquid $\tau_{\text{liq}}$</td>
</tr>
</tbody>
</table>

### 15.8 Design Liquid/ Solid (L/S) Separators

#### 15.8.1 Rotary Drum Filter S201

Stream <246> leaving crystalliser E208 and entering S201 has the following composition:

<table>
<thead>
<tr>
<th>Tabel 15.21: Composition of stream &lt;246&gt; from crystallisers E208</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Liquid</td>
</tr>
<tr>
<td>Solid</td>
</tr>
</tbody>
</table>

* as most of the liquid is sulphuric acid 75 wt%
** calculated from the composition of solid phase and known densities of different components
For this amount of solids, 33.3 wt%, a rotary drum filter will be used. The particles have a uniform size of 200 μm produced by crystalliser E208.

**Dimensions of the Rotary drum filter:**

The Rotary drum filter is assumed to operate at ΔP=68 kPa [25].
As the cake resistance varies from 5.0E+6 (m/kg) for sand and 2.0E+12 (m/kg) for pigments the cake resistance (α) is set to be 1.0E+10 m/kg [25].
Medium/precoat resistance (R_m) is chosen to be 1E+10 m⁻¹ [25].
The drum speed (ω) has been set to 1rpm or 0.105 rad/s, from which the total cycle time t_c is equal to 60s.
Fraction submerged (ψ) is chosen to be 0.3.
Solid concentration (s) in the feed, kg solids/kg slurry is 0.33.
The solids leaving the rotary drum filter will contain 40wt% liquid, from this assumption the cake moisture (m), kg wet cake/kg dry cake, is equal to:

\[ m = \frac{454 + 303}{454} = 1.66 \]  

[eq.15.42]

The filtrate leaving the rotary drum will not contain any solids, the particles leaving the crystalliser, stream <246>, are assumed to have a uniform size of 200 μm.

As most of the liquid is sulphuric acid, the density is 1.84E+03 kg/m³ and the viscosity 28E-3 Pa*s.

From the data and assumptions above the productivity of the above sized rotary drum filter will be calculated using the following formula:

\[ w_r = \frac{[-R_m + (R_m^2 + 4 * k_1 * k_2)^{0.5}]}{(2 * k_1 * t_c)} (kg/m^2s) \]  

[eq.15.43]

where

\[ k_1 = \frac{\alpha}{2} (m/kg) \]  and  \[ k_2 = \frac{\Delta P \cdot c \cdot t_f}{\mu} (m/kg) \]  

[eq.15.52 and 15.44]

t_f is the time required for filtration which is equal to:

\[ t_f = \psi \cdot t_c = 0.3 \cdot 60 = 18s \]  

[eq.15.45]

c is the dry mass of solids per unit filtrate volume:

\[ c = \frac{\rho_s}{(1 - m^*s)} = \frac{1840 \cdot 0.33}{(1 - 1.66 \cdot 0.33)} = 1342.77 kg/m^3 \]  

[eq.15.46]

k_1 and k_2 are calculated from the data above:

\[ k_1 = 5E+09 m/kg \]  

\[ k_2 = 5.87E+10 kg/m^3 \]
The production of dry solids for the specified rotary drum filter will be
As we need to remove 454 kg/h or 0.12611 kg/s solids from stream <246> the area of the drum filter will be 0.12611/0.043 = 2.93 m². A 1.5m long rotary drum filter with diameter of 0.62m has the specified area of 2.93 m².

The filter material should be resistance to sulphuric acid. The filter should be made of metal or ceramics with pore size that can trap particles larger than 150 μm as the particles in the slurry have uniform particle size of 200 μm.

15.8.2 Rotary Drum Filter S202

Stream <255> leaving mixer M201 which is used for dissolving MgSO₄, has following composition:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>ρ (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>1.455E+03</td>
<td>1000*</td>
<td>1.455</td>
<td>89</td>
</tr>
<tr>
<td>Solid</td>
<td>1.70E+02</td>
<td>2881**</td>
<td>0.059</td>
<td>11</td>
</tr>
</tbody>
</table>

* as most of the liquid is water 88 wt%
** calculated from the composition of solid phase and known densities of different components

As the solid ZnO, ZnS, MnO and MnS have not dissolved in the water it is assumed that they have retained their original size of 200 μm produced by the preceding crystalliser.
The liquid contains mostly water with dissolved MgSO₄.

Dimensions of the Rotary drum filter:

The Rotary drum filter is set to operate at ΔP=20 kPa [25].
As the cake resistance varies from 5.0E+6 (m/kg) for sand and 2.0E+12 (m/kg) for pigments the cake resistance (α) is set to be 1.0E+10 m/kg [25].
Medium/precoat resistance (Rₘ) is chosen to be 1E+10 m⁻¹ [25].
The drum speed (ω) has been set to 0.2rpm, from which the total cycle time tₐ is equal to 300s.
The fraction submerged (ψ) is chosen to be 0.3.
Solid concentration (s) in the feed, kg solids/kg slurry is 0.11.
The solids leaving the rotary drum filter will contain 40wt% liquid, from this assumption the cake moisture (m), kg wet cake/kg dry cake, is equal to:

\[ m = \frac{170 + 113}{170} = 1.66 \]  

[eq.15.48]

The filtrate leaving the rotary drum will not contain any solids, the particles leaving the crystalliser, stream <255>, are assumed to have uniform size of 200 μm.

As most of the liquid is water, the density is 1.00E+03 kg/m³ and viscosity 1E-3 Pa·s.
From above data and assumptions the production of solids by the above sized rotary drum filter will be calculated by following formula:

\[
\begin{align*}
    w_r &= \left[ -R_m + \left( R_m^2 + 4 * k_1 * k_2 \right)^{0.5} \right] / \left( 2 * k_1 * k_2 \right) \text{ (kg / m}^2 \text{s)} \quad \text{[eq.15.49]}
\end{align*}
\]

where

\[
    k_1 = \frac{\alpha}{2} (m / kg) \quad \text{and} \quad k_2 = \frac{\Delta \rho \cdot c \cdot t_f}{\mu} (m / kg) \quad \text{[eq.15.50 and 15.51]}
\]

t_f is the time required for filtration which is equal to:

\[
    t_f = \psi * t_c = 0.3 * 60 = 18 \text{s} \quad \text{[eq.15.52]}
\]

c is the dry mass of solids per unit filtrate volume:

\[
    c = \frac{\rho_s}{1 - m * s} = \frac{1000 \cdot 0.11}{1 - 1.66 \cdot 0.11} = 134.57 \text{ kg / m}^3 \quad \text{[eq.15.53]}
\]

k_1 and k_2 are calculated from the above data:

\[
    k_1 = 5E+09 \text{ m/kg} \\
    k_2 = 7.24E+10 \text{ kg/m}^3
\]

The production of solids for the specified rotary drum filter will be

\[
    w_r = \left[ -1 \cdot 10^{10} + \left( 1 \cdot 10^{10} \right)^2 + 4 \cdot 5 \cdot 10^9 \cdot 2.41 \cdot 10^{11} \right]^{0.5} / \left( 2 \cdot 5 \cdot 300 \right) = 0.0201 \text{ (kg / m}^2 \text{s)} \quad \text{[eq.15.54]}
\]

As we need to remove 170 kg/h or 0.047 kg/s solids from stream <255> the area of the drum filter will be 0.047/0.0201=2.25 m^2. A 1.2m long rotary drum filter with diameter of 0.60m has the specified area of 2.25 m^2.

The filter should be made of woven cloth with pore size that can trap particles larger than 150 μm as the particles in the slurry have uniform particle size of 200 μm.

### 15.9 Design Mixers

#### 15.9.1 Design M201

In mixer M201, the solids leaving reactor D201 will be mixed with water to allow MgSO_4 to dissolve. It is assumed that all other solids do not dissolve at all, while MgSO_4 dissolves at a very fast rate. Therefore, the residence time needed in this mixer to dissolve MgSO_4 will be neglected. The only residence time needed is to get an equal distribution of the dissolved magnesium sulphate.

All further calculations are given in (Appendix 15.7).

#### 15.9.2 Design M202

The purpose of the bubble column is to strip off the environmentally hazardous components (sulphuric acid, sulphur trioxide) of the gas stream. The flux of the gas components depends on the solubility of the components in the liquid stream. This
solubility is very complex to determine. Therefore a flux is assumed which is constant throughout the column and which is a typical gas-liquid flux. While the flux is (assumed to be) independent of concentration we assume a total removal of the hazardous gases from the gas stream.

Sulphuric acid is assumed to be the worst soluble gas. This is a justifiable assumption while the amount of sulphuric acid is much larger than the amount of sulphur trioxide.

When assuming a bubble diameter the flow of sulphuric acid to the gas phase can be calculated. Furthermore the concentration, and thereby the amount of sulphuric acid per bubble, are known. This results in a residence time, and at a known rising velocity, a column height needed.

For detailed calculations see appendix 15.8.

**15.10 Design of storage tank**

**Table 15.23: Composition of stream <262> from the evaporator E210**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flow (kg/h)</th>
<th>ρ (kg/m³)</th>
<th>Flow (m³/h)</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>2.28E+02</td>
<td>1000*</td>
<td>0.23</td>
<td>67</td>
</tr>
<tr>
<td>Solid</td>
<td>1.14E+02</td>
<td>2660**</td>
<td>0.04</td>
<td>33</td>
</tr>
</tbody>
</table>

Stream <262> coming from the forced circulation Evaporator E210, contains 33 wt% solid MgSO₄. As the remaining water is not removed and MgSO₄ will form hydrates, the stream <262> will be stored without further processing.

The size of the storage tank to contain weekly production will be 45.36 m³.

**NB.**

For all equipment units specification sheets are filled out. These are attached in appendix D.2.

**15.11 Pumps, blowers and screws**

In this section the places for all pumps and blowers used will be justified and explained. The design specs can be found in the pump data sheets in appendix x.

Pₜ is the pressure drop for liquids due to shear forces and is assumed to be around 0.2 bar = Pₜ, evaporator for pumping from one evaporator/crystallizer to the next and 0.5 bar for other pumps Pₜ, other.

The pressure drop for gases due to shear is assumed to be Pₜ, gas = 0.3 bar.

**Pump P201**

Pumping capacity = φᵥ = 3.77 m³/h.

Naturally a pump is required to pump the Feed flow into our process. For this purpose a standard centrifugal pump is selected. The pump has to create a pressure difference between the flow from the zinc plant and the flow entering the first falling film evaporator of 2.95 bar. Since the flow also has to pumped up to the top of the falling
film evaporator (+1.42 bar, see pump 202 for calculation) and a pressure drop due to shear forces of $P_{s,\text{evap}} = 0.2$ bar, a total pressure of around 4.57 bar is required. In reality pumping it up to the next stage requires a bit less pressure because the density here is lower than at pump P202.

**Pump P202**  
Pumping capacity $= \phi_V = 2.30 \text{ m}^3/\text{h}$.  
The falling film evaporators are 10 meters high. So if a flow has to go from the bottom of one evaporator to the top of the next, there has to be a certain minimum pressure difference to keep the flow going. This minimum pressure difference can be calculated simply if we neglect shear forces. The pressure difference required has to be larger then the pressure coming from gravity. The gravitational pressure drop equals:

$$P_g = \frac{F_g}{A_{\text{pipe}}}$$  \hspace{1cm} [eq. 15.55]

with: $F_g = \text{gravity force} = m \cdot g = \rho \cdot \pi \cdot r^2 \cdot h \cdot g$  \hspace{1cm} [eq. 15.56]

and: $A_{\text{pipe}} = \pi r^2$  \hspace{1cm} [eq. 15.57]

so: $P_g = \rho \cdot h \cdot g$  \hspace{1cm} [eq. 15.58]

If the following values are used in equation 4,  
$\rho = 1450 \text{ kg} \cdot \text{m}^3$  
$g = 9.81 \text{ m} \cdot \text{s}^{-2}$  
h = 10 m  
a minimum required pressure difference of $P_g = 1.42$ bar is found. If $P_{s,\text{evap}}$ is added a pumping pressure of 1.62 bar is required.

**Pump P203**  
Pumping capacity $= \phi_V = 0.65 \text{ m}^3/\text{h}$.  
The steam coming from the final falling film evaporator has a pressure of 1 bar. After condensation at the forced circulation evaporator the condensate has to be pumped away. This means only $P_{s,\text{other}}$ remains here so $\Delta P = 0.5$ bar. Again a normal centrifugal pump is used here.

**Pump P204**  
Pumping capacity $= \phi_V = 0.79 \text{ m}^3/\text{h}$.  
Flow $<227>$ contains a small amount of solids. Because centrifugal pumps can experience problems when pumping suspensions, a disc pump [26] is selected. This kind of pump is able to pump suspensions with little problems. Also the corrosion due to mechanical stress is very little in this kind of pump. This pump is required to accurately control the flow size from the first forced circulation evaporator. Although there appears to be a pressure difference between flows $<227>$ and $<232>$, which would make a pump obsolete, the pump has to pump the flow upwards. Therefore the choice has been made to add a pump here.
**Pump P205**
Pumping capacity $= \phi_V = 0.65 \text{ m}^3/\text{h}$.  
A centrifugal pump is placed here to pump away the condensate from the heat exchanger included in E207. The condensate flow <242> has a low pressure and therefore has to pumped away to a final pressure of 1 bar. Adding of $P_{s,\text{other}}$ leads to a pressure difference of 1 bar.

**Pump P206**
Pumping capacity $= \phi_V = 0.52 \text{ m}^3/\text{h}$.  
A centrifugal pump is placed after the air cooled condenser to pump the evaporated water from E208 away. It is much pump P205 accept a pressure difference of 1.3 bar is required here.

**Pump P207**
Pumping capacity $= \phi_V = 0.070 \text{ m}^3/\text{h}$.  
The reason for installing a disc pump [26] here is that a slurry has to pumped out of the forced circulation evaporator. A pressure difference in flows <235> and <241> plus $P_{s,\text{other}}$ is required, resulting in a total pressure of 1.3 bar.

**Pump P208**
Pumping capacity $= \phi_V = 0.23 \text{ m}^3/\text{h}$.  
See pump p207 accept with a pressure difference of 1 bar.

**Pump P209**
Pumping capacity $= \phi_V = 0.054 \text{ m}^3/\text{h}$.  
Again we pump out a flow containing a small amount of solids so we use a disc pump [26]. The required pressure difference is $0.8 + 0.5 = 1.3$ bar.

**Pump P210**
Pumping capacity $= \phi_V = 0.25 \text{ m}^3/\text{h}$.  
To pump the liquid from the separator S201 a pump is installed. Pump 210 is a centrifugal pump because there are no solids in this flow. A pressure difference of 0.5 bar (= $P_{s,\text{other}}$) is required here.

**Pump P211**
Pumping capacity $= \phi_V = 0.049 \text{ m}^3/\text{h}$.  
A pump has to be installed here to pump the suspension from the mixer to the separator. because there are solids in the flow a disc pump is selected. The required pressure difference equals $P_{s,\text{other}} = 0.5$ bar.

**Pump P212**
Pumping capacity $= \phi_V = 1.23 \text{ m}^3/\text{h}$.  
Here the same reasoning as for pump P210 can be used. The pressure of 0.5 bar is also the same.

**Pump P213**
Pumping capacity $= \phi_V = 1.00 \text{ m}^3/\text{h}$.  
Here the same reasoning as for pump P206 can be used. The pressure now is 0.5 bar.
**Pump P214**
Pumping capacity $= \phi_V = 0.23 \text{ m}^3/\text{h}$. 
This pump pumps the concentrated slurry from the final forced circulation evaporator to the storage where it can dry even further in open vessels. Because it is a slurry a disc pump [26] is used here. The pressure difference here is $P_{\text{other}} = 0.5 \text{ bar}$.

**Blower K201**
Pumping capacity $= \phi_V = 1587 \text{ m}^3/\text{h}$. 
The incoming steam has to be blown into the falling film evaporator. This is done by a turbo blower. The total pressure required here is 0.3 bar to compensate for shear.

**Blower K202**
Pumping capacity $= \phi_V = 102 \text{ m}^3/\text{h}$. 
Here a turbo blower is installed to force the fuel gas to the furnace. Although the gas doesn’t have to be pressurized again a compensation for pressure drop is required so the pressure over this pump is $P_{\text{gas}} = 0.3 \text{ bar}$.

**Blower K203**
Pumping capacity $= \phi_V = 49 \text{ m}^3/\text{h}$. 
The same reasoning as for blower K202 can be followed here. Again a turbo blower is used with 0.3 bar pressure difference ($P_{\text{gas}}$).

**Transporter screw X201**
Capacity $= \phi_V = 3.40 \text{ m}^3/\text{h}$. 
To transport the concentrated slurry from the solid/liquid separator a Transporter screw is installed. This is done because obviously transporting the slurry to the rotary kiln is required. A transporter screw has been selected instead of another transporting device like a transporter belt because it is a slurry and could simply drip off of any other device.
16 Wastes

A big advantage of the evaporation process is that the present waste stream containing magnesium sulphate will no longer have to be dumped.

Because no additional chemicals are added, they also do not have to be removed. This means there is little waste in the evaporation process.

The main waste stream of the process is the off-gas stream of the rotary kiln <263>. The same solution is chosen as in the membrane process. The gas is led through a bubble column with H₂O, where SO₃ will be converted to sulphuric acid.

The only other waste streams in the whole process are the condensed steam, which will be cooled and depressurised, and the burned fuel from the furnaces that consists of carbon dioxide and water.

The total off-gas contains over 1800 t/a CO₂.
17 Health and Safety

17.1 Health

In order to assess the health aspects of a given chemical process it is sensible to start with identifying all chemicals that exist in the plant. These chemicals are listed in table 17.1.

In this table liquid water and steam are listed separately. This is done because there exists an obvious difference in the danger these compounds pose.

For a person to estimate the threats these chemicals pose several data are very useful.

We will try to identify the way these chemicals enter the body, how they work and toxicity levels (LD50, MAC and NOAEL values).

Of course it is also important to get a rough estimate for the probability of contact and the duration of contact should it occur.

In appendix 17.1 some important properties regarding the used chemicals can be found.

From this table we can very roughly say there are three main health concerns in our plant.

As first, the use of steam will be looked upon. The flows of steam are the ingoing steam at E201, E202, E203, E204, E208 and E209 and the outgoing steam at E202, E203, E204, E208, E209 and E211. For safety it is recommendable that these lines are well insulated, kept as short as possible and regularly checked.

Second the existence of concentrated sulphuric acid after the last crystallizing step (equipment E209, S201 and P211; streams 241, 246 and 248) before the rotary kiln.

And as third the dust, exiting the rotary kiln. With this in mind, the designers chose to use a transporter screw instead of a transporter belt. This enables the transportation of solids from the rotary kiln (D201) to the mixer (M201) to be operated as a closed system, which will decrease the amount of dust in the air.

It might also be advisable to spray the solids with a slight amount of water right after they exit the rotary kiln (D201) to reduce the amount of dust in the air.

<table>
<thead>
<tr>
<th>Formula</th>
<th>State</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>l</td>
<td>liquid water</td>
</tr>
<tr>
<td>H2O</td>
<td>g</td>
<td>Steam</td>
</tr>
<tr>
<td>H2SO4</td>
<td>l/g</td>
<td>sulphuric acid</td>
</tr>
<tr>
<td>ZnSO4</td>
<td>s/aq</td>
<td>zinc sulphate</td>
</tr>
<tr>
<td>MgSO4</td>
<td>s/aq</td>
<td>magnesium sulphate</td>
</tr>
<tr>
<td>MnSO4</td>
<td>s/aq</td>
<td>manganese sulphate</td>
</tr>
<tr>
<td>SO3</td>
<td>g</td>
<td>sulphur trioxide</td>
</tr>
<tr>
<td>O2</td>
<td>g</td>
<td>oxygen</td>
</tr>
<tr>
<td>ZnO</td>
<td>s</td>
<td>zinc oxide</td>
</tr>
<tr>
<td>ZnS</td>
<td>s</td>
<td>zinc sulphide</td>
</tr>
<tr>
<td>MnO</td>
<td>s</td>
<td>manganese oxide</td>
</tr>
<tr>
<td>MnS</td>
<td>s</td>
<td>manganese sulphide</td>
</tr>
<tr>
<td>CH4</td>
<td>g</td>
<td>methane</td>
</tr>
<tr>
<td>CO2</td>
<td>g</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>N2</td>
<td>g</td>
<td>nitrogen</td>
</tr>
</tbody>
</table>

Table 8.1: Chemicals occurring in the plant
17.2 Safety

17.2.1 Safety analysis using HAZOP

Before a Hazard and Operability Studies (HAZOP, [27]) is started we first decide which process parts we will analyse. The plant has been divided into 4 sections that will each be analysed as a whole. So the analysis will not be carried out over separate equipment units. This is done because the units within each section are very much alike and experience the same problems.

The sections that will be studied are:
1) The falling film evaporation section.
2) The forced circulation crystallization section.
3) The rotary kiln section.
4) The final crystallization including the boiler furnace.

For each of these sections a HAZOP analysis has been made. This analysis can be found in appendix 17.2.

Several things can be concluded from the HAZOP tables (appendix 17.2). One is that there seems to be little danger of a completely uncontrollable situation. Most problems seem to lead to a problem at the plant, which constitutes no immediate danger.

A list of things that might be desirable to incorporate in the design can now be made.

- Build Storage Vessel to store feed so shutdown can be done gradually.
- For pumps and blowers spares should be installed.
- Pressure relief valves should be installed at several places.
- Install ratio controls at several places. Especially for the ratios between a feed and steam/fuel flow.
- Install flow controls at several places.
- Install volume controls/alarms.
- Develop a good and quick shutdown plan. Shutdown is not a huge problem, because the amount of magnesium in the zinc plant doesn’t build up very fast.
- Patrolling the site can be considered.
- Building an extra heater at the forced circulation crystallisiers might be a good way to compensate if there is not enough water evaporated.
- Building a storage vessel just before the rotary kiln.
- Keep the pipe for stream <263> as short as possible.
- Install vent in rotary kiln.
- Building a concrete foundation under certain parts of the process.

The storage vessel to store feed will not be build because no feed flow, is not a huge danger, and fouling is not a huge problem because the system can be easily cleaned with water.

The spare pumps and blowers will be installed (see equipment sheets).
Pressure relief valves, ratio controls, flow controls and volume controls/alarms will be implemented (see chapter 13).

An extra heater at the crystallization section is not taken up in the process flow scheme, but is highly recommended.
The importance of storage vessel just before the rotary kiln is disputable. A good flow ratio controller between the feed / fuel ratio might be enough to avoid any problems. Therefore it will not be taken up in the design. A concrete foundation to prevent spilling is advisable, also because the equipment already requires a foundation for support anyway.

If a problem arises, certain actions should be undertaken. First try to locate and identify the problem by looking at the controls. If this is insufficient, simply go take a look at the section that has a problem. If there’s a problem with the rotary kiln section, shutdown flow of methane first because this takes away a large part of the danger.

Most of these recommendations will be considered more closely in chapter 13.
17.2.2 Fire and Explosion analysis.

In order to say something about the safety of the process an analysis based on the Dow Fire and Explosion Index can be made (FEI, [27]). First we identify the dangerous sections in the process. A FEI will be calculated for two sections. First the evaporation section, because sulphuric acid becomes increasingly more concentrated up to highly concentrated levels. And second the rotary kiln section because high temperatures and methane are applied here.

This actual analysis consists of two parts. The first part says something about the danger coming from the used chemicals expressed in Material Factors. These factors say something about the reactivity (adiabatic decomposition temperature) and flammability (flash point, heat of combustion and volatility). For further explanation of the FEI method see [27], [10].

Material Factors can be determined using table 17.2:

<table>
<thead>
<tr>
<th>Adiabatic decomposition temperature, ( T_d ) (K)</th>
<th>&lt;830</th>
<th>830 - 935</th>
<th>935 - 1010</th>
<th>1010 - 1080</th>
<th>&gt;1080</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity</td>
<td>Nr</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Flammability</td>
<td>Nf</td>
<td>0</td>
<td>0</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>Flammable factor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This leads to the following material factors:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactivity</th>
<th>Flammability</th>
<th>Material Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>0</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>2</td>
<td>0</td>
<td>24</td>
</tr>
</tbody>
</table>

The second part of a FEI analysis consists of identifying and quantifying process hazards. For these hazards a penalty will be given. It must be said that there are two problems with FEI. First of all the actual plant layout (including equipment placing and piping layout) is not known yet. Second the authors are inexperienced with making a FEI, so the penalties given may deviate from the penalties a more experienced annalist would give.

The following penalties will be given for general process hazards in the Evaporation section:
For special process hazards the following penalties are given:

**Table 17.5: Special Process Hazards Factor, evaporation section.**

<table>
<thead>
<tr>
<th>Base factor</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Toxic materials</td>
<td>0.40</td>
</tr>
<tr>
<td>B: Sub-atmospheric pressure</td>
<td>0.50</td>
</tr>
<tr>
<td>C: Operation in or near flammable range</td>
<td></td>
</tr>
<tr>
<td>1. Tank farms storage flammable liquids</td>
<td>-</td>
</tr>
<tr>
<td>2. Process upset or purge failure</td>
<td>-</td>
</tr>
<tr>
<td>3. Always in flammable range</td>
<td>-</td>
</tr>
<tr>
<td>D: Dust explosion</td>
<td>-</td>
</tr>
<tr>
<td>E: Pressure</td>
<td>-</td>
</tr>
<tr>
<td>F: Low temperature</td>
<td>-</td>
</tr>
<tr>
<td>G: Quantity of flammable/unstable material</td>
<td></td>
</tr>
<tr>
<td>1. Liquids, gases and reactive materials in process</td>
<td>-</td>
</tr>
<tr>
<td>2. Liquids or gases in storage</td>
<td>-</td>
</tr>
<tr>
<td>3. Combustible solids in storage dust in process</td>
<td>-</td>
</tr>
<tr>
<td>H: Corrosion and erosion</td>
<td>0.40</td>
</tr>
<tr>
<td>I: Leakage joints and packing</td>
<td>-</td>
</tr>
<tr>
<td>J: Use of fired heaters¹</td>
<td>0.30</td>
</tr>
<tr>
<td>K: Hot oil heat exchange system</td>
<td>-</td>
</tr>
<tr>
<td>L: Rotating equipment</td>
<td>-</td>
</tr>
<tr>
<td><strong>Special hazards factor</strong></td>
<td><strong>2.60</strong></td>
</tr>
</tbody>
</table>

¹: The final forced circulation evaporator after the rotary kiln is fuelled by methane.

To calculate the final index number, the material factor for H₂SO₄ (the highest material factor here) is multiplied with 1.20 and 2.50, which leads to a number of 74.88.

This process section can now be classified as having a moderate degree of hazard. One suggestion with safety in mind might be to evaporate a bit less water, so the sulphuric acid is less concentrated. However this would make the plant much less effective and more expensive as well. And a decrease in effectiveness would lead to more use of methane, which is less favourable for the environment.

The following penalties will be given for general process hazards in the **Rotary kiln section**:
Table 17.6: General Process Hazards Factor, rotary kiln section.

<table>
<thead>
<tr>
<th>Base factor</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Exothermic chemical reactions</td>
<td>-</td>
</tr>
<tr>
<td>B: Endothermic processes (+ burning of CH₄)</td>
<td>0.40</td>
</tr>
<tr>
<td>C: Material handling and Transfer.</td>
<td>-</td>
</tr>
<tr>
<td>D: Enclosed or indoor process units (dust)</td>
<td>-</td>
</tr>
<tr>
<td>E: Access¹</td>
<td>-</td>
</tr>
<tr>
<td>F: Drainage and spill control.</td>
<td>-</td>
</tr>
<tr>
<td><strong>General Process Hazards Factor (F₁)</strong></td>
<td><strong>1.40</strong></td>
</tr>
</tbody>
</table>

¹: unknown yet, so assumed zero.

For special process hazards the following penalties are given:

Table 17.7: Special Process Hazards Factor, rotary kiln section.

<table>
<thead>
<tr>
<th>Base factor</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Toxic materials</td>
<td>0.20</td>
</tr>
<tr>
<td>B: Sub-atmospheric pressure</td>
<td>-</td>
</tr>
<tr>
<td>C: Operation in or near flammable range</td>
<td>-</td>
</tr>
<tr>
<td>4. Tank farms storage flammable liquids</td>
<td>-</td>
</tr>
<tr>
<td>5. Process upset or purge failure</td>
<td>-</td>
</tr>
<tr>
<td>6. Always in flammable range</td>
<td>-</td>
</tr>
<tr>
<td>D: Dust explosion</td>
<td>-</td>
</tr>
<tr>
<td>E: Pressure</td>
<td>-</td>
</tr>
<tr>
<td>F: Low temperature</td>
<td>-</td>
</tr>
<tr>
<td>G: Quantity of flammable/unstable material</td>
<td>-</td>
</tr>
<tr>
<td>4. Liquids, gases and reactive materials in process</td>
<td>-</td>
</tr>
<tr>
<td>5. Liquids or gases in storage</td>
<td>-</td>
</tr>
<tr>
<td>6. Combustible solids in storage dust in process</td>
<td>-</td>
</tr>
<tr>
<td>H: Corrosion and erosion</td>
<td>0.20</td>
</tr>
<tr>
<td>I: Leakage joints and packing</td>
<td>-</td>
</tr>
<tr>
<td>J: Use of fired heaters</td>
<td>0.30</td>
</tr>
<tr>
<td>K: Hot oil heat exchange system</td>
<td>-</td>
</tr>
<tr>
<td>L: Rotating equipment</td>
<td>0.50</td>
</tr>
<tr>
<td><strong>Special hazards factor</strong></td>
<td><strong>2.20</strong></td>
</tr>
</tbody>
</table>

To calculate the final index number, the material factor for CH₄ (the highest material factor here) is multiplied with 1.20 and 2.50, which leads to a number of 64.68. This process section can now be classified as having a moderate degree of hazard, just like the evaporation section.

The FEI analysis appears to say that the process is ‘limitedly’ hazardous. This is a conclusion, which is deemed acceptable by the authors. However this conclusion should in no way keep anybody (designers, operators, or anybody else) from suggesting safety measures, which could make the process safer.
18 Economy

A description of the factorial method used to estimate the costs of the process can be found in chapter 11. The estimation of the costs of the evaporation process is very straightforward. There are no other chemicals needed and no waste is produced. Remarkable are the very high investment costs in comparison with the membrane process. This is mainly due to the high purchase costs of the evaporation equipment.

An important point, which determines the total costs of the evaporation process, is heat integration. A large amount of heat integration is already calculated, by calculating the multiple-effect evaporation. Because the heat transfer coefficient was highly underestimated, the sum of the investment costs and the steam cost will be reduced by a factor 1.89 (optimalisation factor).

Table 18.1 Economic Criteria of the Evaporation Process

<table>
<thead>
<tr>
<th>Costs</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment costs</td>
<td>10087 k euro</td>
</tr>
<tr>
<td>Operational costs</td>
<td>3289 k euro/yr</td>
</tr>
<tr>
<td>Magnesium removal costs</td>
<td>10.8 euro/kg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Costs corrected for heat exchange coefficient</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment costs</td>
<td>6256 k euro</td>
</tr>
<tr>
<td>Operational costs</td>
<td>2470 k euro/yr</td>
</tr>
<tr>
<td>Magnesium removal costs</td>
<td>7.7 euro/kg</td>
</tr>
</tbody>
</table>

As stated in the table, the costs per kilogram magnesium using the evaporation process equal 7.7 euro (after correction). The error in this value may be estimated to be 10%. Even with this error taken in mind, these costs are considerably lower than the costs in the existing process.

However, there are more possibilities to improve the heat efficiency. The options thought about are described in chapter 20 (Conclusions and Recommendations). Due to lack of time, these options are not implemented in this design.

In appendix 18.1 a detailed calculation of the purchase costs of the major equipment can be found. The economic performance is available in appendix 18.2.
19 Creativity

As part of the project, creativity is used as a tool to approach technological challenges by referring to one's intuition, past experiences, associations and emphasizing the non-linear thinking. To stimulate the creativity, different methods are used which will be outlined below.

19.1 Informal meeting

In the first week of the project to get acquainted, break the ice and exchange views about the project an informal meeting outside the TU building has been organised. In order that the project wouldn't get monotonous, to increase the team cooperation and commitment a second meeting has been organised in presence of ir. P. Swinkels.

19.2 Brainstorm session

Brainstorm session is the first creativity method applied by the group. Brainstorm session was applied as Brain-writing Pool method [C1]. The following question was presented to the team: Write down as many as possible ways to separate magnesium and zinc from each other. The number of ideas generated by each member of the team, has been passed to the next person. The ideas were exchanged several times. After the session, thirty different methods to separate magnesium from zinc have been generated (see Appendix 19.1). The method was very fruitful and praised by the team members. From the generated ideas, promising ideas were selected to be looked upon more closely (see Appendix 19.2) and explored on their applicability by searching the literature and contacting relevant people inside as outside the Chemical Engineering Faculty.

A second brainstorm session has also been organized with assistance of ir. P. Swinkels. The method has been applied to elaborate the demands of an evaporator. The demands were discussed in the group. Brainstorm session applied to demands of an evaporator have been proved useful in that way that the team members were more conscious about the possible drawbacks and demands that needs to be looked upon more closely but also as a way to approach other equipment.

19.3 Contact persons

In the start of the project, in order to acquire ideas, expert knowledge and latest technological advances, different people inside as outside the Chemical Engineering Faculty have been contacted (see References, People contacted). Different persons are approached with similar question: what are the possibilities from their point of expertise and experience to remove magnesium from a zinc sulphate solution.
Sometimes the question has been adapted, specified, in order to explore the possibilities of certain techniques generated by brainstorm session. After extensive literature search and contacts with relevant people, further selection between the promising ideas have been made (see Appendix 19.3). However, evaporation has been chosen as an alternative to the membrane process after delayed appointment with ir. Gärtner [P5], who breathes new life into evaporation, which in the brainstorm session have been mentioned as distillation and later rejected as a possibility (see Appendix 19.2).

### 19.4 Symbolization

With the choice of evaporation as an alternative to precipitation, a symbolization session was held, where the team members were asked to associate evaporation process with a landscape. Two sessions of symbolization about the evaporation process have been held.

First session:
Different landscapes were mentioned such as Iraq, Sahara, Iceland, Ardennes and Maasvlakte. The conclusion of the group was that the evaporation was a dangerous and challenging process. As the overall opinion of the group wasn’t satisfying, the second session of symbolization has been organized to elaborate more on the mentioned landscapes.

Second session:
The members of the group were asked to associate on the mentioned landscape in order to find out the reason the specified landscape have been mention in the first place by the regarding team member. However even after the second symbolization session the method didn’t produced any interesting details or new insights to be looked more upon.

Third session:
As the symbolization on the evaporation didn’t provide results, third symbolization session has been organized in presence of dr. D.Grunwald. It has been asked of the team members to attribute to the different elements (zinc, magnesium, sulphuric acid, water, manganese and fluoride) character types and possibly a person. The group has discussed different character types in order to find new solutions for magnesium removal from sulphate solution. As the group extensively used the creativity to provide the solution to the removal of magnesium from zinc sulphate solution, the last session didn’t provide any new idea.

### 19.5 Visualization

Visualization session was also applied with assistance of dr. D.Grunwald. Each team member has been asked to write down the problem of the process in which he was interested. Afterwards, by closing the eyes for five minutes, each team member had to write down the ideas that emerged. The method was useful in that way that the team members got acquainted with the method, but it didn’t provide any new insights to work on.
19.6 Drawing

Creativity method, drawing, has been applied to the evaporation process. Each team member has been asked to draw the possible flow sheet of the evaporation process. From the drawing session emerged the idea to recycle the sulphuric acid after being separated from solids. However after the calculations were made the idea was rejected. Also the idea appeared to precipitate ZnSO₄ first in order to change the ratio between the amount of ZnSO₄ and MgSO₄, as the solubility of the salts in water is different. This idea, has also been rejected after calculations, it proved to be expensive.

It is worth to mention that at given point by drawing of flow sheet, an air dryer already drawn in the flow sheet has been seen as a rotary kiln by one of the team members. At that point an already chosen furnace for solids heating has been replaced by Rotary kiln.

19.7 Notebook

The notebook has been mainly used in the beginning of the project. Times the notebook has been used differs per person. The idea to directly stoke out the MgF₂ instead of converting to Mg(OH)₂ is coming from the notebook.

19.8 Group Process

In the beginning of the project the team members have been asked to make their profile, to specify their strong and weak points. When compared, the profiles of the team members proved to be very similar. The group seemed to be very homogenous which was not astonishing as all of the team members attend the same study. The group seemed to be very good in systematic thinking and not so well on the aspects of creativity and cost control (see Appendix 19.4). This profile didn’t change during the project.

With the progress of the project a second group profile has been made where each team member has been assessed by the rest of the group. Team members were assessed on his style and role in the group and his strong and weak points. Afterwards, recommendations have been made to each team member in order to improve his weak points. The recommendations made, mostly concerned things that would contribute to better team cooperation and to improve the team spirit. As most of the group members have technical background and little or no experience with creativity, the incorporation of creativity into the Conceptual Process Design has been justified. As creative methods, brainstorming and drawing have been proven to be most useful. This can be explained by the fact that in the beginning of the process the brainstorm session has been chosen as first method.
20 Conclusions

Two different processes to remove magnesium from a zinc sulphate solution are worked out in this CPD report. The objective was to design a process that is capable of removing 250 tonne magnesium each year. The first process to be worked out was a process proposed by J.L. Booster, to which is referred as the membrane process. Using creative methods we created numerous other alternatives of variable quality and selected one promising idea, the evaporation process.

20.1 Membrane Process

In the membrane process, magnesium that is present in the incoming solution will be selectively precipitated to magnesium fluoride by adding zinc fluoride. The formed solid will be converted to magnesium hydroxide after addition of sodium hydroxide, which is converted to sodium fluoride. Calcination of the magnesium hydroxide to magnesium oxide removes the amount of fluoride, which was still present, and makes the magnesium product saleable. Using a membrane reactor the fluoride is recycled yielding new zinc fluoride and sodium hydroxide.

When considering the stream, which is led back to the plant as product, the yield of the feed stream to the product stream is 0.995 t/t. Furthermore, the yield of magnesium oxide is 0.015 t/t.

One of the problems of the process is the removal of fluoride from both the magnesium stream and the stream that goes back to the zinc plant. The fluoride in the magnesium stream is removed during the calcination to magnesium oxide. For the fluoride removal from the stream back to plant no elegant solution is found. The cheapest solution is precipitation by adding silicate and aluminium sulphate. The formed solid will be processed by the AVR Industrial Waste Services.

Another problem described are the uncertainties about the performance of the membranes. From the research of Booster and Schrader [45, 46] most of the uncertainties are taken away. However the membrane lifetime, which can be achieved in industrial practice, and the operational performance (i.e. fouling) is still not completely known.

Some recommendations coming from the HAZOP-analysis have been taken up into the design. Not all recommendations have been taken up in the design though. Partly because the situations which they are to prevent are not extremely dangerous, and partly because they have to be taken into account when actually making the process layout (spacing of equipment, layout of piping, etc.) or operating the plant. The Fire and Explosion Index indicated that the process is not very hazardous. It is classified as having an intermediate degree of hazard (degree 3 on a scale of 1 to 5). This can be considered as a positive outcome.
The loss of zinc for 100% removal of magnesium is 80 t/a or 40 t/a if the membrane process has been designed to remove 50%. The loss of zinc is on average 155 kg zinc per ton magnesium removed. This can be considered to be quite high.

The investment costs for the membrane process are 4333 k€. Because the process was designed to removed twice as much magnesium as necessary, this investment cost are corrected to 3523 k€ by using the step counting method. The operational costs are calculated to be 3753 k€/a. While removing 234 t/a the costs per kg magnesium will be 14.6 €. This price is too high to compete with the existing SRB process. In the next chapter, recommendations will be done that may increase the feasibility of the process.

### 20.2 Evaporation Process

In the evaporation process water in the incoming solution is evaporated in order to achieve precipitation of the metal salts. In the first part of the evaporation no precipitation occurs, which makes it possible to use simple falling film evaporators. In the latter stages where precipitation does occur, forced circulation evaporators are used. After the evaporation the mixture of zinc, magnesium and manganese sulphate is heated to 1173 K in a rotary kiln. At this temperature zinc and manganese sulphate decompose to oxides and sulphides that are insoluble in water. By dissolving in water followed by evaporation, pure magnesium sulphate is obtained. All other fractions are led back to the zinc plant.

Again the stream led back to the plant is regarded as being the product. The yield with respect to the feed is 1.07 t/t. The magnesium sulphate yield is 0.0335 t/t product.

One of the most important issues in the evaporation process is the use of heat integration. To maximise the efficiency of the used steam, multi-effect evaporation is used.

One uncertainty regarding the process is the decomposition in the rotary kiln. Due to unexpected big particles there may be zinc and manganese sulphate that does not decompose. The assumption is made that this problem will not occur in practice. If this assumption may not appear to be correct some possible solutions have been thought of. Grinding of the particles might bring the outcome. In case this doesn’t work, the kiln can be heated until magnesium sulphate melts. After that, the liquid magnesium sulphate can be separated from the other salts by some sort of solid/liquid separation.

Some recommendations coming from the HAZOP-analysis have been taken up into the design. Not all recommendations have been taken up in the design though. Just like in the membrane process this is partly because the situations, which they are to prevent are not extremely dangerous, and partly because they have to be taken into account when actually making the process layout (spacing of equipment, layout of piping, etc.) or operating the plant.

The Fire and Explosion Index indicated that the process is not very hazardous. It is classified as having a limitedly degree of hazard (degree 2 on a scale of 1 to 5). This can be considered as a very positive outcome.
In evaporation process there is no zinc loss.

The investment costs for the evaporation process are 6256 k€. The operational costs are calculated to be 2470 k€/a. In the plant 268 tonne magnesium is removed each year, which leads to the price of 7.7 € for each kg of magnesium removed. This price is lower than the price for the existing SRB process, and can even be lowered by increasing the heat efficiency as proposed in the recommendations. This makes the evaporation a very promising concept.

For the zinc refinery in Budel, the evaporation has an additional advantage. In the roasting unit at the site one tonne 6 bar steam is produced per hour. Up to now, this steam is not used. The amount of steam produces should be enough to supply the multi-effect evaporators, which reduces the costs even further.

20.3 Comparison Membrane/Evaporation Process

Both processes seem to be applicable in practice. The membrane lifetime and the operational performance remain uncertain in the membrane process, while the evaporation process appears to be very robust.

The relative high zinc loss in the membrane process compared to the negligible zinc loss in the evaporation process is another advantage of the evaporation process.

Comparing the costs of both processes the evaporation process comes out as the better alternative. The costs made to remove a certain amount of magnesium using the evaporation process are almost half the costs made in the precipitation process. The economic lifetime of the membrane process might be taken to short, 10 years instead of 15. The influence on the total costs is however quite small.
21 Recommendations

21.1 Membrane process

As stated in the previous chapter, the membrane process in the current form cannot compete with either the existing SRB process or the evaporation process. Some time is spent to think about opportunities to enhance the concept. The most promising improvement is the concept of direct calcination.

Instead of calcination of the magnesium hydroxide the magnesium fluoride can be calcined directly yielding magnesium oxide and hydrofluoric acid. This calcination process can be done by using the Ruthner Spray Roasting process or a Fluidised Bed process [51]. The hydrofluoric acid can be recycled to the precipitation section. The addition of zinc oxide is needed in order to compensate for the hydrofluoric acid.

Figure 21.1: Simplified flowsheet of the direct calcination process
yielding a pH above 2 (see section 5.1.5 and [7]). The problem of fluoride removal in the stream back to plant still remains. This can be solved in the same way as is done in the membrane process. A simplified flowsheet of the process is shown in figure 21.1.

The process of direct calcination omits the use of the expensive membrane reactor and makes the process very promising. It would be very interesting to be able to compare the performance of this process to the process of evaporation. However, after consultation of the principal the assignment wasn’t changed.

21.2 Evaporation process

Although the evaporation process is already quite cost-effective, the designers think taking a closer look at the heat integration of the process can reduce the cost. This is not fully worked out due to lack of time. When the design is inspected it can be seen that the process has both cooling/condensing units as well as heating/evaporating units. Instinctively it can be recognized that this is odd.

For instance the first suggestion has to do with the preheating of the incoming purified solution <201>. In the design a furnace (F201) is installed to heat this stream from 315 to 413 K. Other sources of heat for this may be found in several coolers and condensers or the outgoing steams of the rotary kiln.

The second suggestion concerns evaporator E210. In order to get pure magnesium sulphate in hands, one single forced circulation evaporator (E210) is used. This is quite a costly unit in the process regarding the operational costs, which are caused by the large amount of natural gas required. To reduce the cost of this evaporator it can be included in the multi-effect sequence. A fraction more steam will be needed to run the evaporators, but the furnace with natural gas can be omitted.
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for her time and assistance with experiments.
List of Symbols

Chapter 4:

\( H \) : Enthalpy (J/mol)
\( C_p \) : Heat capacity (J/molK)
\( T \) : Temperature (K)
\( A \) : Constant for heat capacity equation
\( B \) : Constant for heat capacity equation
\( C \) : Constant for heat capacity equation
\( D \) : Constant for heat capacity equation
\( H_f \) : Formation Enthalpy (J/mol)
\( \phi_n \) : Molar flow (mol/s)
\( \rho_{slurry} \) : Density (kg/m\(^3\))
\( x_{solid} \) : Fraction solids (-)
\( x_{liquid} \) : Fraction liquid (-)

Chapter 5:

\( Q \) : Liquid flow rate (m\(^3\)/s).
\( u_g \) : Terminal velocity of the solid particles settling under gravity (m/s).
\( \Sigma \) : Sigma value of the centrifuge (m\(^2\)).
\( \rho \) : Density (kg/m\(^3\)).
\( g \) : Gravitational acceleration (m/s\(^2\)).
\( d_s \) : Cut off size, 50% of the particles of this size will be removed, (m).
\( \mu \) : Viscosity (Pa*s)

Chapter 8:

\( Re \) : Reynolds (-)
\( D \) : Impeller Diameter (m)
\( D_T \) : Tank Diameter (m)
\( p \) : Blade Pitch (m)
\( N \) : Revolutions (1/s)
\( \rho \) : Density (kg/m\(^3\))
\( N_p \) : Power number (-)
\( P \) : Power input (W)
\( t \) : Residence time (h)
\( V_s \) : Volume (m\(^3\))
\( \phi_v \) : Flow (m\(^3\)/h)
\( V_{tot} \) : Total Volume (m\(^3\))
\( v_{gas} \) : Gas velocity (m/s)
\( Q \) : Heat (J/s)
\( U \) : Overall heat transfer coefficients (W/m\(^2\)K)
\( A \) : Area (m\(^2\))
\( T_m \) : Mean temperature (K)
\( T_{air,in} \) : Temperature air in (K)
\( T_{air,out} \) : Temperature air out (K)
\( T_{\text{air-int}} \) : Temperature air intermediate (K)
\( T_{\text{L,in}} \) : Temperature gas in, to be cooled (K)
\( T_{\text{L,out}} \) : Temperature gas out, to be cooled (K)
\( T_{\text{L,avg}} \) : Average Temperature gas, to be cooled (K)
\( p \) : Pressure (kPa)
\( H_{\text{packed bed}} \) : Height packed bed (m)
\( U_{\text{inf}} \) : Minimum fluidization velocity (m/s)
\( Q \) : Liquid flow rate (m³/s).
\( u_g \) : Terminal velocity of the solid particles settling under gravity (m/s).
\( \Xi \) : Sigma value of the centrifuge (m²).
\( g \) : Gravitational acceleration (m/s²).
\( d_s \) : Cut off size, 50% of the particles of this size will be removed, (m).
\( \mu \) : Viscosity (Pa*s)
\( d_{50} \) : Particle diameter for which the cyclone is 50 % efficient (μm)
\( D_c \) : Diameter of the cyclone chamber (cm)
\( \mu \) : Liquid viscosity (Pa*s)
\( L \) : Feed flow rate (l/min)
\( \rho_L \) : Liquid density (g/cm³)
\( \rho_S \) : Solid density (g/cm³)
\( H \) : Height (m)
\( V_c \) : Centrifuge volume (m³)
\( \omega \) : Rotational speed (rpm)
\( r_1 \) : Inner radius (m)
\( r_2 \) : Outer radius (m)
\( u_t \) : Terminal velocity of the solid particles settling under gravity (m/s)

**Chapter 12:**

\( V \) : Steam flow (kg/h)
\( L \) : Liquid flow (kg/h)
\( C_p \) : Heat Capacity (J/kgK)
\( U \) : Overall heat transfer coefficient (W/m²K)
\( A \) : Area (m²)
\( H_{\text{vap}} \) : Evaporation Enthalpy (J/kg)
\( \eta \) : Effectivity (-)
\( f \) : Correction factor (-)
\( c \) : constant (-)
\( A \) : Area (m²)
\( i \) : Number of units
\( n \) : index

**Chapter 15:**

\( H_r \) : Enthalpy of reaction (J/kg)
\( Q \) : Heat duty (J/h)
\( \Phi_m \) : Flow rate (kg/h)
\( C_p \) : Heat capacity (J/kgK)
\( \text{LMTD} \) : Logarithmic mean temperature difference (K)
\( A_{\text{tube}} \): Area of tube (m²)
\( D_{\text{tube}} \): Diameter of tube (m)
\( L_{\text{tube}} \): Length of tube (m)
\( n_{\text{tube}} \): Number of tubes (-)
\( \delta_{\text{tube-wall}} \): Thickness of tube (m)
\( v_{\text{liq}} \): Liquid velocity (m/s)
\( \phi_{\text{m}} \): Flow (kg/s)
\( \rho_{\text{avg}} \): Average density (kg/m³)
\( D_{\text{film}} \): Diameter of film (m)
\( U \): Overall heat transfer coefficient (W/m²K)
\( h_{\text{inside}} \): Film coefficient inside (W/m²K)
\( \lambda \): Heat conduction coefficient (W/mK)
\( \text{Re}_L \): Reynolds number, Liquid (-)
\( \text{Re}_V \): Reynolds number, Steam (-)
\( \text{Nu} \): Nusselt number (-)
\( \text{Pr} \): Prandtl number (-)
\( \eta \): Efficiency (-)
\( H_{\text{vap}} \): Enthalpy of evaporation (J/kg)
\( t \): Residence time (h)
\( V_s \): Volume (m³)
\( \phi_v \): Flow (m³/h)
\( V_{\text{tot}} \): Total Volume (m³)
\( v_{\text{gas}} \): Gas velocity (m/s)
\( T_{\text{comb}} \): Combustion temperature (K)
\( x \): Thickness of shell (m)
\( v_{\text{vap,in}} \): Steam velocity in (m/s)
\( v_{\text{vap,out}} \): Steam velocity out (m/s)
\( \rho_L \): Density liquid (kg/m³)
\( \rho_S \): Density solid (kg/m³)
\( \mu \): Viscosity (Pa*s)
\( L \): Length (M)
\( P \): Pressure (kPa)
\( \alpha \): Cake Resistance (m/kg)
\( R_m \): Precoat resistance (m⁻¹)
\( \omega \): Drum speed (rpm)
\( \Psi \): Fraction submerged
\( s \): Solid concentration in feed (kg solid/kg slurry)
\( m \): Cake moisture (kg wet cake/kg dry cake)
\( w_r \): Productivity of rotary kiln (kg/m²s)
\( t_f \): Filtration time (s)
\( c \): Dry mass of solids per unit filtrate volume (kg/m³)
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