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Conceptual Process Design

Process Systems Engineering
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Subject

Slag treatment process in the magnesium recycling industry

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Summary

This conceptual process design is the result of a three-month project during project commissioned by the Delft University of Technology. The assignment originated from Remag Alloys, which is a magnesium recycling company, located in Delfzijl in the Netherlands, and is about improvement of the magnesium recycling process in such way, that only environmentally acceptable waste and saleable product streams are formed, either by improving the existing process or extending the process. The purity of the metal oxides stream (250 tpa) is about 99.5 w%, and can be sold to the cement industry. The salt stream, free from metal oxides, has a size of 144 ton per annum and can be sold for de-icing at a price of € 0.20 per kg.

The slag treatment plant that was designed processes the waste stream from the magnesium recycling industry. After crushing and sieving, the smallest slag fraction of 305 tpa, contains mainly salts, oxides, magnesium nitride and metallic magnesium. The oxides are separated from the salts by dissolving the slag in water, filtration and drying. The salts are recovered through crystallisation in a eutectic freeze crystalliser. Though this technique is not yet applied commercially no further development is necessary since there is a pilot plant at the API which has sufficient capacity for this design.

The total investment costs for this design are calculated at a price of k€ 403. The variable costs of the process are calculated at k€ 41.9 per annum. When this is compared to the costs for dumping the slag, which are € 150 per ton, it can be calculated that the rate of return on investment is roughly 3.8 years. The total life span of the design is 15 years. The plant is designed to operate continuously for 8000 hours per annum.

The key conclusion is that it is possible to process the slag that is formed during the magnesium recycling process in an environmentally safe and economically feasible way. From industrial point of view this is very attractive. However, from this research can also be concluded that there are several parts of the design that have to be elaborated further before the process can be commercially applied. This research should be focused mainly on the design of the eutectic freeze crystalliser, on which several reasonable assumptions are made.

From the research that has been performed during the making of this design several recommendations follow, which are mentioned in paragraph 13.2. The most important recommendation is worth mentioning in this summary and deals with slag cooling. It is strongly recommended to cool the slag in absence of air to prevent the formation of magnesium nitrides in the slag, which are the cause of ammonia formation in the downstream slag processing. This can simply be done by covering the slag with a hood and creating an argon atmosphere under the hood. In this way roughly 50% of the magnesium nitride formation can be prevented.

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1 Introduction

1.1 Background

Magnesium is a material that is mainly used in the automotive industry. Since it is very light and strong it can fulfil a variety of functions in for instance the automotive industry or the aeronautics industry. However, due to the high environmental impact of the waste streams of the recycling process, magnesium is not used as much as desired industry. Magnesium can be used in wheels, gearboxes, steering wheels, indoor mounting structures and several other applications. Future developments include using magnesium in roof panels, engine blocks, hoods and the like. Clearly, a sustainable recycling process can increase the use of magnesium. Especially since the European Union has decided that 80 percent of car parts must be recyclable by 2006, rising to 85 percent by 2015 [Reuters, May 2004].

A lot of companies around the world are focussing on magnesium recycling for exactly this reason, but none of them have found the optimal way to recycle magnesium. No good solution has as yet been found to dispose of the waste stream (slag), which contains salts, oxides and nitrides. This is also the problem of Remag Alloys in Delfzijl. Remag Alloys owns and operates a magnesium recycling plant in Delfzijl in the province of Groningen in the north of the Netherlands. The plant is situated on an industrial estate called the "Metaal Park".

Remag started recycling magnesium in November of 2003 and their aim is to produce 10 kilotons of magnesium alloys per year in 2005 through recycling. The current production is about 5 kilotons of magnesium alloys. Remag Alloys buys magnesium scrap from different companies, mostly from Volkswagen and BMW. The scrap is melted in batches in a crucible, which is heated with an induction oven. The temperature in the crucible is about 700 °C. Remag produces different kinds of alloys, such as AZ91D, AM50A and AM60B. Other magnesium alloys are also possible depending on the requests of the customer. The heating requirement is about 1 kWh per kg scrap. Finely distributed magnesium reacts easily with water, so the workplace is kept free of water. At all times the exothermic reaction with water (equation 4-1) has to be prevented.

The molten magnesium is sprinkled with a salt mixture called Emgesal or flux. The components of the salt are: NaCl (28.3 w%), KCl (22.8 w%), MgCl₂ (39.5 w%), MgO (3.0 w%) and CaF₂ (5 w%) [Inzunza, 2003]. The flux has two functions. The first is to create a protective layer of salt on top of the melted magnesium in order to prevent the magnesium from reacting with oxygen in the air. The second is to extract the impurities (mainly metal oxides) from the molten magnesium. The production process of Emgesal

is as follows. First the individual components are mixed and subsequently the mixture is melted in order to evaporate all the water that is present in the lattice of the components. During the cooling the components of the salts form bonds which gives Emgesal its properties.

When comparing the magnesium recycling process with the aluminium recycling process several differences become apparent. First of all the aluminium recycle process is far further developed. Aluminium and magnesium have two features that are worth mentioning [Boin, July-Aug. 2001]. First of all aluminium and magnesium are both easily oxidized. Secondly, the oxides in both processes formed can't be reduced to metal again. The main difference is that a solution has already been found for the aluminium industry, or as it is described in the article, the aluminium recycle loop has already been closed. In spite of the similarities between magnesium and aluminium, the composition of the salt mixtures used for melting and refining of the alloys are totally different for both processes, which means that there is no solution yet for the magnesium recycle process.

1.2 Current process description

At Remag the magnesium is currently recycled in a batch process. Magnesium scrap is melted in a crucible at 700 °C under atmospheric conditions. One batch contains roughly 2200 kg of scrap material. Per batch about 50 kilograms of Emgesal is added, this amount of course depends on the impurities in the scrap. The batch time is about 4 to 5 hours. The volume of the crucible is about 1.25 m³. One batch produces around 2000 kg of magnesium alloy and 250 kg of slag.

To separate the slag from the magnesium the slag is brought to the top of the crucible by an agitator, creating a sort of vortex in the crucible. With a lance argon is injected at the bottom of the crucible and the agitator distributes the argon in small bubbles to bring the salt slag to the top of the crucible where it can be skimmed off (Appendix 1-1: Crucible with agitator and argon inlet). Argon is currently consumed at a rate of about 7000 m³ per year, which is about 13 ton per year of argon.

The solid slag and dross are put in a large drum and taken to the consolidator. The consolidator is basically a big stirrer. During the stirring of the slag and dross in the consolidator the temperature rises to 900 °C, far above the melting temperature of magnesium. The result is that the magnesium residue is located at the bottom of the drum and the salts are on top. The drum is "punctured" at the bottom and some of the remaining magnesium flows out and is caught in a box. Another 10 kg of magnesium per batch is recovered in this way. The remaining salt slag, which still contains metallic

magnesium, is allowed to cool in contact with air. It is then stored in big bags onsite. There is currently no application for the slag.

The purified liquid magnesium in the crucible is poured into a storage vessel and then into ingots, solidified and stored for sale. This is the process as it is currently applied at Remag. For details on the process see figure 1.1.

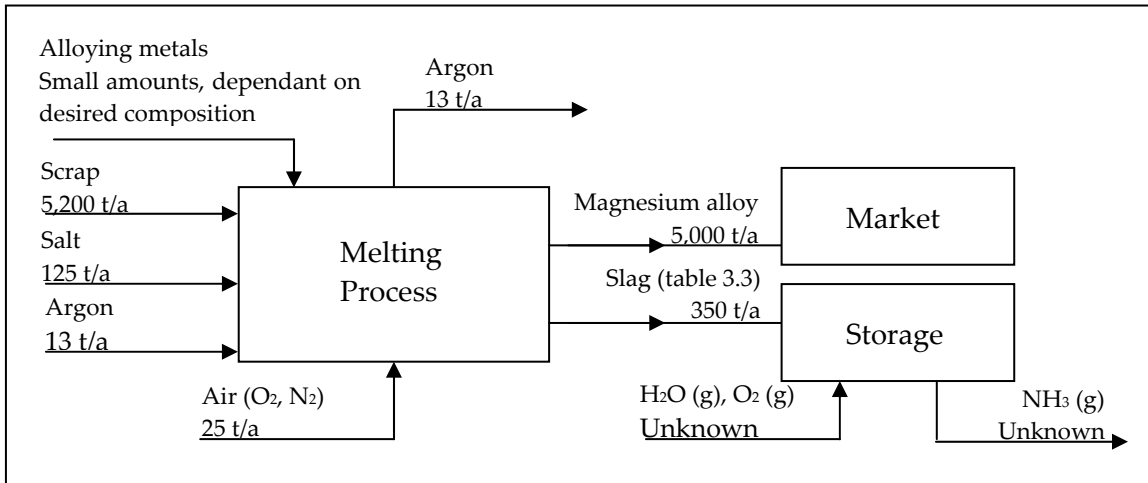


Figure 1.1: Current process at Remag Alloys, Delfzijl.

Remag is further planning to install a crushing and sieving process that will be fully operative by mid 2004. Crushing and sieving of the slag is a very effective way to roughly separate the metallic magnesium from the salts and metal oxides. For a detailed flow sheet of the crushing and sieving process see Appendix 1-2: Crushing and sieving process flow sheet.

1.2.1 Crushing and Sieving

Crushing and sieving of the slag is a very effective way to roughly separate the metallic magnesium from the salts and metal oxides. The largest sieve fractions (> 5 cm, > 1 cm and > 5 mm) are reintroduced into the melting process, because these fractions mainly contain metallic magnesium. The middle sieve fraction (5 mm to 0.5 mm), can be sold for desulphurisation. As of yet there is no market for the smallest sieve fraction (< 0.5 mm), therefore this is the feed stream for this design. The crushing and sieving process will be installed on site and is planned to be fully operative by mid 2004.

The salts and metal oxides are rather brittle. When these are processed by the crushing unit they crumble into smaller particles. The metallic magnesium however is not brittle and merely deforms. After crushing the larger particles can be separated from the smaller ones by sieving, and thus a rough separation is performed between the metallic particles and the non-metallic ones. The process has to be repeated several times to obtain fractions that can be either processed again in the crucible (the large metallic particles) or the salt recovery process (the small non-metallic particles).

Detailed information on the compositions of the slag fractions is given in table 1.1. The data is based on analyses that Steef Steeneken performed on the slag ([Steeneken, 2004], Appendix 1-3: Composition of sieved slag fractions).

Table 1.1: Sieved slag fraction streams in tpa (Appendix 1-3)

	Total	Metal	Soluble components					Insoluble components		
	tpa	Mg	Mg ₃ N ₂	MgF ₂	MgO	Al ₂ O ₃	MnO	MgCl ₂	KCl	NaCl
To crucible (>6 mm)	10.89	10.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Desulphurisation (0.5 – 6 mm)	34.50	8.09	3.02	0.31	9.49	5.06	0.71	2.12	2.08	3.62
To dissolving (<0.5 mm)	304.61	16.99	32.94	3.43	103.34	55.06	7.75	23.06	22.61	39.43

As clearly can be seen from this data the > 6 mm fraction only contains metal and can be reintroduced to the crucible (see recommendations, paragraph 13.2). Although a considerable amount of metallic magnesium (about 70%) of the slag leaves the system in the smaller fractions, this will not be retrieved for the main reason that it is not a lot of magnesium compared to the total production (~ 4 ‰). Since it is not economically feasible to extract that magnesium it will be considered as a loss.

1.3 Problems with current process

Currently Remag Alloys faces several problems. As described in paragraph 1.1 there is a need for a magnesium recycling process that contains the following aspects:

- Magnesium should be recovered from the scrap with a minimal loss of magnesium.
- The salts in the slag should be cleaned from the remaining magnesium and should ideally be dried for reuse.
- The remaining waste stream should be free from reactive components and if possible be saleable.

The main problem is located in the slag stream. This slag stream contains:

- Metallic magnesium
- Several metal oxides (such as MgO and Al₂O₃)
- Salt components (such as NaCl, KCl and MgCl₂)
- Reactive components (such as Mg₃N₂)

During the scrap melting process the properties of the Emgesal change, components in the slag are therefore not the same as the components in Emgesal. CaF_2 , for instance leaves the crucible as MgF_2 , while only trace amounts of calcium are found in the slag. The composition of the slag stream is therefore determined by experiments rather than making a mass balance over the melting process.

Obviously it is desirable to recover the metallic magnesium in order to obtain a higher yield. The metal oxides could be used in construction; the oxides also have to be removed if the salt is to be recycled. Furthermore, the salt is preferably recovered because it can be reused or resold and can't be dumped [Elzinga, 2004]. Lastly some very reactive components, which are formed during the melting process, have to be removed because they cause an environmental impact. The most reactive components in the salt slag are metallic magnesium and Mg_3N_2 , which make dumping of the slag impossible.

Another issue is that the slag is very hygroscopic and reactive, which creates several storage problems. For details on the slag composition see chapter 3, table 3.3. Several options, such as landfill, conversion to fertilizer, the use of salt to prevent ice formation on the roads in the winter and dumping into sea, have been considered and rejected, mainly because of the slag's reactivity and environmental impact. Currently this slag stream, about 350 tons per annum, is stored, which is not a sustainable solution. An increase in production of magnesium, from 5,000 tons per year to 10,000 tons per year in 2005 at Remag is desired, which would also bring about a larger slag stream (700 t/a in 2005).

Because Remag has not found a solution yet for the slag it is stored, as can be seen in figure 1.2. The slag is stored in big bags and is exposed to the air. The metallic magnesium that is still in the slag can react with the oxygen in the air. Magnesium nitride, which is also present in the slag reacts with moisture to form ammonia. During our visit to Remag there was the typical smell of ammonia in the storage hall. For more information on these reactions see chapter 4 on thermodynamics.

1.4 Problem definition

If one considers the recycling process and the aspects mentioned in the previous paragraph there are two possible ways of achieving the stated aspects. Either the process itself can be optimized, or the process can be extended with a slag treatment process. Of course, a combination of both ways is also possible. The area of focus is therefore widespread. Since only a limited amount of time was available (12 weeks), the design team chose to focus mainly on the slag processing.

The design team had two goals in mind during the making of this Conceptual Process Design. The first was to find a solution for the slag problem in the magnesium recycling industry. The second goal was to find a solution for the slag problem at Remag Alloys.

With the considerations stated above in mind, the design team formulated the following problem definition:

“Use creativity to improve the magnesium recycling process either through minimising the production of slag, or through designing an extension to the current process at Remag Alloys.”

In order to ensure that the design is feasible it will be assessed in terms of Safety, Health and Environment (chapter 10), and an economic evaluation will be made (chapter 11). Furthermore the design team will perform some experiments at Remag and at the faculty of Applied Earth sciences, first of all to get a better insight of the current process, secondly to discuss with well founded arguments about the current process and thirdly to do research for improvements or come up with recommendations for the current process.

1.5 Key solutions

1.5.1 Short process description

To render the reactive components in the smallest slag fraction harmless this fraction is first dissolved. This causes the harmful components to react to inert substances. The chloride salts that are present in the slag will dissolve in the water stream. The ammonia that is formed will be led to a scrubber where the ammonia will be converted to ammonium and led back into the dissolving tank. The brine will then be separated from the solid particles, which are the metal oxides. The metal oxides are washed with clean water and dried to make the saleable. The concentrated brine is fed to a eutectic freezer where the chloride salts are separated from the water through crystallisation. The salt stream is then dried to make it saleable.

The process as described in the preceding paragraph yields two saleable product streams. The first is a stream of metal oxides, which can be sold to the cement making industry. Four basic oxides in the correct proportions make solid grains, better known as cement: calcium oxide (65%), silicon oxide (20%), alumina oxide (10%) and iron oxide (5%). These elements mixed homogeneously (called “raw meal” or slurry) will combine when heated by the flame at a temperature of approximately 1450 °C. New compounds are formed: silicates, aluminates and ferrites of calcium. The second is a stream of chloride salts, which can be used in the manufacturing of de-icing salt.

1.5.2 Nitride and oxide formation

Cooling the slag under argon will help to decrease the formation of Mg_3N_2 and MgO , as can be seen from the results of the experiments done by the design team (Appendix 14-1, Magnesium nitride experiments). The sample of magnesium cooled with argon and not treated with the consolidator is the one with the lowest concentration of nitrides.

Remag is planning to install the crushing and sieving process in mid 2004. With this installation running it is doubtful whether the consolidator fulfils a useful purpose, since metallic magnesium will also be recovered through crushing and sieving. The experiments done by the design team show that the slag after the consolidator contains more nitrides than the slag before the consolidator. The temperature in the consolidator rises to 900 °C and there is a constant burning of magnesium, which indicates a loss of product. One advantage of the consolidator is the small particle size of the slag (if cooled under argon) in contrast to the agglomerated ones, which need a more intense crushing and sieving process.

2 Process Options

In paragraph 1.4, Problem definition, it was chosen to mainly focus on the design on slag processing. In this chapter the choice for the different steps in the designed slag process will be discussed. These process steps are schematically presented in Appendix 2-1: Process route options magnesium and slag recycling. The dissolving, filtration and drying were logical results from relatively simple reasoning. However in the case of the separation of the salts from water, several options were considered to be applicable. An in depth discussion within the design team was held on general aspects of the possible options of this separation step in order to draw a well founded conclusion on what option would be the best.

2.1 Dissolving

In the process of this design a dissolving step is planned for the separation of the non-metallic components from the salts, to initiate a controlled formation of magnesium oxide out of magnesium-nitride with ammonia as a by-product. This seemed to be the most logical step after the crushing and sieving steps that were already planned for the slag processing at Remag and will be in process by mid 2004, see also Appendix 1-2: Crushing and sieving process flow sheet.

Controlled contact of slag with water will let the reactive components, such as magnesium nitride and metallic magnesium react to inert components, magnesium hydroxide, magnesium oxide and off-gasses ammonia and hydrogen, see also chapter 4 for further details on these reactions. To let the reactions take place in a controlled manner has several advantages. Firstly, the exothermic reactions will not take place anymore after a controlled dissolving, because the reactants are formed into inert components. Secondly, ammonia can leave the slag in a controlled manner, which is desirable from an environmental point of view. Thirdly, the inert components will not dissolve and the salts will, in this way the metal oxides can easily be separated.

To minimise the effort of separating the water from the salts again in a later stage, a minimum amount of water will be used. The amount added during this step will be such that the salts form a 25 wt% solution.

2.2 Removal of the oxides

The obvious way to separate the oxides from the saturated solution is through filtration. The small size of the particles could be a disadvantage, since it could necessitate a high pressure drop over the filter. Other techniques for the removal of the oxides could be settling of the oxides followed by pouring out of the brine. The 'wet' oxides could be dried by air or by evaporation. Although this could be an interesting solution, filtration followed by washing has the advantage that the oxides are almost free of salts.

2.3 Salt recovery

After filtration of the oxides the salts need to be separated from the water again for two reasons. Firstly the salt solution can't be dumped in the ground water or the sea. Although no harmful components are present, the environmental impact of the surrounding industries is already of such intensity that the local government has decided to turn down any requests for salty wastewater drainage. Secondly, some valuable components are present in the solution. If it is possible to recover the salts from the solution, they could be sold or reused.

So, the main decision that has to be made concerns the separation of the water from the salts, when all inert components have already been removed. To separate salts from water, four separation possibilities were considered and investigated more in depth. The four possibilities can be seen in the overview in Appendix 2-1: Process route options magnesium and slag recycling, they are:

- Membranes
- Zeolites
- Eutectic freezing
- Evaporation

2.3.1 *Membranes*

The first technique that was considered to be of interest is membrane technology. Various types of membranes can separate various types of impurities from water. With osmosis and reversed osmosis techniques it is possible to produce pure water from brine. Unfortunately this technique works only with low concentrations, producing pure water and highly concentrated brine. In this particular process the aim to use as little water as possible in the dissolving unit, hereby producing concentrated brine, which can only be processed by membranes under very high osmotic pressures. Subsequently a

crystalliser will be necessary to retrieve the salts from this concentrated solution. Therefore it is not a solution in this case.

However, this membrane technology can be useful for treatment of the purge water that has to be drained into the ground water or the sea. For this particular use it is sufficient to know at this moment that it is possible to produce salt free water that satisfies the local environmental restrictions.

2.3.2 Zeolites

Zeolites can be used as ion exchangers. Cations and anions can be exchanged for Na^+ and Cl^- ions respectively. In this way other ions that are in solution can be separated from the solution. After loading the zeolite it can be used as landfill. The main advantage of this technique is that the zeolite is very cheap, and therefore regeneration is not necessary. Nevertheless, this technique will not solve the problem because it will not separate the ions from the water; it will only replace them by sodium and chlorine, which are already present in the brine in large concentrations. For this particular reason, the zeolites technique was not assessed in the decision making process.

Perhaps, future developments in the magnesium recycling industry can make use of this technique if the magnesium scrap contains ions that cannot be separated (well) with the chosen technique. One could think of heavy metals that cannot be crystallised and need to be separated from the process water after the high concentrate salts (NaCl , KCl and MgCl_2) have been removed. In that particular situation all process variables have to be reconsidered, but ion exchange by zeolites could provide a suitable solution.

2.3.3 Eutectic Freezing and Evaporation

Although eutectic freezing and evaporation of water are both forms of crystallisation techniques, the process conditions vary in many ways. For this reason they are considered separately in the rest of this chapter.

In all cases of crystallisation, the state of super saturation must be achieved. The method used to obtain super saturation depends on the characteristics of the crystallising system. Some solutes are readily deposited from solution when cooled (eutectic freezing), whereas others may crystallise only after some solvent has been removed through heating (evaporation).

Crystallisation is carried out in many organic and almost all inorganic, chemical-manufacturing plants where the desired product is a finely divided solid, which is also desired in this conceptual process design. The unit operation of crystallisation is governed by very complex, interacting variables. It is a simultaneous heat- and mass transfer process with a strong dependence on fluid and particle mechanics. Nucleation

and growth kinetics are the key processes in this operation and are often heavily influenced by traces of impurities. More information on these interacting variables of the salts that are present in the slag of Remag can be found in Appendix 2-2: Crystallisation.

The four possibilities can be seen in the overview in Appendix 2-1: Process route options magnesium and slag recycling. This important figure is all about the basis of design and the different processes investigated such as, scrap pre-treatment, scrap and slag processing and the salt recovery, which are separated by dashed lines in appendix 2.1. In paragraph 2.4 a decision is made for the salt recovery section and in paragraph 2.5 an option is chosen. In the subsequent chapters the chosen option is further worked out and detailed process scheme with numbers in ton per annum are developed, see figures 3.1 and 3.2.

2.4 Decision making

In order to make a well-founded choice as to what process is best and most applicable the design team decided to define what aspects of the technology are most important for the design. These are given in table 2.1. The aspects are all interrelated, but in this way the design group tried to unravel the situation and tried to gain insight into the argumentation for certain techniques.

Table 2.1: Description of factors for comparison of separation techniques

Factor	Description
Process costs	What are the costs of running the process under normal conditions? (proportional costs such as energy usage)
Investment costs	What are the costs of acquiring and installing the necessary equipment (fixed costs)
Proven technology	Is the technology widely used and proven to be feasible?
Information availability	Is a good source of information readily available?
Throughput	Can the process meet the throughput required for the design?
Size	Does the process require a lot of space and is it therefore not applicable in the case of Remag?
Safety	What are the safety requirements for the technology?
Labour intensity	Does the technology require extensive supervision or a large amount of manual labour?
Energy efficiency	Is the process efficient in terms of energy usage?
Energy sources	What possible sources are able to supply the energy needed for the process?
Product quality	Can the technology reach the required product specs?
Environment	Is the process hazardous to the environment?
Waste streams	What are the waste streams and do they pose problems?
Heat Integration	Is it possible to make heat integration steps within the technology or with the current process at Remag?
Legal restrictions	Could the use of the technology lead to breaking legal restrictions due to energy usage, waste streams etc.
Robustness	Is the equipment robust for a long period of time?

These aspects will be valued by the design team with the marks 0 (bad), 1 (moderate) or 2 (good) in order to compare the techniques with respect to the different aspects.

The different aspects could also be categorized in important aspects from the point of view of a design team and important aspects from the point of view of Remag. For instance the factor of proven technology could be of minor importance for a design team, but is a very important decision criterion for a company, while uncertainty in this area is a risky investment. An unproven technology could cause problems in the future that are not yet known. For a process design environmental, risk and sustainability criteria are of importance to ensure a process that satisfies future needs for society and industry, but a company does not necessarily share those interests and does not feel this responsibility to the same extent, while the first priority for a company is profitability. Long term interests for a whole industry or even society are usually of minor importance compared to short-term profitability.

2.4.1 Eutectic freezing

Process costs

The process costs for eutectic freezing are relatively low compared to other separation methods [van der Ham, 1999]. Some calculations were performed on the minimum amount of work that is necessary to separate the salt from the water. In that case a minimum amount of work of 205 kJ/kg salt is necessary. For a stream of 250 ton salt/a and an efficiency of 0.5 of the equipment this results in a minimum amount of work of 112 MWh. At a cost of 0.08 € per kWh, this results in an electricity cost of 9 k€ per annum, which is negligible compared to other process costs (see also appendix 8-10).

Investment costs/ proven technology

The investment costs for the eutectic freezing equipment of sufficient size are not exorbitantly high. One of the drawbacks of the use of a eutectic freezer is that the technology has not proven itself in practice. For this reason alone the implementation of this process brings about a certain risk. However, a lot of information on the subject (theoretical knowledge, practical knowledge and data from pilot plant scale experiments) is readily available.

Throughput/ Size

The experiments mentioned above have proven that it is possible to separate large process streams of 1,000 ton/a with acceptable size equipment [van der Ham, 1999]. Increasing throughput through up scaling of the equipment is possible [Genceli, 2004].

Safety

Apart from the dangers that the chemicals that are processed bring about, no additional hazards have to be dealt with.

Energy/ Product quality

As mentioned before, the main advantage is that the energy input of the eutectic freezer is very low. A drawback on the other hand is that it can only operate with electrical energy. The quality of the product (and waste-) streams is very good. Water can be formed with almost 100% purity. The salt crystals can contain water in the lattice structure, depending on the salts that are present in solution.

Environment/ Waste streams

From an environmental point of view the eutectic freezing process is very interesting. Compared to other evaporation it uses relatively small amounts of energy and no hazardous chemicals are used/produced in the process, other than the compounds that have to be separated.

Heat integration

The eutectic freezer operates at low temperatures. It might be possible to cool the feed to the eutectic freezer with the product streams. No integration with other units is possible.

Robustness/ Labour intensity

The equipment for the eutectic freezer consists of some mechanically moving parts. In comparison with other separation methods that do not have these moving parts the eutectic freezer is a risk, because of the possibilities of a breakdown or malfunctioning equipment, which would cost man-hours and money to repair.

Since this technology is still unproven for usage in industry, not much can be said about long-term utilisation problems. What can be said is that it has run on pilot plant scale with appreciable volumes (1000 tpa). Also it has to be analysed whether the process is flexible enough to cope with changes in composition of the process water.

Legal restrictions

No problems with legislation are expected since no hazardous materials are either produced or used in the process.

Table 2.2: Factors applied to eutectic freezing

Factor	Mark	Keywords
Process costs	2	Low energy usage
Investment costs	1	Not exorbitantly high
Proven technology	0	Pilot plant scale
Information availability	2	Contact with experts on the subject
Throughput	2	Pilot plant scale large enough, scale up possible
Size	2	Small enough for site
Safety	2	No additional hazardous chemicals or process conditions
Labour intensity	1	Operators necessary, breakdown risk
Energy efficiency	2	Low energy usage
Energy sources	0	Electricity
Product quality	2	Pure water and pure salts
Environment	2	No additional hazardous waste streams, low energy usage
Waste streams	2	Water and salt recycling opportunities
Heat Integration	1	Some heat integration possible
Legal restrictions	2	Pure product/waste streams, fortunate outlook to future legislation
Robustness	1	Unproven, but expected to be robust

2.4.2 *Evaporation of water*

Process costs

In order to determine the process cost a simple calculation was made based on the energy costs of evaporating the water (appendix 2-3, Evaporation calculations). It turned out that, while taking into account an overall energy efficiency of 50%, about 530,000 kWh a year is necessary for the current process (2.500 batches a year). When the cost of 1 kWh is assumed to be € 0.08, this leads to process costs of around 42.5 k€ a year. When this is compared to the annual cash flow, which is 11.5 M€ the costs are very acceptable.

Investment costs/ Proven technology/ Information availability

An industrial evaporator is not a very expensive piece of equipment, particularly on the scale that is needed here; this means the investment costs will also be very acceptable. Evaporation technology was one of the first ways to separate dissolved salts from watery streams. It is a well-known technology that has been in use for many years. This also means that a lot of information is available on evaporation.

Size/ Throughput

Because the scale of the current process is relatively small it will be quite easy to design an evaporation step that can handle the necessary scale, even if the production is doubled as Remag intends to do. The size of an industrial evaporator is not extraordinarily large. This means that it will be possible to place one within the plant area.

Safety

An industrial evaporator can get very hot since the heating element will reach a high temperature. However the temperature of the heating element will still be lower than the temperature of melted magnesium. Therefore, compared to other process steps of this magnesium recycle process, evaporation will be a relatively safe process step.

Labour/ Energy

Because the technology is so well known it means that a high level of automation is probably also possible. The question is however if that is feasible for such a small scale. It is well known that the energy efficiency of an evaporator is not high. The energy sources are however closely related to this issue; the efficiency will be different when a different energy source is used. When electricity is used as a source, the efficiency could be quite high. When natural gas is burned to generate the necessary amount of energy the energy efficiency could drop.

Product quality

The water that is evaporated is almost 100% pure. Also in the evaporated water some ammonia could be present that originates from the nitrides in the cold slag. It is very

likely that the residual salts will contain at least some water. It is at this moment unknown whether this is a problem and if so whether a second drying step is necessary.

Environment

The main environmental impact is the heating of the environment due to heat loss of the process. We can however assume the heat loss to be negligible when compared to the heat loss incurred during the process of magnesium melting.

Waste streams

As no extra components are needed to separate the salts and water there are no extra waste streams. It is possible to recycle the water without problems and it will also be possible to sell the salts as a useful product.

Heat integration

With the steam from the evaporator heat integration will not be feasible; the temperature will be too low to use it elsewhere in the process. However heat integration could be feasible when heat from elsewhere is used to heat up the evaporator for instance when heat from other processes at the 'Metaal Park' where Remag is located could be used or making use of the high temperatures of the magnesium melting process. In the latter case, care must be taken that the magnesium melting process will not be in contact with water.

It might be possible to prevent the water from cooling down completely before recirculation, but as can be seen from the calculations in appendix 2-3 the main energy sink is the evaporation of water and not heating it to its boiling point.

Legal restrictions

Since there are no waste streams and it is not likely that in future there will be legislation that forbids the use of evaporation as a technology for separating salts from water. Therefore the design team expects no problems in this area.

Robustness

A high concentration sodium and potassium salts is very aggressive at high temperatures. The equipment will corrode due to the aggressive properties. Utilisation of an evaporator to crystallise the salts in the solution is not preferable from this point of view.

Table 2.3: Factors applied to evaporation

Factor	Mark	Keywords
Process costs	2	Low when compared to turnover
Investment costs	2	Low
Proven technology	2	Done for years
Information availability	2	Books available on subject
Throughput	2	Possible to achieve required throughput
Size	2	Not extraordinarily large
Safety	1	Could be hot (colder than crucible)
Labour intensity	2	Some supervision
Energy efficiency	0	No opportunity for reuse of heat
Energy sources	1	Multiple sources available
Product quality	1	Perhaps some residual water in salts
Environment	1	Heat effect
Waste streams	2	No waste streams, only heat
Heat Integration	1	Perhaps warm slag could be dissolved, otherwise no
Legal restrictions	2	No legal restrictions
Robustness	0	Solution will be very corrosive for the equipment

2.5 Option Chosen

In the first place the objective of the decision making factors was to investigate whether the technique could realise a separation between salts and pure water or at least contribute in a way to this objective. During the in depth research into the different techniques it became clear that eutectic freezing and evaporation are the only two techniques that could be compared on the different decision aspects.

Table 2.4 shows that eutectic freezing and evaporation are more or less equal for application as a separation step when all the criteria are considered to be of equal importance. The table is a rough qualitative overview of possible application of the techniques with respect to the different factors. A more in depth comparison is necessary in order to come up with a final decision. The two techniques will be compared on each separate factor.

Table 2.4: Comparison of separation techniques

Factor	Eutectic freezing	Evaporation of water
Process costs	2	2
Investment costs	1	2
Proven technology	0	2
Information availability	2	2
Throughput	2	2
Size	2	2
Safety	2	1
Labour intensity	1	2
Energy efficiency	2	0
Energy sources	0	1
Product quality	2	1
Environment	2	1
Waste streams	2	2
Heat Integration	1	1
Legal restrictions	2	2
Robustness	1	0
Total	24	23

To make a first rough distinction between criteria that have to be discussed more in depth, we can say that:

Legal restrictions do not play an important role in the decision making, because there are no restrictions with respect to these two different techniques

Information availability will not cause problems in the developing of the design

Size is not a problem for the implementation

Throughput is feasible for both techniques because of the small scale

This leaves costs, product quality, proven technology, safety, health and environment, robustness and energy open for a more in depth discussion.

Costs

Very important criteria for a company are the costs, which can be divided in proportional costs and fixed costs. The process costs are proportional and are for eutectic freezing and evaporation respectively €9,000.- and €42,500.- (see chapter 2.4.1 and 2.4.2). Although both were judged to be good when compared to the turnover (11,5 M€), the process costs of eutectic freezing are less than 25 % of the process costs of evaporation. It can be concluded that although both techniques have a good score on process costs, eutectic freezing is by far the best.

Fixed costs are not expected to be high for either eutectic freezing or evaporation. Although no exact data on the fixed costs are known, based on the proportional costs and fixed costs together there is much in favour of eutectic freezing.

Product quality

Since the subject of the discussion is separation, we have to deal with at least two outgoing streams. When water is evaporated it will be 100% pure and it can directly be used for recycling. The same with respect to water can be said for eutectic freezing. With respect to the crystallised product both techniques crystallise in the same way. Both crystallisation techniques are equal with respect to product quality.

Proven technology

Evaporation is a technique that has been proven for many years. Eutectic freezing on the other hand is still in an experimental phase in the laboratory of API of the TU Delft. Eutectic freezing has been tested in a pilot plant of 1000 tpa. So, although eutectic freezing is not yet proven technology, it is not likely that at this scale problems will arise since the scale necessary for this application is already in continuous operation at API of the TU Delft, so time for further development is not required.

Robustness

Concentrated salt solutions are very aggressive at high temperatures and relatively harmless at low temperatures. Although both, eutectic freezing and evaporation are crystallisation techniques, the process takes place at very different temperatures. This difference in process conditions has an enormous influence on the aggressiveness of the solution and the extent of corrosion of the equipment. The high temperature of the evaporation process causes corrosion of the evaporator and therefore is not a very robust technique for this particular separation process.

Safety, Health and Environment

The two techniques are relatively safe compared to the melting process of magnesium. Using the two techniques is not unhealthy, and the environment will not be harmed.

Energy

Eutectic freezing is far more energy efficient than evaporation, which is shown by the calculated process costs. For eutectic freezing the only possible energy source is electricity. For evaporation there are more possible energy sources, such as combustion of natural gas. This makes evaporation a more flexible technique with respect to energy sources and in that way could perhaps save costs. But the energy advantage of the eutectic freezer (on this scale less than 10% compared to evaporation) is such that it is very hard to overcome this difference when using evaporation.

The above discussion of the two techniques shows that with respect to costs, robustness and energy there is much in favour of eutectic freezing. Product quality and safety is equal for both techniques. With respect to proven technology evaporation is in favour.

The robustness is considered to be a very important criterion, because of possible corrosion of evaporation equipment the costs will increase even more, while the cost criterion was already in favour of eutectic freezing. The proven technology criterion does not seem to be a big disadvantage at this process scale. Now that these two crystallisation techniques are compared, it can be concluded that there is very much in favour of eutectic freezing. The cost criterion and robustness criterion were the main reason for choosing eutectic freezing to separate the salts and water.

3 Basis of Design

3.1 Description of the design

3.1.1 Background information

Magnesium is recycled by melting magnesium scrap in a crucible at 700 °C and atmospheric conditions. Salt is added to extract the impurities, mainly metal oxides, from the liquid magnesium. The solid slag is skimmed off from the crucible. The purified liquid magnesium is poured into ingots, solidified and stored for sale. This is the process as it is currently applied at Remag.

The main problem is located in the slag stream. This slag stream contains in the first place some magnesium, which is desired to get out, secondly several metal oxides, which have to be removed from the slag for both environmental and recycling reasons, thirdly salt, which preferably is recovered, and last some very reactive components that cause an environmental impact, which makes dumping of the slag impossible. Also this slag is very hygroscopic and reactive, which creates several storing problems.

Several options, such as land filling, converting it to fertilizer material and dumping into sea, have been considered and rejected, mainly because of the slag's reactivity and environmental impact. Currently this slag stream, about 350 tons per annum, is stored, which is not a sustainable solution. A larger production of magnesium (10,000 t/a in 2005) from scrap is desired, which would also bring about a larger slag stream.

As described above there is need for a magnesium recycling process that contains the following aspects:

Magnesium should be recovered from scrap with a minimal loss of product

The salts in the slag should be cleaned and dried for reuse

The remaining by-product stream should be free from reactive components and saleable

3.1.2 Points of focus

If one considers the recycling process and the aspects above there can be two possible ways of achieving the stated aspects. Either the process itself can be optimized, or the process can be extended with a slag treatment process. (Of course, a combination of both is also possible.) The area of focus is therefore widespread. It was chosen by the group to focus mainly on the slag processing. However, if the group runs into solutions that concern melting process improvements that appear to be viable and the time-span of the project appears to be long enough, both will be elaborated.

3.1.3 *What will be done*

For the melting process itself, a process scheme will be developed. It will be tried to innovate the melting process in such way that the stated problems are reduced and the stated goals are (easier) met. This process scheme can be based on both generated theoretical ideas as well as practical improvements that are found in literature.

The viability of creating an innovated process scheme will be tested by several experiments. Three types of slag (slag directly from the crucible, slag after processing by the consolidator and slag after cooling at the air) from the same batch will be analyzed on their composition. From the results of these analyses conclusions can be drawn on the effect of the consolidator process on the slag, and whether this process unit should be implemented in the conceptual process design or not.

For The slag treatment a process scheme will be developed. The physical qualities and compositions of the flows will be based on the basic assumptions as stated in paragraph 3.3. As in the melting process the elements of this process scheme can be based on both generated theoretical ideas and practical process units that are found in literature. The basic flow scheme follows from the route that was chosen in appendix 2-1, which is described in chapter 2.

Several experiments will be performed on crushing and sieving the slag. The masses and compositions of the fractions will be analyzed. With the results of these analyses conclusions can be drawn on the use of these fractions in both the process itself (recycling of salts) and other processes (sell the fractions for other use).

For the recovery of the salts several conditions have to be met. Since the presence of water has to be avoided, the drying of the salt stream is of crucial importance. Also the removal of the metal oxides that are present in the slag is an objective from a recovery point of view. The salt recovery process is done by dissolving the slag, followed by filtering of insoluble metal oxides and eutectic freezing of the salt solution to separate the salt from the water again. It will also be investigated whether it is possible, both physically and economically, to recycle the water stream.

3.1.4 *What will not be done*

While in future developments the pre-treatment of the scrap can become an important step in the recycling of magnesium, it will not be investigated in this project. For now Remag only uses certain types of scrap that do not require pre-treatment. Pre-treatment of magnesium can be necessary in the future, for example, to remove paints or coatings from the magnesium scrap.

Fluxless melting, that is the melting of the magnesium without the use of any salts (Emgesal), will also not be considered in this process design. Fluxless melting under argon conditions can only be applied the cleanest type of scrap, which is not the case Remag is dealing with.

3.2 Process definition

It was chosen by the design team to mainly focus on the design of slag processing. Since Remag is planning to install a crushing and sieving process, discussed in paragraph 1.2.1. The design team shall investigate to what extent the smallest sieve fraction (< 0.5 mm), for which no market has yet been found, can be further processed towards salts, metal oxides and a small as possible waste stream. This is done by doing experiments, at Remag and the faculty of Applied Earth Science, by having meetings with experts in the field of magnesium recycling and by extensively literature search.

In the process, the most logical step after the crushing and sieving step is a dissolving step to separate the non-metallic components from the salts, to initiate a controlled formation of magnesium oxide out of magnesium-nitride with ammonia as a waste. The design team will make a process scheme for the dissolving and separation of the smallest slag fraction. To do this, the components of the slag fraction have to be known. Raw data, as can be seen in table 3.1, was obtained through XRF and XRD analysis of the slag. A rough idea of the composition was obtained from Steef Steeneken [Steeneken, 2004]. This was used to calculate the composition in the slag.

Table 3.1: Slag composition before crushing sieving (from report: [Steeneken 2004])

Component	Slag before C&S			
	Mass (g)	Mass (%)	Mole	Mole (%)
Mg (metal)	10.10	10.3%	0.4156	21.8%
MgCl ₂	7.07	7.2%	0.0743	3.9%
Mg ₃ N ₂	10.10	10.3%	0.1001	5.2%
MgF ₂	1.05	1.1%	0.0337	1.8%
MgO	31.70	32.2%	0.7863	41.2%
KCl	6.93	7.1%	0.0930	4.9%
NaCl	12.09	12.3%	0.2069	10.8%
Al ₂ O ₃	16.89	17.2%	0.1656	8.7%
MnO	2.38	2.4%	0.0335	1.8%
Sum	98.32	100.0%	1.9091	100.0%

Currently this slag stream, about 350 tons per annum, is stored, which is not a sustainable solution. An increase in production of magnesium, from 5,000 tons per year

to 10,000 tons per year in 2005 at Remag is desired, which would also bring about a larger slag stream (700 t/a in 2005). An overview of the current process at Remag is schematically given in figure 1.2. The crushing and sieving process and dissolving step are schematically given in figure 3.1. The flows can be determined in ton per year (tpa) and in yield values, between brackets, in ton per ton salts (t/t), see figure 3.1.

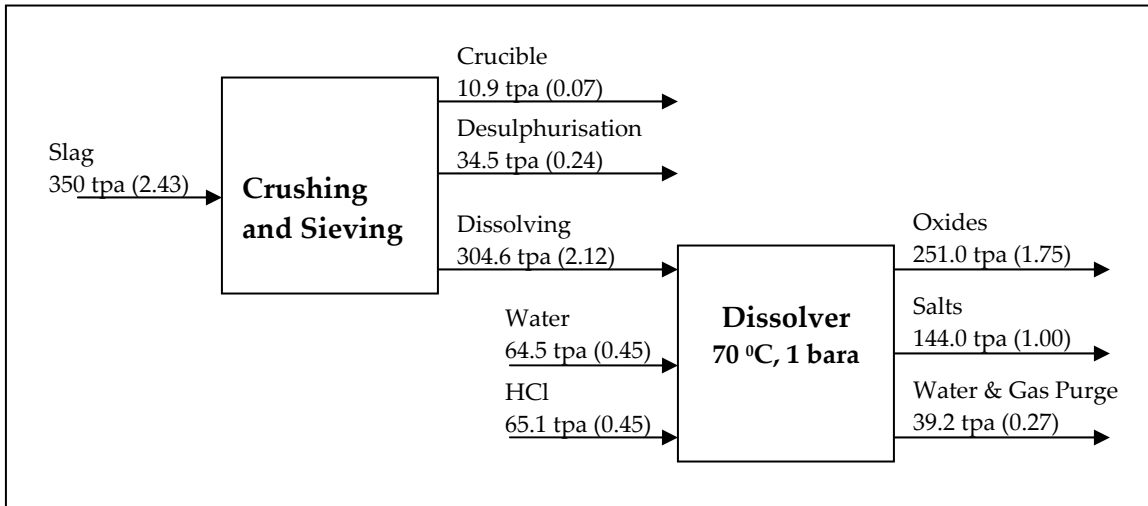


Figure 3.1: Dissolving process with Yield in ton per ton salts (t/t).

The same figure can be produced for in the yield values in ton per ton oxides, between the brackets, since the oxides are also a product stream.

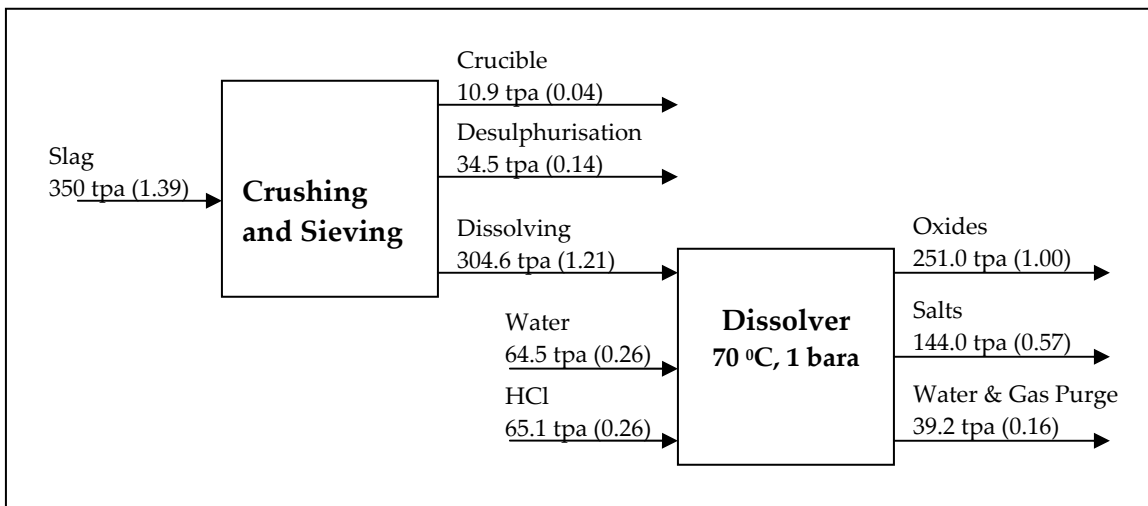


Figure 3.2: Dissolving process with Yield in ton per ton oxides (t/t).

During the dissolving stage there are two main reactions that take place. First of all metallic magnesium reacts with water to form magnesium hydroxide and hydrogen and secondly magnesium nitride reacts with water to form magnesium oxide and ammonia.

Both reactions are very exothermic. The reaction of metallic magnesium with water has an enthalpy of about -353 kJ/mole and the reaction of magnesium nitride with water has an enthalpy of about -577 kJ/mole, (see also appendix 4-1).

Furthermore, the only components in the slag as described in table 3.1 that are easily dissolved are MgCl_2 , NaCl and KCl . Therefore an easy separation can be made on the basis of solubility. All the necessary information about every component can be seen in appendix 3-1, the pure component property list.

To prevent ammonia from escaping the solution, acid is added to the dissolver. For this purpose hydrogen chloride is used to prevent the formation of insoluble salts with the acids anion.

3.3 Basic assumptions

3.3.1. Plant capacity

Remag Alloys is a magnesium recycling facility in Delfzijl in the province of Groningen in the north of the Netherlands. The plant is situated on an industrial estate called the "Metaal Park". All generally used utilities are readily available.

The company started recycling magnesium in November of 2003 and aims to produce 10.000 tons of magnesium alloys per year through recycling, for this report 5.000 tons of magnesium alloys per year is taken for the design. The magnesium scrap, ready for melting, consists mainly of die-cast AZ91 and AM60, which is oxidized to a certain extent. Oxidation of the metals also takes place in the process. However, it is assumed that all metal oxides that leave the process are already in the scrap. The properties of the concerning types of scrap are given in table 3.2.

Table 3.2: Content of magnesium alloy scrap [magnesium.com, 2004]

Component	AZ91	AM60
Aluminium	9.0 wt%	6.0 wt%
Zinc	0.7 wt%	-
Manganese	0.13 wt%	0.15 wt%
Metal oxides	3.7 wt%	3.7 wt%

The melted magnesium is sprinkled with a salt called Emgesal 5 (flux). The components of the salt are listed in table 3.3.

Table 3.3: Emgesal 5 salt composition [Inzunza, 2003]

Component	wt%
NaCl	28.3
KCl	22.8
MgCl ₂	39.5
MgO	3.0
CaF ₂	5.0
H ₂ O (max)	0.5

Since this report focuses mainly on a part of the Remag Alloys production facility, it is more convenient from the point of view from the design to define the battery limits accordingly. However for the financial part of the design it is better to define the battery limits as the whole process since this gives greater insight. Because of these reasons the design team has decided to define two battery limits, one for the purpose of the design, and one for the purpose of the process economics.

3.3.2 Battery limits for the design

For the purposes of the design the smallest fraction of the slag that leaves the crushing and sieving part of the plant is taken as the input. The outputs are salt, metal oxides, water purge (steam) and off gasses. It is assumed that all feed streams are readily available and furthermore that all product and waste streams are directly carried off. A schematic overview is given in figure 3.2.

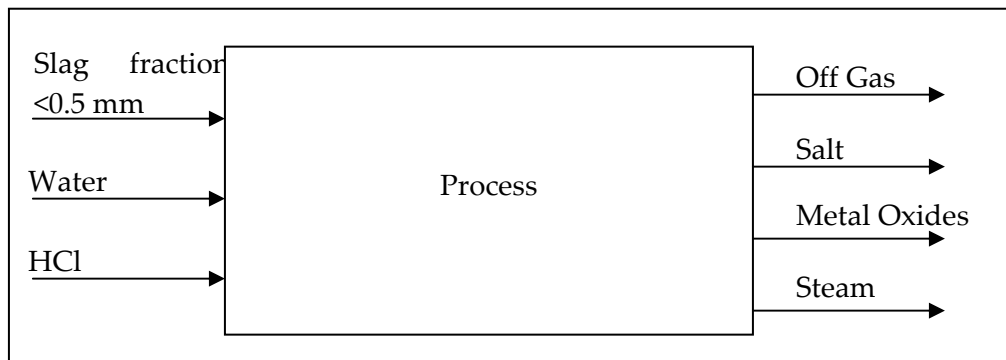


Figure 3.3: Battery limits for the purpose of the design

For the rest of this report, except in chapter 11, when the battery limits are mentioned the statement refers to figure 3.2.

3.3.3 Battery limits for the economics

Within the battery limits of the plant are the magnesium melting and purifying step and the slag treatment step. A schematic representation of the battery limits is given in figure 3.3.

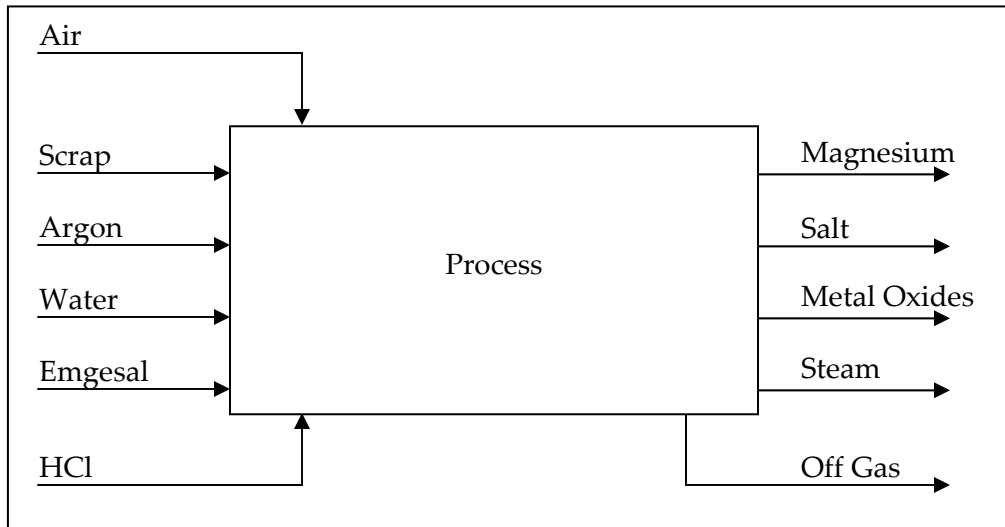


Figure 3.4: Battery limits for the economics

Scrap, emgesal (salt) and water enter the plant and magnesium (alloys), metal oxides, some salt and some water leave the plant. The aim is to recycle the salt and the water, however to prevent a build-up of impurities a purge is necessary.

3.3.4 In-going streams

As can be seen from figure 3.2 there are three in-going streams, the slag fraction <0.5 mm, water and hydrochloric acid.

The first in-going stream is the slag stream, which is the feed of the recycling process. It is the smallest fraction after crushing and sieving the slag stream. The composition of this slag stream is given in table 3.4.

Table 3.4: Composition of the slag stream <0.5 mm (Appendix 3-2)

Stream Name : Slag (<0.5 mm)					
Comp.	Units	Specification		Notes	Additional Information (also ref. note numbers)
		Available	Design		
Mg	%wt	5.6	5.6	(1)	(1) This composition follows from the experiments done by Steef Steeneken on the composition of the slag and on crushing and sieving (2) Atmospheric conditions (3) Unknown, and not important since it is not part of the economical considerations
Mg ₃ N ₂	%wt	10.8	10.8	(1)	
MgF ₂	%wt	1.1	1.1	(1)	
MgO	%wt	33.9	33.9	(1)	
Al ₂ O ₃	%wt	18.1	18.1	(1)	
MnO	%wt	2.5	2.5	(1)	
MgCl ₂	%wt	7.6	7.6	(1)	
KCl	%wt	7.4	7.4	(1)	
NaCl	%wt	12.9	12.9	(1)	
Total		100.0	100.0		
Process Conditions and Price					
Temp.	°C		20	(2)	
Press.	Bara		1	(2)	
Phase	V/L/S		S		
Price	euro/kg		-	(3)	

The water stream is taken to be composed of pure water. The reasoning behind this is that impurities that are likely to be present in this stream have no effect on the process. The price of this stream is based on the information in the design instruction manual [Grievink, Luteijn and Swinkels, 2003]. See table 3.5.

Table 3.5: Composition of the water stream (Appendix 3-2)

Stream Name : Water					
Comp.	Units	Specification		Notes	Additional Information (also ref. note numbers)
		Available	Design		
Water	%wt	100.00	100.00	(1)	(1) Take to be 100 % water, since impurities have no effect on process
Total		100.00	100.0		
Process Conditions and Price					(2) Atmospheric conditions (3) Based on appendix 3 of the CPD instruction manual
Temp.	°C		20	(2)	
Press.	Bara		1	(2)	
Phase	V/L/S		L		
Price	euro/kg		0.05	(3)	

The third ingoing stream is the hydrochloric acid feed, the properties of this stream are given in table 3.6.

Table 3.6: Composition of the HCl stream (Appendix 3-2)

Stream Name : HCl					
Comp.	Units	Specification		Notes	Additional Information (also ref. note numbers)
		Available	Design		
Water	%wt		64.00		(1) Atmospheric conditions (2) [ichem.org,2004]
HCl	%wt		36.00		
Total			100.0		
Process Conditions and Price					
Temp.	°C		20	(1)	
Press.	Bara		1	(1)	
Phase	V/L/S		L		
Price	euro/kg		0.19	(2)	

3.3.5 Out-going streams

As can be seen from figure 3.3 there are 4 out-going streams, off gas, salt, metal oxides and the water purge.

There is no specification for the composition requirements of the off gas, since the local authorities review each case separately. Therefore it is assumed that as long as the NH₃ output on an annual basis does not exceed 1000 kg environmental regulations will be met. This corresponds with a maximum concentration of 0.06%.

Table 3.7: Composition of the off gas stream (Appendix 3-2)

Stream Name : Off Gas					
Comp.	Units	Specification		Notes	Additional Information (also ref. note numbers)
		Available	Design		
NH ₃	%wt		0.06	(1)	(1) Based assumption of environmental regulations. (2) Atmospheric conditions (3) Assumed no permit required
H ₂	%wt		0.24	(1)	
Air	%wt		99.70		
Total			100.00		
Process Conditions and Price					
Temp.	°C		20	(2)	
Press.	Bara		1	(2)	
Phase	V/L/S		V		
Price	euro/kg		0.00	(3)	

The composition of the salt stream is based on the assumption that all components that are soluble leave the process with this stream. The salt will be packaged into plastic bags, which will each hold 10 or 20 kg.

Table 3.8: Composition of the salt stream (Appendix 3-2)

Stream Name : Salt					
Comp.	Units	Specification		Notes	Additional Information (also ref. note numbers)
		Available	Design		
MgCl ₂ .6H ₂ O	%wt		33.7	(1)	(1) The composition of this stream is on there being no more than 0.5 % of water in this stream. (2) Atmospheric conditions (3) Based on estimation by the design team
KCl	%wt		15.4	(1)	
NaCl	%wt		27.0	(1)	
NH ₄ Cl	%wt		23.4	(2)	
H ₂ O	%wt		0.5	(1)	
Total			100.0		
Process Conditions and Price					
Temp.	°C		20	(2)	
Press.	Bara		1	(2)	
Phase	V/L/S		S		
Price	euro/kg		0.20	(3)	

The composition of this stream is based on the assumption that all insoluble components leave the process in this stream.

Table 3.9: Composition of the metal oxides stream (Appendix 3-2)

Stream Name : Metal oxides					
Comp.	Units	Specification		Notes	Additional Information (also ref. note numbers)
		Available	Design		
MgF ₂	%wt		1.4	(1)	(1) Based on no water and a maximum of 0.5 percent salts in this stream (2) Maximum allowed concentration (3) Atmospheric conditions (4) Price unknown
Mg(OH) ₂	%wt		16.2	(1)	
MgO	%wt		56.9	(1)	
Al ₂ O ₃	%wt		21.9	(1)	
MnO	%wt		3.1	(1)	
Salts	%wt		0.5	(2)	
Total			100.0		
Process Conditions and Price					
Temp.	°C		20	(3)	
Press.	Bara		1	(3)	
Phase	V/L/S		S		
Price	euro/kg			(4)	

The composition is assumed to be completely composed of water, it does not contain any impurities since it is assumed that water is the only component that will be evaporated.

Table 3.10: Composition of the water purge stream (Appendix 3-2)

Stream Name : Water purge				
Comp.	Units	Specification		Additional Information (also ref. note numbers)
		Available	Design	
Water	%wt		100.0	(1)
Total			100.0	(2)
Process Conditions and Price				(3)
Temp.	°C		20	(2)
Press.	Bara		1	(2)
Phase	V/L/S		L	
Price	euro/kg		0.00	(3)

3.4 Economic Margin

The following text is a description for the finance for Remag, Delfzijl. In this chapter the costs that were discussed during our visit at Remag shall be discussed [Elzinga,2004]. The opening of Remag Alloys took place in November 2003. At the moment of writing the plant has only been online for six months, so it is hard to say something about Remags finance. The costs and profits are determined as good as possible for the total magnesium treatment at Remag, including the dissolving process, designed by the team.

3.4.1 Equipment costs

The total investment to build the plant including the office facilities is about 6,0 M€, discussed during our meeting at Remag. The crushing and sieving installation is build from secondary equipment and costs about 250 k€ [Steeneken, 2004]. Remag is planning to install the crushing and sieving process in mid 2004.

The total new equipment costs, as can be seen in the process flow sheet in figure 5.1, can be calculated. The fixed capital for the new equipment is about 403.3 k€ and are planned to put into use in 2005.

3.4.2 Feed and energy streams

The process at Remag is a batch process containing per batch roughly 2200 kg of scrap with 50 kg flux, the salt Emgesal, to produce roughly 2000 kg of magnesium and 250 kg slag. The costs of the raw material are not constant but the mean price is for the type I scrap, € 1.40 per kg, for the salt Emgesal € 0.90 per kg and for the argon gas € 0.70 per m³ [Elzinga, 2004].

The energy costs that were calculated consist mainly of the heat that is required to warm up the crucibles. The heating coil produces an induction heat to warm the crucible up to a temperature of 700 °C. At Remag about 1 kWh is needed to melt 1 kg of scrap, which

agrees with the thermodynamics when heat losses are taken into account. The cost of the industrial price of 1 kWh is about € 0.08. Assuming that Remag is using 11,000 tons of scrap per year, this means 880 k€ for only the melting process energy costs.

Table 3.11: Variable operating costs

Variable costs	Price per unit (€)	Unit per year 2003	Total costs (k€/a)	Total costs (€/ton product)
Raw material				
Argon gas (m ³)	0.70	7100	5	1
Salt Emgesal (ton)	0.90	125	113	23
Scrap type I (ton)	1.40	5214	7,300	1,460
Miscellaneous materials	10% of the Maintenance		60	12
Utilities				
Electricity (kWh)	0.08	5214000	417	83
Shipping and packaging	5% of the Maintenance		30	6
			7,925	1,585

3.4.3. Personnel costs

The personnel costs are divided into the costs for the office personnel and the personnel at the work floor. There are in total 4 people working at the office at Remag, working from 9:00 till 17:00, from Monday till Friday. The magnesium production process is a batch process that lasts 24 hours for 7 days a week. Working with 7 people per shift and a shift is about 8 hours. In total there are working 21 people per day at Remag. The total personnel costs for 2003 are about 742.12 k€. The fixed operating costs are determined as a percentage of the fixed capital and the operating labour, which is determined in appendix 11-4.

The total operating costs per annum can now be calculated, when adding up the variable costs and the fixed costs, as can be seen in table 3.13.

Table 3.12: Fixed operating costs

Fixed costs	for 2003	Total costs (k€/a)	Total costs (€/ton product)
Maintenance	10% of the fixed capital	600.0	120.0
Operating labour	calculated in appendix 11.4	742.1	148.4
Laboratory costs	20% of the operating labour	148.4	29.7
Supervision	20% of the operating labour	148.4	29.7
Plant overhead	50% of the operating labour	371.1	74.2
Capital charges	15% of the fixed capital	900.0	180.0
Insurance	1% of the fixed capital	60.0	12.0
Local taxes	2% of the fixed capital	120.0	24.0
Royalties	1% of the fixed capital	60.0	12.0
		3,150.0	630.0

Table 3.13: Total production costs for 2003

	Total costs (k€/a)	Total costs (€/ton product)
Total production costs	11,074.2	2,214.8

3.4.4. Net cash flow

Remag can sell the magnesium for about 2,25 €/kg. Remag produces ingots of a weight of 8 to 12 kg, which are sold in bundles from 700 to 1000 kg. The price for a bundle is about €1,575.- to €2,250.- selling most back to the automotive industry. The net cash flow is calculated in table 3.14.

Table 3.14: Net cash flow for 2003

	k€	€/ton product
Total income	11,250	2,250
Total operating costs	11,074	2,215
Net cash flow	176	35

This is the net cash flow for 2003, so without the crushing and sieving equipment and the dissolving process equipment.

Table 3.15: Results for the two different options

	Option 1		Option 2	
	Costs per year (k€)	Revenue per year (k€)	Costs per year (k€)	Revenue per year (k€)
From C&S	91.38			
Desulphurisation		unknown		unknown
Water			0.01	
Hydrochloric acid			24.80	
Oxides				unknown
Salts				57.86
Electricity			17,13	
Total:	91.38	0.00	41,94	57.86

If we assume Remag have two different options. Option 1 is to crush and sieves the slag and transports it to the waste disposal. Option 2 is to crush and sieve and dissolve the remaining slag. We can determine table 3.15 below, roughly represented are the costs and profits for the two options.

Some important assumptions are first of all no more personnel is needed if the dissolving process is running. The current personnel will be sufficient. The shipping and packaging costs are negligible.

As can be seen in table 3.15, the costs of option 1 are about 91.4 k€, not taken into account the revenue for the desulphurisation. Option 2 yield a profit of about 15.9 k€, not taken into account the revenue for the desulphurisation and the oxides. If Remag decides to build the dissolving process it also saves the costs for the waste disposal, saving per year about 107.3 k€. The total new equipment costs are determined to be about 403.3 k€. A very rough calculation gives a pay back time of about 3.8 years.

The discounted cash flow rate of return can be determined for the whole plant, included the crushing and sieving and the dissolving process.

Table 3.16: Cumulative cash flow and Cumulative discounted cash flow with crushing and sieving and the dissolving process.

Year	Investment	Net cash flow	Cumulative cash flow	Discounted percentage	Investment	Discounted cash flow	Cumulative discounted CF
2001	-€ 3,000,000.00	-	-€ 3,000,000.00	1.00	-€ 3,000,000		-€ 3,000,000
2002	-€ 3,000,000.00	-	-€ 6,000,000.00	0.93	-€ 2,777,778		-€ 5,777,778
2003		€ 176,000.00	-€ 5,824,000.00	0.86		€ 150,892	-€ 5,626,886
2004	-€ 250,000.00	€ 176,000.00	-€ 5,898,000.00	0.79	-€ 250,000	€ 139,714	-€ 5,737,172
2005	-€ 403,333.00	€ 3,307,000.00	-€ 2,994,333.00	0.74	-€ 403,333.00	€ 2,430,744	-€ 3,709,761
2006		€ 3,307,000.00	€ 312,667.00	0.68		€ 2,250,689	-€ 1,459,072
2007		€ 3,307,000.00	€ 3,619,667.00	0.63		€ 2,083,971	€ 624,899
2008		€ 3,307,000.00	€ 6,926,667.00	0.58		€ 1,929,603	€ 2,554,501
2009		€ 3,307,000.00	€ 10,233,667.00	0.54		€ 1,786,669	€ 4,341,171
2010		€ 3,307,000.00	€ 13,540,667.00	0.50		€ 1,654,323	€ 5,995,494
2011		€ 3,307,000.00	€ 16,847,667.00	0.46		€ 1,531,781	€ 7,527,275
2012		€ 3,307,000.00	€ 20,154,667.00	0.43		€ 1,418,316	€ 8,945,590
2013		€ 3,307,000.00	€ 23,461,667.00	0.40		€ 1,313,255	€ 10,258,846
2014		€ 3,307,000.00	€ 26,768,667.00	0.37		€ 1,215,977	€ 11,474,823
2015		€ 3,307,000.00	€ 30,075,667.00	0.34		€ 1,125,905	€ 12,600,727
Total	-€ 6,653,333	€ 36,729,000	€ 30,075,667		-€ 6,431,111	€ 19,031,838	€ 12,600,727

4 Thermodynamic properties

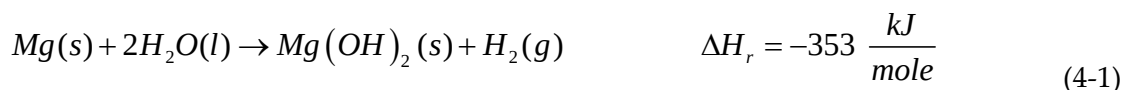
When making a conceptual process design it is essential to have a clear view of the thermodynamic properties that are important in the process. Within the battery limits as they are stated in paragraph 3.3 there are several properties of interest. First of all two reactions take place during the dissolving of the slag in water. Secondly during the same process step it is important to know the solubility in water of all the components in order to determine what components end up in what stream. Thirdly the experiments done by the design team to determine the magnesium nitride content in the slag are discussed.

4.1 Dissolving

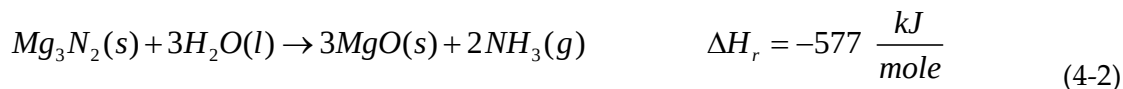
In the final process as it is described in chapter 2 there is a need for a dissolving step in order to separate the chloride salts from the oxides. In this paragraph the thermodynamic phenomena that are of interest in this step are briefly explained.

4.1.1 Reactions

During the dissolving stage there are two main reactions that take place. First of all metallic magnesium reacts with water according to reaction equation 4-1:



Secondly magnesium nitride reacts with water according to reaction equation 4-2:



Both reactions are very exothermic, the reaction enthalpies were calculated based on enthalpies of formation as found in [Binas, 1992], see also appendix 4-1, Calculation of the reaction enthalpies.

Unfortunately, the kinetics for the above reactions are unknown. Based on the fact that these reactions are both exothermic and that in both of the reactions one of the products is a gas it will be assumed that for both reactions the extent of reaction is 1.

4.1.2 Solubility of salts

The solubility of most of the components of interest is given in table 4.2. Metallic magnesium and magnesium nitride are not given because they react with water.

Table 4.1: Solubility of components in water [Binas, 1992]

Component	Solubility mole/kg
MgF ₂	<0.01
Mg(OH) ₂	<0.01
MgO	<0.01
Al ₂ O ₃	<0.01
MnO	<0.01
KCl	4.81
NaCl	6.15
MgCl ₂ ·6H ₂ O	5.77
NH ₄ Cl	7.34

As can clearly be seen from the above table the only components that are easily dissolved are MgCl₂, NaCl, KCl and NH₄Cl. Therefore an easy separation can be made on the basis of solubility.

4.1.3 Solubility of ammonia

A well-known property of ammonia is that its solubility in water is heavily dependant on the temperature. Ammonia is very soluble in water at low temperature but at high temperature it doesn't dissolve well. Another effect of interest is salting out. When the water becomes saturated with salts (for instance NaCl, KCl or MgCl₂), the solubility of ammonia also decreases. Since the aim is to make a high concentration salt solution this last effect heavily influences the dissolving step.

Normally the equilibrium concentration of a liquid and the vapour phase is calculated using Henry's Law (equation 4-3), where p is the partial pressure of the gas in atmospheres, K_H is the Henry constant and X is the concentration of the gas in the aqueous solution.

$$X = K_H \cdot p \quad (4-3)$$

In an article by Hedengren et al. [Hedengren, 2000], the Schumpe model is described and assessed. This model relates the Henry constant in for a gas in water with the Henry constant for a gas in solution according to equation 4-4. Where h_i and h_g are the ion and gas specific coefficients and c_i is the concentration of ion "i" in the salt solution.

$$\log\left(\frac{K_{H,G}(\text{water})}{K_{H,G}(\text{solution})}\right) = \sum_i (h_i + h_G) \cdot c_i \quad (4-4)$$

where $h_G = h_{G,0} + h_T \cdot T$

Values for the constants in this formula are given in the article. The article also mentions an equation that relates the temperature to the Henry constant for ammonia in water (equation 4-5).

$$K_{H,NH_3} = \exp\left(-8.0964 + \frac{3917.50}{T} - 0.00314 \cdot T\right) \quad (4-5)$$

With help of the above equations and the constants given the article by Hedengren et al. [Hedengren, 2000] the solubility of ammonia in salt solutions can be calculated.

4.1.4. Solubility of ammonium

There is equilibrium in the dissolver between ammonia and ammonium.



The equilibrium constant for this equation is given in equation 4-7.

$$5.8 \cdot 10^{-10} = \frac{[NH_3][H^+]}{[NH_4^+]} \quad (4-7)$$

With this equation and the Schumpe model explained above (equations 4-3 through 4-5) the maximum ammonium concentration in salt solutions can be calculated.

4.2 Scrubber

In the scrubber equation 4-6 is also valid. In order to minimise the release of ammonia the equilibrium needs to be shifted to the left. For this purpose hydrochloric acid is added. This results in the formation of more H^+ , which causes the equilibrium of reaction 4-6 to shift to the left as desired. The goal of this shift is to neutralise the formation of ammonia in such a way that it is not expelled into the air, but rather contained in a harmless form. The salting out effect mentioned in paragraph 4.1.3 (equations 4-3 through 4-5) also has an effect in this process step. However since the salt

concentration in the scrubber is a lot lower, the effect is also smaller. And of course there is also equilibrium between ammonia and ammonium

4.3 Eutectic freezing

4.3.1 Introduction

The eutectic freezing process [Van der Ham, 1999] is a technique that makes it possible to separate a salt solution into a stream of solid salt and a water stream. The relatively low energy consumption is mostly due to the fact that the heat of evaporation is roughly six times as high as the heat of crystallisation.

The principle of eutectic freeze crystallisation is founded on creating a supersaturated concentration by removing the water from the saline solution by cooling the solution and creating ice crystals. In this supersaturated solution also salt crystals precipitate. The conditions at which this three-phase equilibrium exists are called 'eutectic'.

The ice crystals float to the top of the solution and the salt crystals sink to the bottom due to density differences with the solution. When the ice and salt crystals are washed product streams with a purity of 99.9% [Genceli, 2004] can be obtained.

4.3.2 Minimal amount of work for separation

In order to perform the crystallisation process of the ice and the salt, a minimal amount of work has to be withdrawn from the solution. This amount of work is equal to the heat of crystallisation that is released when the salt and ice crystals are formed, i.e. the heat of melting. Heat also has to be withdrawn from the feed stream to lower the temperature to the eutectic temperature in the crystalliser.

This minimal amount of heat that has to be withdrawn is expressed in equation (4-8).

$$W_{Min} = \Phi_{Feed} * C_{p,Feed} * (T_{Feed} - T_{Eut}) + \Phi_{Ice} * \Delta H_{Water} + \Phi_{Salt} * \Delta H_{Salt} \quad (4-8)$$

With:

W_{Min}	=	Minimal amount of work (kW)
Φ_{Feed}	=	Feed of the solution (kg s ⁻¹)
Φ_{Ice}	=	Ice stream (kg s ⁻¹)
Φ_{Salt}	=	Salt stream (kg s ⁻¹)
$C_{p,Feed}$	=	Specific heat of the solution (kJ kg ⁻¹ K ⁻¹)
T_{Feed}	=	Feed temperature (K)
T_{Eut}	=	Eutectic temperature (K)
ΔH_{Water}	=	Heat of crystallisation of water (kJ kg ⁻¹)
ΔH_{Salt}	=	Heat of crystallisation of salt (kJ kg ⁻¹)

Actual amount of work for separation

To perform the thermodynamic process of crystallisation there needs to be a driving force, and therefore some amount of the work will be lost. Work will also be lost due to dissipating heat from the environment. It is assumed that the actual amount of work has to be multiplied by an efficiency factor η to overcome these heat losses, as can be seen in equation (4-9).

$$W_{Act} * \eta = W_{Min} \quad (4-9)$$

With:

W_{Act}	=	Actual amount of work (kW)
η	=	Efficiency factor (-)

5 Process Structure & Description

In this chapter the main units in the process are briefly elaborated upon, and their design criteria are stated. Subsequently the Process Flow Scheme and the Process Stream Summary are presented and briefly explained. Next the utilities required for the process will be presented and finally the process yields will be discussed.

5.1 Criteria and selections

In chapter two, Process Options and Selection, a selection was made for a separation step to separate salts and water. Eutectic freezing works more efficiently when it is operated in a continuous fashion. Since the Eutectic Freezer has the largest energy consumption of all the units envisaged, the design team decided to design the whole process as a continuous one. Fortunately this decision does not pose any problems with respect to the other process steps.

5.1.1 *Dissolving*

In chapter two, the decision to dissolve the slag was substantiated with the following reasons:

- Decrease of reactivity
- Controlled elimination of ammonia

The feed streams of the dissolving step will be water (L), recycled from downstream operations and the smallest slag fraction of the sieving process (S). When the slag is brought into contact with water exothermic reactions occur and NH_3 (g), H_2 (g), $\text{Mg}(\text{OH})_2$ (s) and MgO (s) are formed, see paragraph 4.1 for more details on these reactions. The chloride salts that are present in the slag fraction will dissolve when slag and water are well mixed in this step, which will reduce the mass of solids present and will result in a concentrated salt solution.

In order to determine the reactivity of the slag some slag was added to water. The highly exothermic reaction was over in a matter of minutes. In order to mitigate the hazardous side effects associated with the highly exothermic nature of the reaction it is decided to use a large volume of water, which will be stirred vigorously. This will ensure that the temperature rise is not large and therefore manageable. This large volume has the added benefit that the residence time will also be large, which gives the salts plenty of time to enter into solution.

The gases that are formed during the reactions in the dissolver will be lead into a scrubber in order to convert the ammonia into ammonium salt, which can subsequently be reintroduced into the dissolver. The conversion of ammonia into a salt makes it possible to remove the ammonia from the process in downstream operations together with the other salts.

The slurry of non-metallic components and salts is highly concentrated salt brine. At high temperatures this brine can be very aggressive; this must be taken into account when designing the dissolver, since it has consequences for the operating temperature and the construction material.

To minimise the amount of effort required for separation further downstream, it is important to minimise the amount of water that is used in this process step.

Design criteria for the dissolving tank:

- Operating temperature: 70 °C
- 25 wt% salt solution
- Operating pH: 7
- Equipment material: must be able to resist metallic corrosion
- Hydrogen concentration in air must be outside explosion limits

In-going streams:

- Smallest slag fraction from crushing and sieving (<0.5 mm) (S), stream <1>
- Water containing ammonium salt from scrubber (L), stream <2>

Out-going streams:

- NH_3 and H_2 gas (g) , stream <3>
- Slurry containing salts and oxides (S+L) , stream <4>

In the dissolver two heterogeneous reactions take place (solid, liquid contact) and salts have to be dissolved. These processes demand good contact between the liquid phase and the solid phase, which is realised by agitation. The reactions that take place in the dissolver take precedence over the dissolving of the salts with respect to the amount of water that is added, since these reactions are more dangerous than the dissolving of the salts. When necessary the dissolving of the salts can be adjusted in a next tank where no reactions will occur and dissolving can be more carefully monitored.

5.1.2 *Scrubbing the off-gases*

The reason for scrubbing the off-gases is to dissolve ammonia and in the mean time promote the formation of ammonium. Scrubbing is done by diffusion of ammonia gases into water and subsequently shifting the equilibrium between ammonia and ammonium

through addition of a sufficient amount of acid. In this way the ammonia is not emitted, which is desirable in environmental point of view.

In terms of phases there will be a gas-liquid contact in this step. Since both phases are well mixed and as no real reaction is taking place the diffusion of the ammonia from gas to liquid is assumed to be rate limiting. Good mixing of the phases increases the surface area and thus also the speed of the mass transfer step.

Design criteria of the scrubber:

- Operating temperature: 20 °C
- Operating pH: 7 (adjustment by adding hydrochloric acid)
- $\text{NH}_3(\text{g})$ - $\text{NH}_3(\text{aq})$ equilibrium is rate limiting

In-going streams:

- Hydrochloric acid (L), stream <7>
- Water (L) (from eutectic freezing), stream <22>
- Ammonia (G) (from dissolver), stream <3>

Out-going streams:

- Water containing salts (aq), stream <2>
- Off-gas H_2 , NH_3 (G), stream <8>

5.1.3 Filtration

Filtration of the slurry that comes from the dissolver is necessary to separate the oxides from the brine. The oxides, when isolated, can be sold. The filtrate only contains water and salts.

Design criteria of the belt filter:

- Cake contains 30 wt% salt solution

In-going streams:

- Slurry from dissolver (S+L), stream <21>

Out-going streams:

- Water containing 25 wt% salts (L), stream <9>
- Cake of which 30 wt% is salt solution (S+L), stream <10>

5.1.4 Washing

The washing of the cake that comes from the filtration step is necessary it is desirable to minimise the amount of impurities that are present in the metal oxide product stream.

The filtrate of the washing step contains dissolved salts, which can be reintroduced into the process.

Design criteria of the washing step (belt filter):

- Wash water can be reintroduced into the process (scrubber)
- Cake of which 30 wt% water

Ingoing streams:

- Cake of which 30 wt% is salt solution (S+L), stream <10>
- Fresh wash water (L), stream <30>

Outgoing streams

- Wash water containing salts (aq), stream <6>
- Cake of which 30wt% is water (S+L), stream <13>

5.1.5 Eutectic freezing

The objective of this step is to separate water and salts. Crystallisation of the salts can be done through controlled freezing. The salts and water will crystallise when cooled, at the eutectic temperature crystallised salt and water split into two separate phases.

Design criteria for the eutectic freezer:

- Eutectic point -34°C
- Ingoing stream at 0°C

Ingoing streams:

- 25 wt% salt solution (aq), stream <24>

Outgoing streams:

- Salts (S), stream <18>
- Ice (S), stream <25>

In order to save energy in the eutectic freezer, the ingoing stream is pre-cooled to 0°C . The outgoing ice stream at the top of the eutectic freezer has a temperature far below zero. Heat integration with the ingoing salt stream is efficient in the point of view of pre-cooling of the ingoing stream and can also contribute to the melting of the outgoing ice stream.

5.1.6 Drying Salts

For the salts to be saleable they need to be dried. The dryers will work on electricity since there is no gas available. The Magnesium melting crucible also uses electricity.

Since the salts are hygroscopic, they need to be packaged in plastic bags to keep them dry.

Design criteria for the salt oven

- All water is evaporated
- Salt market: de-icing salt

5.1.7 *Drying Oxides*

In order to make the metal oxides saleable they need to be dried. The dryers will work on electricity since there is no gas available.

Design criteria for the oxide oven

- All water is evaporated
- 0.5 w% salts remains in the dry oxides
- Oxides market: Concrete

5.2 Process flow scheme

The process flow scheme can be seen in figure 5.1.

The feed of the process <1>, the smallest slag fraction from crushing and sieving enters the process via hopper (H01) and is lead to the dissolver (V04) by conveyer belt (B01). The ammonia that is formed leaves the dissolver <3> and is lead into a scrubber (V01). The slurry <4> containing salts and oxides is lead into the filtration feed buffer tank (V05) for water <28> and pH adjustment <29> adjustment if necessary.

The slurry <21> is filtered and subsequently washed with a belt filter (BF01). The washing is done with water recycled from the eutectic freezer <12> and augmented with fresh water <11> if necessary. The washed oxides <13> are sent to the dryer (D01) before they leave the process <15>.

The filtrate from the filtration step <9> will be pre-cooled (E01 and E02) before it is sent to the eutectic freezer (EF01) for separation of water <25> and salts <16>, the salts <16> are also sent to a dryer (D02) before they leave the process.

The wash filtrate <6> and the water from the eutectic freezer <5> can both be reintroduced into the process via the scrubber (V01) since the wash filtrate <6> contains some salts and the water from the eutectic freezer (EF01) is very cold, which is beneficial for the diffusion process in the scrubber (V01). The pH in the scrubber (V01) is adjusted with hydrochloric acid <7>.

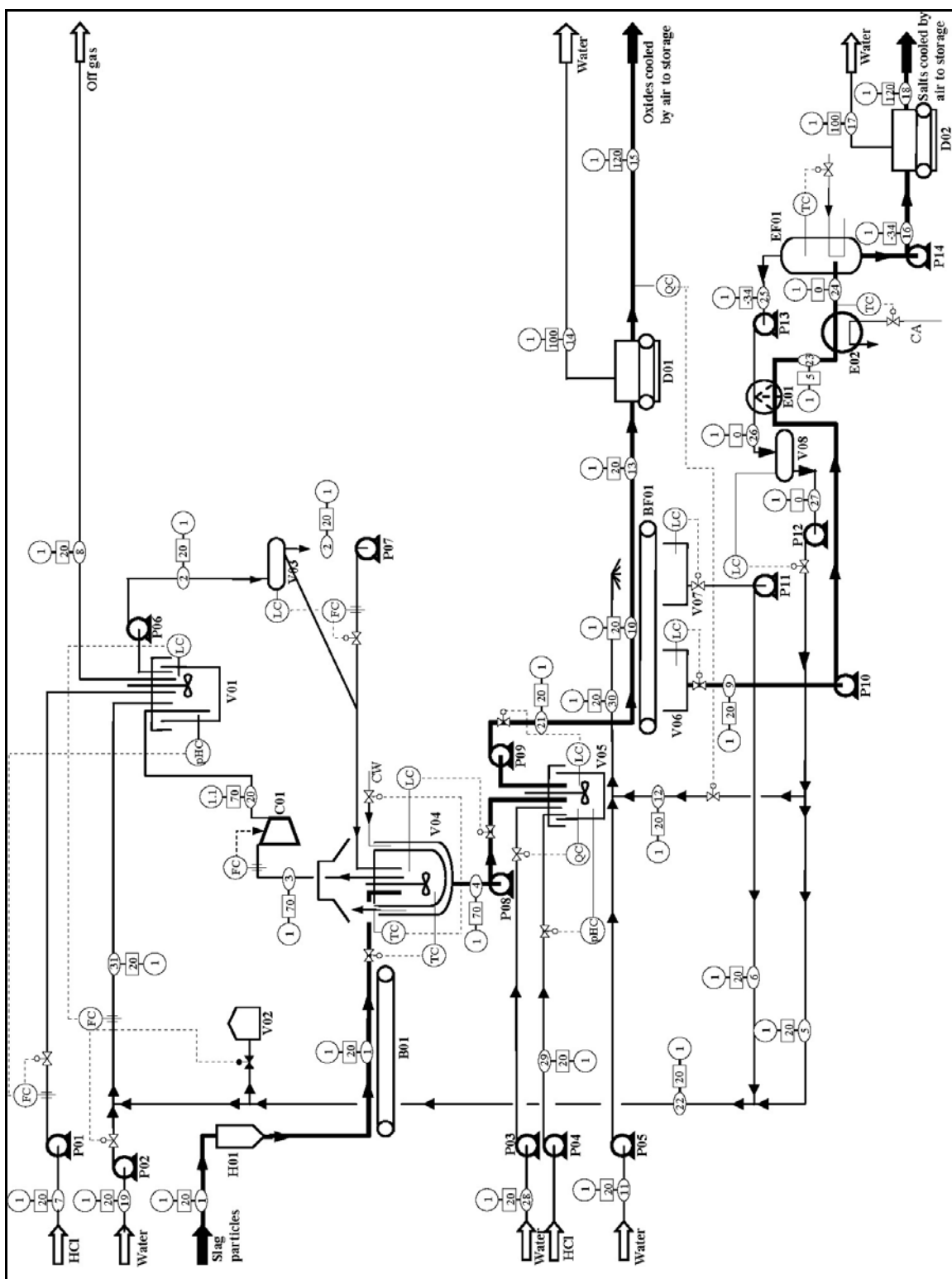


Figure 5.1: Process Flow Scheme

The ammonia that is removed by the scrubber is reintroduced into the dissolver (V04) as ammonium salt <2> after passing a buffer vessel (V03). The off gases <8> leave the process via the scrubber. The dryers (D01 and D02) evaporate water, which leaves the process by air, stream <14> and <17>.

5.3 Process stream summary

The complete process stream summary is given in Appendix 5-1, Process stream summary. The ingoing and outgoing streams are given below in table 5.1.

Table 5.1: In-going and out-going stream summary (Appendix 5-1)

STREAM Nr. :		0	IN	0	OUT
Name :		Total plant		Total plant	
COMP	MW	kg/h	kmol/h	kg/h	kmol/h
Mg	24.31	2.12	0.0873	0.00	0.0000
Mg ₃ N ₂	100.93	4.12	0.0408	0.00	0.0000
MgF ₂	62.29	0.43	0.0069	0.43	0.0069
Mg(OH) ₂	58.31	0.00	0.0000	5.09	0.0873
MgO	40.31	12.92	0.3205	17.85	0.4429
Al ₂ O ₃	101.96	6.88	0.0675	6.88	0.0675
MnO	70.94	0.97	0.0137	0.97	0.0137
MgCl ₂	95.21	2.88	0.0303	2.88	0.0303
KCl	74.55	2.83	0.0379	2.83	0.0379
NaCl	57.44	4.93	0.0858	4.93	0.0858
HCl	36.45	2.92	0.0801	0.00	0.0000
NH ₄ Cl	53.45	0.00	0.0000	4.28	0.0801
NH ₃	17.00	0.00	0.0000	0.03	0.0015
H ₂	2.00	0.00	0.0000	0.17	0.0873
H ₂ O	18.00	13.28	0.7376	7.93	0.4405
Total	0	54.27	1.5083	54.27	1.3817

5.4 Utilities

Below there is an overview of the energy requirements of the main process units (table 5.2). As can be seen from this table the energy requirements for the process are low.

Table 5.2: Overview of the energy requirement for major process units

Equipment	Type	Requirement		Reference
Scrubber	Stirring	0.6	kW	Appendix 8-3
Dissolver	Stirring	1	kW	Appendix 8-1
Dryer (D01)	Heating	7.24	kW	Appendix 8-12
Dryer (D02)	Heating	3.59	kW	Appendix 8-12
Eutectic Freezer	Cooling	14.04	kW	Appendix 8-10
HE (E02)	Cooling	0.29	kW	Appendix 8-13
Total		26.8	kW	
Per Annum		214098	kWh	

The other utilities required are of course the cooling requirements these are cooling water for the dissolver and cooling agent for the eutectic freezer. The cooling water flow will be 0.38 m³/h (Appendix 8-1), which will not be recycled. The flow of the cooling agent, Freezium, is 5.4 m³/h (Appendix 8-11). The volume of coolant in the discs during normal operation is about 50 litres. In order to ensure continuous operation it will be necessary to use around 200 litres of Freezium in total.

5.5 Process Yields

The crushing and sieving process and dissolving step are schematically given in figure 3.1. With the flow stream summary the yield values when compared to salts can be determined, these are given in the figure between brackets, in ton per ton salts (t/t).

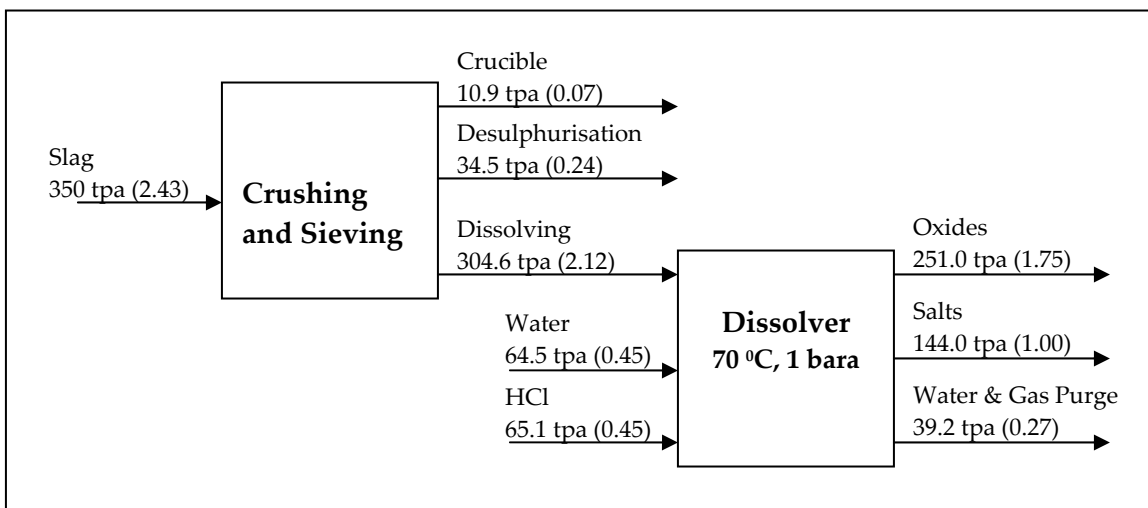


Figure 3.1: Dissolving process with yields in ton per ton salts (t/t).

The same figure can be produced for in the yield values in ton per ton oxides since the oxides are also considered to be a product stream.

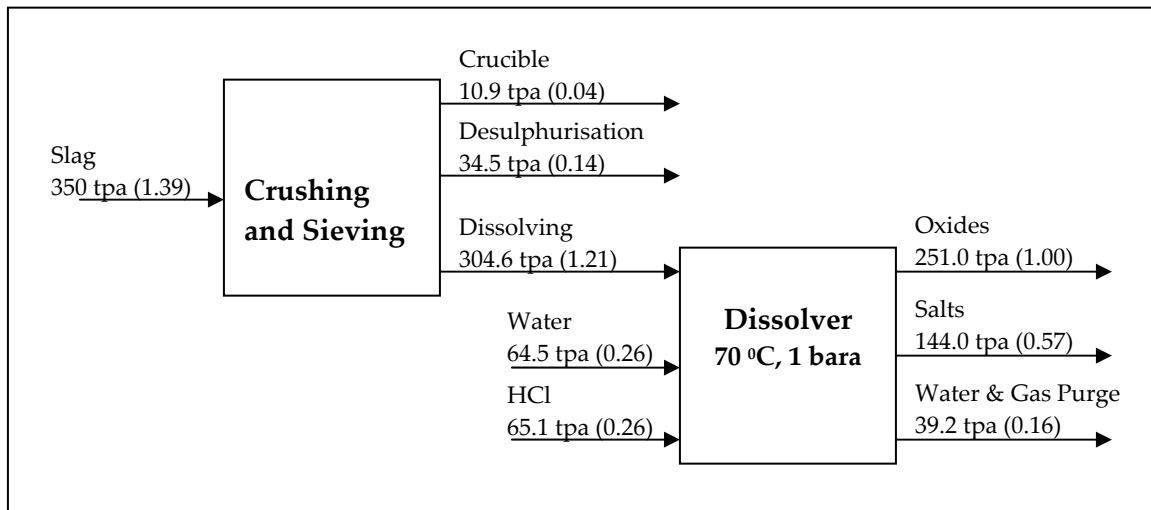


Figure 3.2: Dissolving process with yields in ton per ton oxides (t/t).

6 Process Control

In this chapter a description will be given of the control as presented in the process flow scheme. The process units will first be discussed separately. In the last paragraph of this chapter the process as a whole will be discussed with respect to the control of the whole plant.

6.1 Scrubber (V01)

In the scrubber two processes take place. The ammonia dissolves into the water followed by conversion of ammonia into ammonium salt by adding hydrochloric acid. Ammonia dissolves best at low temperatures. Therefore, the ingoing water stream has to be cold enough (at most 20 °C). This is automatically realised since the recycled water from the eutectic freezer is cold. The amount of acid that is added is adjusted by ratio control based on the pH measured in the scrubber.

6.2 Dissolving vessel (V04)

Temperature rise in the dissolving vessel must be controlled from the point of view of safety but also to ensure a faster exothermic reaction. Control of the temperature is done through cooling the vessel with a cooling jacket. The temperature of the out-going cooling water is measured and controlled by adjusting the in-going cooling water stream.

The operating temperature is also controlled by controlling the ingoing slag stream. Bringing the slag inlet to stop when the temperature becomes too high is the fastest way to decrease the reaction rate in the dissolver.

A stop on the slag inlet will automatically reduce the ammonia formation, which will result in a lower pH in the scrubber and subsequently less water will flow through the scrubber back into the dissolving vessel. In this way the whole process will slow down.

A level control is necessary to prevent the vessel from flowing over or pumping dry. The control is realised by adjusting the outgoing slurry flow, which is the most effective way since this stream has the biggest volume.

6.3 Filtration feed buffer vessel (V05)

Controlling the temperature, the pH and the extent of solution at the same time in the dissolving vessel is very difficult. The amount of disturbances can't be covered by the amount of manipulating variables in the dissolving step.

Therefore the control has to take place according to priority. Since the dissolving is less important relative to the exothermic reactions that take place, it was decided to focus the control in the dissolver on the rising temperature instead of the extent of saturation. So, the amount of slag that enters the dissolver depends on the temperature. Vessel (V05) takes care of the adjustment of pH and dissolving of the salts if necessary. The extent of solution in this tank is verified and if required water will be added in order to dissolve all the salts present, also the pH is measured and hydrochloric acid is added if required.

6.4 Eutectic Freezer (EF01)

The temperature of the eutectic freezer is controlled to ensure the temperature is at the eutectic point of the salt solution as to let separation between the crystallised salt phase and the crystallised water phase take place. The freezing process takes less energy if the ingoing salt stream is pre-cooled to a temperature of 0 °C.

6.5 Belt Filter (BF01)

The purpose of the belt filter is to filter and wash the oxides. It is very important that the oxides are salt free to a certain extent, therefore the amount of wash water has to be adjusted if it is not sufficient for the removal of the salts from the oxides. This adjustment is done with backward control while in principle the amount of wash water required is fixed because adjustment of the salt composition takes places in vessel (V05) to ensure 25 w% solution.

6.6 Vessels (V03), (V06), (V07) and (V08)

These buffer vessels in the process are level controlled to prevent them from flowing over or pumping dry. Vessel (V06) and vessel (V07) are easiest controlled with forward control. Since stream <5> coming from vessel (V08) will be part of a combined recycle stream, forward control has almost no consequences for other process steps. Vessel

(V03) is forward controlled with a level control that is related to a flow control in order to minimise the consequences for the scrubber (V01) and to have influence on water stream <2> that goes into the dissolver.

6.7 Conclusions, the process as a whole

When the basic process steps were lined up and the possible control was reviewed it became clear at which points in the process it was desired to add buffer vessels. These will ensure that possible disturbance upstream will have only a minimal effect on downstream processes.

The basic process steps are dissolving (V04), scrubbing (V01), filtration (BF01) and eutectic freezing (EF01). Vessels (V02), (V03), (V05), (V06), (V07) and (V08) were added for reason mentioned above.

With respect to the dissolving of the salts and the amount of oxides suspended there is control when there is too little water to realise the dissolving, but no control when too much is added. This is a likely situation since it is very likely that the slag composition is subject to fluctuations depending on the processed scrap in the magnesium recovery process.

The consequences for this design are that the cake on the belt filter will be thinner than assumed and it will be washed with more water than necessary, which is a waste of filtration effort. Also the effort of the eutectic freezer is in that case unnecessarily high.

The slag composition can be monitored by applying a regular quality check on the mass of oxides coming from the dryer (D01) and the extent of saturation of the salt solution in vessel (V05). If this does not satisfy the requirements on a regular basis it must be considered to reduce the amount of water that is recycled in order to save energy and process effort. If this occurs it is likely that this is due to a change in the scrap type, an improvement in the magnesium recovery process or the magnesium slag has been exposed to an external disturbance.

7 Mass and heat balances

In this section the mass and heat balances for the process within the battery limits will be explained, they will be treated in the order in which they were calculated. The results of these calculations can be found in appendix 7-1, Mass balance calculations. After the calculations described above a check was performed for every component within every process step and over the whole of the process to ensure that the mass balances were correct. The designations between brackets refer to the process flow sheet as it is given in figure 5.1.

7.1 Crushing and sieving

The calculation of the mass balances starts at the crushing and sieving. The composition of the slag stream was assumed to be as it is given in table 1.1. This composition was combined with the results from the sieving experiments done by Steef Steeneken (Appendix 1-3) to calculate the composition of the outgoing streams of the crushing and sieving section. It was assumed that the crushing and sieving section only separates metals from non-metals.

The size of the total slag stream is based on information from Remag. The amount of slag produced in one batch is around 150 kg. This equals 375 tons of slag produced in 2003/2004 (2500 batches). For each batch around 10 kg of magnesium is recovered in through the consolidator. This equals 25 tons a year. All this means that the total slag stream that goes to the crushing and sieving process is 350 tons per annum. The smallest fraction leaves the crushing and sieving step and goes to the dissolver. The size of this stream is about 305 tons per year.

7.2 Dissolver (V04)

In the dissolver two reactions take place; metallic magnesium is converted to magnesium hydroxide and hydrogen (equation 4-1) and magnesium nitride is converted to magnesium oxide and ammonia (equation 4-2). Since the conversion for both reactions is assumed to be 100 percent the resulting products are easily calculated. The gasses that are formed during the reaction leave the dissolver to go to the scrubber.

The rest of the components in the dissolver go to the filtration step. This stream is required by the design to be a 25 w% solution of salts in water. The water that is

required for this composition enters the dissolver from the scrubber. The size of the water stream that enters the dissolver from the scrubber depends on two things. Firstly it must contain enough water to create a 25 w% solution of the soluble components and secondly it must contain enough water for the reactions to take place. The stream from the dissolver also contains dissolved NH_4Cl , which is formed in the scrubber, and some chloride salts, which come from the washing step.

7.3 Scrubber (V01)

The task of the scrubber is to catch the ammonia that is formed in the dissolver and ensure that it stays in solution in the form of ammonium. Around 11 tons of ammonia is formed each year, to convert this to sal ammoniac 24 tons of hydrochloric acid is needed. This is added in the form of a 36 w% solution, of which 66 tons is needed yearly. The water needed for the scrubber comes mostly from the washing step (300 tpa), however some comes directly from eutectic freezing (77 tpa). The hydrogen leaves the gas scrubber in gas form.

7.4 Filtration (V06)

During filtration the solids are separated from the solution. In order to calculate the streams leaving this step it was assumed that the filtercake contains 30 percent liquid by volume. Furthermore it was assumed that the solution is the same whether it remains in the filtercake or goes to the eutectic freezer. The filtercake leaves this step to go to the washing step.

7.5 Washing (V07)

The assumption that the residue contains 30 percent liquid by volume is also made for the washing step. In order to calculate the outgoing streams it was assumed that there is perfect mixing in this step so that all the solution which leaves this step has the same composition, whether in the residue or in the filtrate.

The assumption of perfect mixing is of course inaccurate. It can however be inaccurate in two ways. It could be that the washing liquid efficiently flushes out the solution that remained in the filtercake. This means that the amount of water needed in this step is overestimated. The other possibility is that the solution clings to the solid particles and is

therefore difficult to wash of in which case the amount of water needed in this step is underestimated. Since it is not known which of these effects is stronger it is not possible to make a further distinction.

In order to calculate the amount of water needed for this step, under the condition of perfect mixing, the ratio of water to salts in the solution needs to be calculated. The basis for this ratio is the desired product composition. The metal oxides stream must not contain more than 0.5 w% other components. On the basis of the eventual composition (after the remaining water has been evaporated) the ratio of water to salts is about 7. 300 tpa of water is required to achieve this ratio.

The water required for washing comes from the eutectic freezer. Unfortunately this stream contains a small amount of soluble components. However since this is a small amount (less than 2 wt%) it can still be used to dilute the solution that is present in the filtercake. This means more water is used than is ideal (washing with clean water is always better) but in the interest of water recycling it is the best approach.

To help minimise the above problem any water that is needed as make up, which is around 60 tons a year is added in this step. In this way the amount of water required from the eutectic freezer is minimised.

7.6 Oxide drying (D01)

In this step, the water that remains in the residue of the washing step is evaporated to obtain a dry product. The final product is about 251 tons of metal oxides; the composition is given in table 7.1.

Table 7.1: Composition of the metal oxide product

Component	Percentage (w%)
MgF ₂	1.4
Mg(OH) ₂	16.2
MgO	56.9
Al ₂ O ₃	21.9
MnO	3.1
MgCl ₂	0.1
KCl	0.1
NaCl	0.2
NH ₄ Cl	0.1
Total	100.00

Assumed is that all the water is evaporated by the dryer, this means the product streams that come from the oxide dryer are only pure salts and pure water that is evaporated. This also means no hydrates are present in the product stream, this in contrast with the products that come from the eutectic freezer.

7.7 Eutectic freezing (EF01)

The ingoing stream of the eutectic freezer contains 25 weight percent dissolved salts. The process separates this into a stream of salt crystals and a stream of water crystals. These streams both contain about 5 weight percent of the mother liquor, which is the in-going stream. This means that the water stream contains some salts and the salt stream contains some water.

The other phenomenon of interest here is that magnesium chloride crystallises as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. This means that there is also a water loss here.

7.8 Salt Drying (D02)

In this step the salt product is dried in order to make it suitable for sale as de-icing salt. This means that 5.9 tons of water is evaporated each year. The salt stream is 144 tons a year and has the composition as it is given in table 7.2.

Table 7.2: Composition of the salt product

Component	percentage (w%)
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	34.16
KCl	15.69
NaCl	27.37
NH_4Cl	22.78
Total	100.00

7.9 Heat balances

There are only four units within the process flow scheme where the heat balances are of real interest. These are, of course, the two heat exchangers, (E01) and (E02). The third is the dissolver, where two exothermic reactions take place, and finally the eutectic freezer.

7.9.1 Heat exchangers (E01) and (E02)

The heat balances over the heat exchangers are very simple, the enthalpy flows from one stream to the other:

$$Q_{duty} = \phi_{mass,1} \cdot C_{p,1} \cdot (T_{in,1} - T_{out,1}) = \phi_{mass,2} \cdot C_{p,2} \cdot (T_{out,2} - T_{in,2}) \quad (7-1)$$

In this case stream 1 is cooled while stream 2 is heated. Both heat exchangers will be designed according to this equation.

7.9.2 Dissolver

A significant amount of heat is generated in the dissolving tank. Both reactions are assumed to reach complete conversion. This means that the total amount of heat that is generated is:

$$Q_{reactions} = \phi_{mass,Mg} \cdot M_{w,Mg} \cdot \Delta H_{r,4-1} + \phi_{mass,Mg_3N_2,in} \cdot M_{w,Mg_3N_2} \cdot \Delta H_{r,4-2} \quad (7-2)$$

It is assumed that this heat is used for three purposes. The first is to heat up the incoming slag <1>:

$$Q_{slag} = \phi_{mass,slag} \cdot C_{p,slag} \cdot (T_{dissolver} - T_{in,slag}) \quad (7-3)$$

The second is to heat the incoming water stream from the scrubber <2>:

$$Q_{water} = \phi_{mass,water} \cdot C_{p,water} \cdot (T_{dissolver} - T_{in,water}) \quad (7-4)$$

In the third place it is also taken into account, that a small amount of the water in the dissolving tank is evaporated.

$$Q_{evap,water} = \phi_{mass,water} \cdot \Delta H_{evap} \quad (7-5)$$

With these four equations the amount of heat that is still must be dissipated through the cooling jacket, Q_{cool} , can be calculated with:

$$Q_{cool} = Q_{reactions} - Q_{slag} - Q_{water} - Q_{evap,water} \quad (7-6)$$

With the cooling requirement the amount of cooling water can be calculated through:

$$Q_{cool} = \phi_{mass,cool} \cdot C_{p,cool} \cdot (T_{out} - T_{in}) \quad (7-7)$$

Since in the Netherlands it is stipulated by law that cooling water can't be discharged at more than 40 °C, and it is assumed that the water is taken in at 20 °C, the amount of cooling water can easily be calculated.

7.9.3 Eutectic freezer

In paragraph 4.3 the actual amount of work that has to be withdrawn from the crystalliser could be calculated with equation (4-9). This heat is withdrawn by means of a coolant that flows through cooling plates in the eutectic freeze crystalliser. The amount of heat that is withdrawn heats the coolant according equation (7-8).

$$Q_{coolant} = \dot{\phi}_{mass,coolant} \cdot C_{p,coolant} \cdot (T_{coolant,out} - T_{coolant,in}) \quad (7-8)$$

with this equation the cooling duty is related to the coolant flow, which can subsequently be calculated.

In appendix 8-1 the cooling requirements can be found. The temperature of the ingoing water stream is 15 °C while the outgoing water stream is about 40 °C.

8 Process and equipment design

In this chapter the design for the process and the equipment will be explained. No tools were used to simulate the process, as will be explained in paragraph 8.1. Paragraph 8.2 is about the design of the units themselves. Successively, the dissolver, the scrubber, the belt filter, the eutectic freezing unit, the drying units, the pumps and the heat exchangers will be designed.

Special attention is paid to the design of the eutectic freezer, because this is not a common apparatus and no design models are available for this type of equipment. Most of the data and design specifications are optimised through trial and error by researchers at the API department of the Delft University of Technology. All relevant data is taken from reports by Van der Ham [Van der Ham, 1999] and Vaessen [Vaessen, 2003]. Detailed information on the exact design of the individual parts of the eutectic freezer can be found there. E. Genceli MSc, who is presently doing research in this area, provided further advice and information.

It is assumed that no equipment is present on site. This means that all equipment has to be newly installed.

8.1 Integration by process simulation

No process simulation tools were used during the development of this report. In the dissolver (V04) it was assumed that 100% conversion takes place, due to the excess of water present and the exothermic nature of the reaction. In this particular case there seemed to be no need for simulation.

It was considered to use Aspen to simulate the crystallization process. However, Aspen has no possibilities to simulate multiple crystallisation processes in one crystalliser. Creating a user-defined component, including all ions in stoichiometric ratio, could solve this problem. In that case, all properties of this (user defined) component have to be estimated. Since the calculations for the minimal amount of work (paragraph 4.3) and the actual amount of work of the eutectic freezer that is necessary to perform the crystallization already give a reasonable estimation, this was not done.

8.2 Equipment selection and design

8.2.1 *The dissolver*

The first step in the process scheme as it is given in figure 5.1 is the dissolver. The dissolver is a vessel (reactor) with a cooling jacket, an agitator (stirrer) and an extractor fan. The dissolving vessel has four main functions:

- Ensure complete conversion of metallic magnesium (equation 4-1)
- Ensure complete conversion of magnesium nitride (equation 4-2)
- Ensure that the heat generated by the reactions is dissipated in a safe way
- Ensure that all the soluble components dissolve completely

There are several properties of the vessel that have to be determined so that the reactor can do its tasks as required. These properties are treated below, the calculations associated with the design can be found in appendix 8-1, Dissolver enthalpy calculations, and appendix 8-2, Ammonia solubility in the dissolver.

Reactor temperature

So as to facilitate cooling the reactor and to lessen the solubility of ammonia the reactor temperature is chosen to be 343 K. Later it will become obvious that this is a convenient temperature for the dissolver.

Space-time

As was stated in paragraph 4.1 no kinetics are known for these reactions. Since the reactions are not infinitely quick some time will have to be allowed for the components to react and for the gas to leave the solution. Time also needs to be allowed for the soluble components to completely dissolve. Both these factors mean that the space-time has to be sufficiently high. Fortunately the throughput of the dissolver is not very high (around 70 litres an hour) this means that a long space-time does not lead to a high reactor volume.

Since both reactions are very exothermic it is desirable to add only a small amount of slag to a large amount of water (or solution). With this in mind the design team decided to set the dissolver volume to 0.5 m³. This would mean that around 44 kg of slag an hour is added to 500 litres of water, a ratio of about 1 to 10 by weight. The adiabatic temperature rise that could occur with this ratio is around 25 degrees. This means that if by accident the feed is dramatically increased and the cooling jacket of the reactor is blocked the temperature rise due to the reactions would still be less than the boiling temperature of water and therefore not be overly dangerous.

When the reactor volume is set at 0.5 m³ and is a Continuous Stirred Tank Reactor (CSTR). The reactor space-time becomes just over seven hours. This is ample time for the reactions to run their course and for the soluble components to dissolve.

Agitator

A propeller stirrer is fitted to the vessel to ensure mixing, which helps the reactions take place, helps dissolve the soluble components and increases heat transfer. The stirring power is estimated to be 2.0 kW per m³ tank [Sinnot, 1999]. In this case that means 1 kW stirrer is required.

Extractor fan

On top of the reactor an extractor fan will be placed to transport the fumes from the dissolver to the scrubber (paragraph 8.2.2). To specify the size of this air blower it is necessary to determine what concentration of ammonia is desired above the dissolver. If the ammonia concentration in the air is too low the equilibrium between ammonia and ammonium in the dissolver will shift to ammonia, which would mean that the solution in the dissolver would become caustic. For more information on the thermodynamics behind this see paragraph 4.1.3 and 4.1.4.

The desired concentration of ammonium in the dissolver is 1.8 mole/litre (see appendix 8-2). According equation 4-7 this is in equilibrium with NH₃ at a concentration of 0.011 mole/litre. According to the Schumpe model (see paragraph 4.1.3), this would be in equilibrium with an ammonia partial pressure of 0.009 atm. In order to be on the safe side an ammonia partial pressure of 0.01 atm is chosen. If it is assumed that the air above the dissolver is perfectly mixed then this is also the composition of the air stream that leaves the blower. Since 1.4 kg of ammonia is produced each hour, the air stream has a required size of 50 litres per second.

Heat exchange area

Since both reactions that take place in the dissolver are very exothermic the dissolver needs a cooling jacket. To calculate the required heat exchange area it is important to first calculate the cooling duty. The total amount of heat that is produced in one hour by the reactions is:

$$Q_{\text{reactions}} = \phi_{m,Mg} \cdot M_{w,Mg} \cdot \Delta H_{r,4-1} + \phi_{m,Mg_3N_2} \cdot M_{w,Mg_3N_2} \cdot \Delta H_{r,4-2} \quad (8-1)$$

with:

$\phi_{m,i}$ = mass flow [kg/h]

$M_{w,i}$ = molar mass [kg/mole]

ΔH_i = reaction enthalpy [kJ/mole]

The heat produced in one hour is 54 MJ (see appendix 8-1). This heat is used to heat up the incoming stream of water (13 MJ) and to heat up the incoming slag (1.8 MJ). This leaves an excess heat of almost 40 MJ, which is the cooling duty.

Cooling water is taken in at 15 °C and is not allowed to leave the plant at more than 40 °C. This combined with the cooling duty means that a cooling water stream of 382 litres an hour is required (see appendix 8-1).

The required heat exchanger area is calculated with:

$$Q = U \cdot A \cdot \Delta T \quad (8-2)$$

with:

Q = cooling duty [W]

U = heat transfer coefficient [W/(m²K)]

A = heat exchanger area [m²]

ΔT = temperature difference [K]

The heat transfer coefficient is estimated at 525 W/(m²K). This value was taken from figure 12.1 in Coulson and Richardson [Sinnot, 1999]. The value for the heat transfer coefficient according to the figure 12.1 is between 525 and 640 W/(m²K). So as not to underestimate the required heat exchange area the lower value is used in the calculations. The temperature difference is assumed to be 42.5 K, which is based on the average temperature difference between the cooling water and the solution in the dissolver. With these values in mind the required heat exchange area is 0.5 m².

Vessel material

The solution contains a large amount of dissolved salts. At high temperatures this causes metallic corrosion. To minimise the amount of corrosion, the dissolver vessel will be made of glass lined carbon steel.

8.2.2 The scrubber

The scrubber receives the off gas from the dissolver. Its function is to shift the equilibrium between ammonia and ammonium to the left according to equation 4-6.



In the liquid phase in the scrubber there will be equilibrium between ammonia and ammonium (equation 4-6). In order to shift the equilibrium to the left, hydrochloric acid is added. The acid must be added in the right (stoichiometric) quantity to maintain pH 7.

In order to help the ammonia dissolve the scrubber will be operated at ambient temperature. For the purposes of the calculations this will be taken as 20 °C. The equilibrium concentrations in the liquid and gas phase inside the scrubber are calculated in appendix 8-3, Scrubber calculations.

Liquid Phase

As can be seen from the mass balances (appendix 7-1), the total production of NH₃ is 1.39 kg an hour. Ideally this would all be converted to NH₄⁺ this would mean an ammonium production of 1.47 kg an hour. The concentration inside the scrubber is then 1.64 mol/litre. This concentration is in equilibrium with the ammonia concentration in accordance with equation 4-7. This means that the ammonia concentration is 9.5.10⁻³ mole/litre (pH = 7).

Gas Phase

The Schumpe model (paragraph 4.1.3, equations 4-3 through 4-5) is used to calculate the corresponding gas phase partial pressure of ammonia. The KH for the solution in the scrubber is 49.85, which means that the partial pressure of ammonia in the gas phase is 19 Pa. With the flow of the gas (50 litre/s) it can now easily be calculated that the remaining ammonia mass flow in the off gas will be 0.21 tpa.

If the ambient temperature were to be lower than is assumed here, the ammonia solubility would be higher, which means that the scrubber would operate more efficiently than the results according to the calculations above (for instance the remaining ammonia mass flow would be 0.16 tpa at 15 °C).

Mass transfer

To get an idea of the required reactor size it is important to know the mass transfer rate per unit of area. From Ullmann's encyclopaedia [Ullmann's, 2000] an equation was obtained to estimate the mass transfer in scrubbers. When making the estimation the design team took a large safety factor on the side of caution. The mass transfer coefficient is estimated to be 2.03·10⁻⁴ m/s. It is now possible to calculate the mass transfer rate in the scrubber per unit of interfacial area. To do this the mass transfer coefficient must be multiplied with the driving force. Again a large safety factor is taken on the side of caution, the driving force was taken as 0.25 times the inlet concentration minus the equilibrium concentration. This results in:

$$\text{Mass transfer rate} = k_g (0.25 \cdot C_{in} - C_{eq}) = 1.05 \cdot 10^{-5} \frac{\text{kg}}{\text{s} \cdot \text{m}^2} \quad (8-3)$$

If this value is combined with the desired mass transfer rate, being the rate at which ammonia enters the scrubber, the required interfacial area can be calculated. This results in a required area of nearly 40 m².

Scrubber volume

Now the interfacial area is known the reactor volume must be calculated. The gas enters the scrubber in the liquid phase at the bottom of the vessel. The liquid and gas are stirred to create a good mixing effect. This results in gas bubbles within the liquid. At a conservative estimate the gas bubbles are 2 cm in diameter. It now becomes possible to calculate the interfacial area of one bubble and the volume of one bubble ($p = 1 \text{ atm}$). With these two values the volume of gas inside the scrubber can be calculated:

$$V_{\text{gas}} = A_{\text{exchange}} \frac{V_{\text{bubble}}}{A_{\text{bubble}}} = 39.68 \cdot \frac{4.19 \cdot 10^{-6}}{1.26 \cdot 10^{-3}} = 0.13 \text{ m}^3 \quad (8-4)$$

From the gas volume it is easy to calculate the liquid volume through the ratio of gas and liquid entering the scrubber. It transpires that the liquid volume is slightly larger than the gas volume, 0.15 m^3 . This means that the reactor volume must be at least 0.28 m^3 . To be on the safe side the scrubber volume will be designed to be 0.30 m^3 .

The feed, the gas and liquid streams that enter the scrubber can control the gas hold-up. If the gas hold-up is too large, the flux of feed streams will be decreased. The pH controller and level controller in the scrubber will control the gas hold-up. If the gas hold-up in the tank is too high, it is assumed that the level is too high due to a larger volume of gas in the liquid, the water stream will be closed and the pH controller will immediately react and the salt supply will be closed. When the level is decreased the water supply will open and in this way the gas hold-up is regulated.

Pressure drop

The pressure drop is an important characteristic of the scrubber since it determines the pressure of the gas inlet stream. The outlet pressure is the same as in the scrubber, 1 bar. The pressure drop is completely dependant upon the height and density of the liquid above the gas inlet. In this case the fluid is water and the liquid height is a function of the bottom area of the vessel. This means that within reasonable limits the pressure drop can be chosen. When the vessel is chosen to be round, which is favourable for stirring, and the diameter is set at 0.5 meters the pressure drop will be 0.08 bar, which is very reasonable. The required height of the reactor in this case would be 1.53 meters (based on 0.30 m^3). In order to minimise the loss of liquid through entrainment the vessel height should be a bit bigger, it will be designed to be 1.75 meters.

Agitator

To facilitate the conversion the vessel will be stirred to promote mixing. The required stirring power is 2.0 kW/m^3 (Coulson and Richardson, volume 6, table 10.14 [Sinnott, 1999]). This means that the power requirement for the stirrer is 0.6 kW.

For equipment data sheet of the dissolver see Appendix 8-4, Equipment data sheets (Vessels, hopper, EF).

8.2.3 The belt filter

Assuming that a belt with a width of one meter (typically) has to filter the slurry with a pressure drop of $6.0 \cdot 10^4$ Pa, the length of the belt and the belt velocity can be designed using Darcy's law for viscous flow, equation 8-5 [Scarlett, 1997]. Darcy's law expresses the linear relationship between the superficial velocity of the filtrate and the overall pressure drop, which gives us insight in the bed permeability, if the viscosity of the fluid is known. Subsequently, Ruth's equation is a parabolic relationship following from Darcy's law that describes the residence time as a function of the filtrated volume at a constant pressure drop.

$$u = \frac{1}{\eta} \cdot k \nabla p \quad (8-5)$$

where

u = superficial velocity

η = viscosity of the filtrate

k = permeability of the bed

∇p = macroscopic pressure gradient

Belt velocity

In chapter 7, Mass and Heat balances, the amount of slurry entering the filtration step was calculated, namely 97.7 kg/h. In order to process the calculated amount of salt slurry the belt velocity can be calculated with equation 8-6.

$$\text{belt velocity} = \frac{\text{flow}}{\text{belt width} \cdot \text{cake thickness}} \quad (8-6)$$

Assuming that a belt with a width of 1 meter and the cake thickness is 0.02 m, the belt velocity can be calculated to be 0.039 m/s. The calculations can be found in appendix 8-7, Filtration calculations.

Filtrate volume per unit area

The filtrate flow to the eutectic freezer <9> was calculated to be 62.1 kg/h. The composition can be found in appendix 5-1. Together with the width and the belt velocity the filtrate volume per unit area can be calculated with equation 8-7.

$$Q = \frac{\Phi_{V_filtrate}}{\text{belt width} \cdot \text{belt velocity}} \quad (8-7)$$

Bed permeability

Darcy's law can be rewritten in terms of mean pore size and is then called the Kozeny-Carman equation [Scarlett, 1997]. The mean pore size can be calculated from the mean particle size using the bed porosity with equation 8-8.

$$\bar{m} = \bar{l} \frac{\varepsilon}{1 - \varepsilon} \quad (8-8)$$

The Kozeny-Carmen equation in terms of the mean pore size is given in equation 8-9.

$$\frac{u}{\varepsilon} = \frac{1}{16C} \bar{m}^2 \frac{1}{\eta} \nabla P \quad (8-9)$$

Specific cake resistance

For cake filtration with constant pressure drop Darcy's law can be derived from mass balances which describe the cake thickness in terms of porosity [Scarlett, 1997]. Darcy's law then becomes as in equation 8-10.

$$u = \frac{1}{\alpha(1 - \varepsilon)\rho_s} \frac{1}{\eta} \nabla P \quad (8-10)$$

In equation 8-10 the α is the specific cake resistance which can be calculated with equation 8-11.

$$\alpha = \frac{1}{k(1 - \varepsilon)\rho_s} \quad (8-11)$$

Residence time

The Ruth equation, equation 8-12, follows from the mass balance of mass of solids per unit area. With this equation the residence time can be calculated.

$$\frac{\eta f \alpha}{\Delta P} \frac{Q^2}{2} + \frac{\eta R}{\Delta P} Q = t_{\text{residence}} \quad (8-12)$$

The filter resistance R is assumed to be 10% of the specific cake resistance. The f value in formula 8-12 represents the ratio of m over Q , where m is the mass of solids per unit area.

$$f = \frac{\rho_l}{\frac{1-S_s}{S_s} - \frac{1-S_c}{S_c}} \quad (8-13)$$

Bed length

The residence time of the particles on the belt filter and the belt velocity, that was determined from the slurry flow, make it possible to determine the bed length by multiplying these values. This results in a bed length of 8.29 m for the filtration step.

The length of the washing section was calculated in the same way as filtration (but with viscosity of water and a flow of wash water), assuming that washing is comparable with respect to the cake properties (see appendix 8-8). The result is a smaller belt velocity calculated for washing than for filtration, which gives an idea about the rate limitation of the washing step, when the design criteria (Paragraph 5.1.3) are taken into consideration. The belt velocity for filtration was adjusted with the rate limiting belt velocity for washing to be able to use the same belt for both processes. This resulted in a bed length of 5.48 m for the subsequent washing step. The total bed length of the belt filter is therefore 13.77 m.

8.2.4 The eutectic freezer

The eutectic freezer is a relatively new type of equipment that is not applied commercially yet [E. Genceli, 2004]. It's basically a crystalliser vessel with several cooling disks inside, on which the ice and salt crystals are formed, due to crystallisation at the eutectic point. These crystals are scraped of the disks by rotating wipers and can move freely through the crystallisation column due to orifices in the cooling disks. The low-density ice crystals float to the top of the vessel and the high-density salt crystals sink to the bottom, where both are removed from the column. Fresh feed enters the crystalliser in the middle. A schematic overview is given in figure 8.1a. A picture of the apparatus at the API building is given in figure 8.1b.

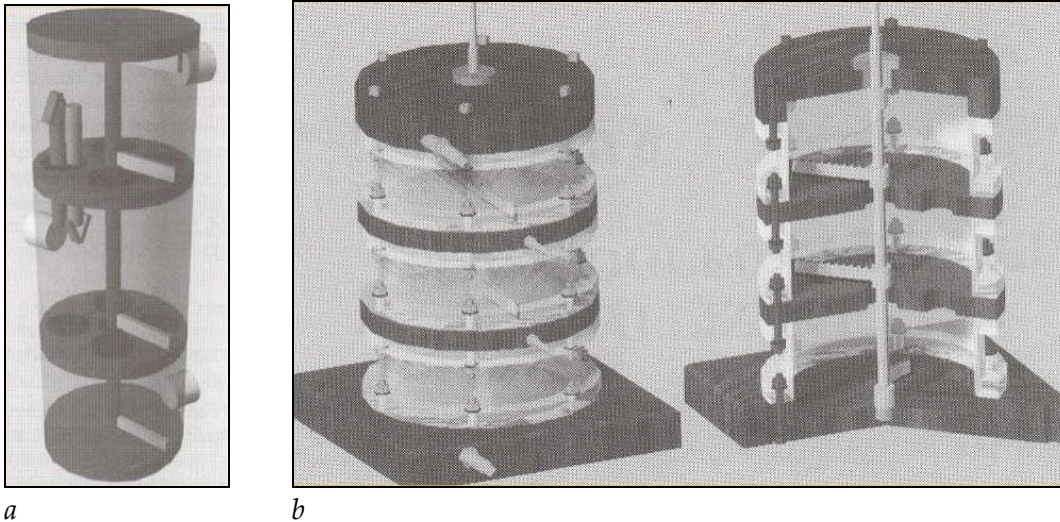


Figure 8.1: Schematic representation of the eutectic freezer column (a) and the apparatus at the API building (b)

The design of the eutectic freezer focuses on three criteria, namely:

- Quality of the ice crystals (purity, shape, size, distribution)
- Quality of the salt crystals (purity, shape, size, distribution)
- Throughput of the apparatus

The quality of the ice crystals is not the primary objective in this case. It is not desired to produce purified water. The water is used for washing of the metal oxides stream and is allowed to contain some amount of salts, namely 2.0 w% (paragraph 7.5), because the metal oxides are allowed to contain a small amount of salts. Also no particular shape or size distribution of the ice crystals is preferred.

The quality of the salt crystals is also not restricted to stringent boundary conditions in this design. The salt crystals that are being produced are a mixture of all present salts in solution, and therefore the purity is not an issue. Since the salt is used for the prevention of ice formation on the roads, it is assumed there are no restrictions to its shape and size distribution.

The capacity of the apparatus has a certain minimal value. It has to be large enough to process the solution that comes from the upstream units. This means that it has to be large enough to process a stream of 500 t/a (See Appendix 7-1).

To accomplish satisfactory operation the 11 design parameters [F. van der Ham, 1999], which are listed below, have to be evaluated.

1. Height/diameter ratio of the vessel
2. Cooling surface
3. Type and construction material used for the disk wiper
4. Construction material for the cooling disk
5. Wiping frequency
6. Agitation supplied inside the column disk (related to wiper rotation speed)
7. Fraction void orifice space present in disk
8. Type and flow rate of coolant through the disks
9. Temperature of the coolant entering the disks
10. Flow rate of salt and ice outlet flows
11. Average residence time of the process fluid in the crystallizer

These design parameters will be treated point by point. The extended explanation on this design is presented in Appendix 8-9. The results are given below.

Height/diameter ratio

A ratio of 1.4 is used.

Cooling surface

A theoretical cooling surface of 1.56 m² surface is needed. It is assumed that the actual cooling surface is twice the size of the theoretical value, i.e. 3.12 m². See also appendix 8-10.

Type and construction material used for the disk wiper

The disk wipers are made of ultra-high molecular weight polyethylene (UHMPE).

Construction material for the cooling disk

The cooling disk is made of polished stainless steel (AISI 316).

Wiping frequency

A typical value for the wiping frequency is around 80 rpm.

Agitation supplied inside the column (related to wiper rotation speed)

No other stirring mechanisms are applied within the column.

Fraction void orifice space present in disk

Typically about 15% of the disk surface is void.

Type and flow rate of coolant through the disks

As a coolant Freezium (50 w% potassium formate in water) is chosen with a flow rate 900 litre/h through every disk. See appendix 8-15.

Temperature of the coolant entering the disks

It can be calculated that the coolant inlet has a temperature of $-43\text{ }^{\circ}\text{C}$. The calculations on the coolant inlet temperature can be found in Appendix 8-11.

Flow rate of salt and ice outlet flows

The flow rate of the top stream (ice) is 349 t/a and the bottom stream (salt crystals) is 151 tpa (See appendix 5-1 for the exact values and compositions).

Average residence time of the process fluid in the crystallizer

A residence time of two hours is assumed.

All above results, and results that can be derived from these, are presented the equipment data sheet of the eutectic freezer in Appendix 8-4 and Appendix 8-9.

8.2.5 Drying

Two dryers are necessary to dry the product streams. Both dryers work on the same principle; the product stream is put into containers that in turn are put into the dryer, which is basically an oven. Two streams will leave the oven, one dried product stream and a stream of vapour. Since the vapour mostly consists of water it will be released to air. To ensure that all the products are dry the temperature in the oven will be $120\text{ }^{\circ}\text{C}$.

Energy requirement

Since the compositions of the in-going streams are known, the heat requirement is easily calculated (appendix 8-12, drying calculations). For the calculations it is assumed that the product stream is heated to $120\text{ }^{\circ}\text{C}$ and the water is heated to $100\text{ }^{\circ}\text{C}$ and subsequently evaporated, after that the vapour is free to leave the oven and therefore not heated any further. This leads to the following equation for calculating the heat requirement per hour of operation:

$$Q_{req.} = \phi_{mass, prod} \cdot C_{p, mix, prod} \cdot (T_{120} - T_{in}) + \phi_{mass, H_2O} \cdot (C_{p, H_2O} \cdot (T_{100} - T_{in}) + \Delta H_{evap, H_2O}) \quad (8-14)$$

This equation holds for both product streams. Since there is an inevitable loss of heat during the operation of an oven, an efficiency of heating is assumed of 0.5:

$$Q_{operation} = 0.5 \cdot Q_{req.} \quad (8-15)$$

The energy required for the metal oxide product stream is 7.24 kW and the energy requirement for the salt product is 3.59 kW.

8.2.6 Heat exchangers

To help save on the energy costs of the Eutectic freezer, the outgoing ice stream <25> is brought into contact with the ingoing feed <9>. In the heat exchanger (C01) the feed is cooled from 20 °C to 5 °C. It was assumed that this was the maximum amount of heat exchange that was possible since stream <25> is largely comprised of ice crystals and therefore does not easily lend itself to being used in a heat exchanger.

The outgoing stream <23> from the eutectic freezer is assumed to be a sort of slurry of ice crystals and liquid. In the heat exchanger the temperature of stream <23> is rising while the ingoing stream <9> is cooled. The outgoing temperature of stream <23> is assumed to be about 5 °C, just above the temperature for the formation of ice crystals otherwise the heat exchanger can be blocked by these ice crystals.

If the above is assumed then the heat exchanged is 1.17 kW (cooling stream <9> from 20 to 5 °C). This is equal to the energy needed to heat the whole of stream <25> to 0 °C, and to melt 0.112 kg/h of ice. From Coulson and Richardson [Sinnott, 1999] a value was obtained for the overall heat transfer coefficient, which was conservatively estimated at 600 W/(m²K). This leads to a heat exchange area of 0.12 m², which is very small. There may be possibilities to improve on the operation of this heat exchanger, but the design team did not explore these any further.

The feed for the Eutectic freezer <24> should ideally be at 0 °C. In theory the eutectic freezer can be used to cool the feed to its eutectic temperature and then start crystallisation. However the eutectic freezer is not designed to be the most efficient cooling apparatus in the world, its primary use is to ensure a controlled cooling of the feed, so that the crystallisation process is also well controlled. Therefore it is wise to install a further heat exchanger (E02) to cool the feed to 0 °C.

The feed needs to exchange another 0.29 kW in order for the temperature to drop to zero. This is accomplished through use of a cooling agent. Again using Coulson and Richardson [Sinnott, 1999] the overall heat transfer coefficient is determined at 600 W/(m²K). Again the area is calculated, which is 0.05 m². The reason both areas required for heat exchange are so small is that the throughput of the heat exchangers is very small. Were the streams to be larger a higher heat exchange rate would be required and thus a larger area. For the complete calculations on the heat exchangers see appendix 8-13, heat exchanger calculations, for the equipment data sheets see appendix 8-5, Equipment data sheets (heat exchangers and dryers).

8.2.7 *Pumps and compressor*

Several pumps are present in the process flow sheet for gases, liquids and slurries. No complete design was done on the pumps necessary for this process flow scheme. Several points however require attention.

- Pumps (P01) and (P04) must be able to handle a low pH, since they will be pumping a solution of concentrated HCl.
- Pumps (P08) and (P09) must be able to handle a stream that contains solids. This could cause attrition within the pumping mechanism and reduce the pumps time on stream. It might be wise to consider installing a second pump, as a back up.
- Pump (P08) must also be constructed of material, which resists metallic corrosion. The stream it will be pumping is a brine at elevated temperature, which causes corrosion.

Since the compressor is a very essential piece of equipment within the design, it was more thoroughly looked at. The compressor needs to be able to deliver a pressure increase of 0.1 bara. This is by all means a small increase in pressure. The pressure increase is nevertheless essential because otherwise the dissolver off gas would not be scrubbed. The power needed for the said pressure increase is 0.72 kW (when pumping efficiency is assumed at 0.7). The stream going through the compressor needs to be 50 litres per second.

For full specifications of the compressor and an overview of the pumps see also appendix 8-6, Equipment data sheets (Pumps and compressor).

8.2.8 *Vessels and hopper*

The hopper is designed to have a capacity of 15 m³, this is sufficient to store the slag production of 2 months magnesium recycling, at current levels (2003-2004). All vessels ((V06), (V07) and (V08)) in contact with the eutectic freezer were designed to have a residence time of 3 hours. All other vessels ((V02), (V03) and (V05)) were designed to have a residence time of 2 hours. The reason for this difference is that the eutectic freezer is not a proven technology, therefore it is more likely to break down and the extra capacity could be convenient.

8.3 Special issues

8.3.1 *Flexibility of the eutectic freezer*

As assumed earlier, the salt solution <24> enters the eutectic freezer at 25 w%. If, at any time, this concentration is lower than 25 w% it is possible that the eutectic conditions are not met. This means that there is no three-phase equilibrium possible at given concentration and temperature. In that case the eutectic freezer becomes a freeze crystalliser, crystallising only the water, until the eutectic composition, i.e. higher concentration of salts, is reached again. The eutectic freezer is therefore a flexible unit that can cope with fluctuations in feed composition (See also paragraph 13.2, Recommendations).

Another flexibility advantage of the eutectic freezer is that the disks inside the column can be placed/moved at any desired height, creating differently sized compartments. The big advantage of this is that the cooling can be concentrated on the area where it is needed most (near the solution inlet). The compartments that contain the ice (top) and salt (bottom) crystals have less need for cooling and can therefore be bigger. The exact position depends on the performance of the column and can be optimised during time on stream.

8.3.2 *Seeding of the eutectic freezer*

If it should be the case that the salt crystals that are formed in the eutectic freezer are too small, i.e. either the settling behaviour is not adequate or the crystals carry too much solution when tapped at the bottom (see the section on coolant temperature in paragraph 8.2.4), the eutectic freezer can be seeded. By adding salt crystals to the column nucleation can be prevented and crystal growth on already existing particles can be stimulated. In this case larger salt crystals are formed.

8.3.3 *Disk design of the eutectic freezer*

The disk-shaped cooling elements have flat horizontal cooling surfaces on top and bottom sides. The plates are constructed of stainless steel (SS316). A picture of one of these cooling elements with three wipers is given in figure 8.2.

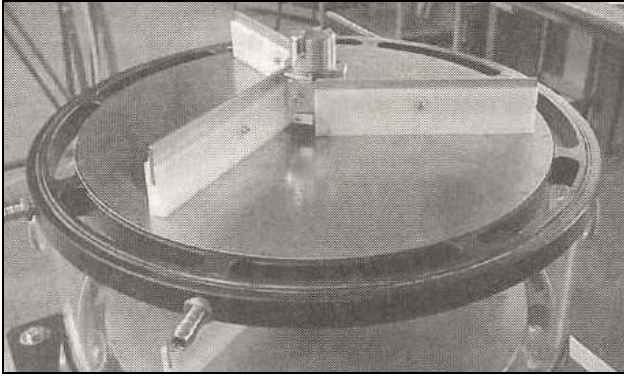


Figure 8.2: Picture of a cooling disk with three wipers

The orifices that provide the void space for the crystals to travel to higher or lower compartments are located on the outside of the disk and occupy typically about 15% of the total disk surface.

An even distribution of coolant flow through every part of the disk is obtained with a labyrinth-like path for the coolant, which is schematically shown in figure 8.3.

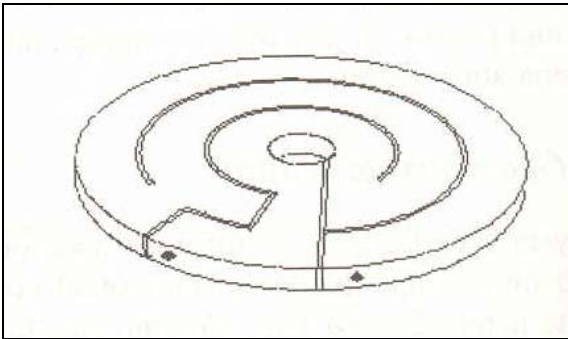


Figure 8.3: Coolant flow through the disk

Currently researchers at API are optimising the design of the disk. But very good results have already been obtained with the present model. The dimensions that are required in this column design are given in the data equipment sheet for the eutectic freezer (Appendix 8-4). A disk is typically 5 cm high and is bound to a maximum outer diameter of 2 m for manufacturing reasons [Vaessen, 2003].

9 Wastes

This chapter deals with the waste streams that are caused by operation of the process. As can be seen from the process flow sheet in figure 5.1 the main waste stream is the gaseous waste. However there is of course the possibility of some spillages, which will be dealt with in the chapter 10 on process safety.

9.1 Gaseous waste stream

The gaseous waste streams contain mainly hydrogen, which is formed in the reaction section of the slag treatment process (See paragraph 4.1, equation 4-1). The other possible component of this stream is ammonia, which is also formed in the reaction section (equation 4-2). To ensure that the ammonia is not released to the air the off gas of the reaction section is scrubbed. However, because not all equipment can be sealed of from the environment and the ammonia is dissolved in water, and therefore in equilibrium with ammonia in air, some part of the ammonia will be released to the atmosphere. This will occur in several parts of the process, mainly in the scrubber (V01), but also from the drying units (D01) and (D02), the reaction vessel (V04), belt filter (BF01) and collection vessels (V07) and (V08) releases will inevitably occur. (Furthermore, in the upstream process of crushing and sieving the slag ammonia will also be released in a certain unknown amount).

It is assumed that the main release of ammonia is present in the gas purge stream <8>. From solubility calculations (see appendix 8-2 and 8-3) and mass balance calculations (see appendix 7-1) it can be derived that this release is 0.2 ton per annum. Ignoring the unknown releases from the units mentioned above, the rest of the ammonia will leave the process as ammonium salts in stream <18>. The other chemical component that is present is hydrogen that is formed in the dissolver (V04). Within the process there is no use for this hydrogen, neither as a chemical reactant nor as feedstock for combustion. See also chapter 10 on process safety.

After being treated by the scrubber the gas purge <8> contains mainly air. The composition of this stream is given in table 9.1.

Table 9.1: Gaseous waste stream from the slag treatment process

Component	Fraction (w-%)	Amount (t/a)
NH ₃	0.012	0.21
H ₂	0.077	1.40
Air	99.911	1820

As stated above it is assumed that the exhaust gas streams <14> and <17> from respectively the metal oxides drier and the salt drier contain only water (See Appendix 7-1 on mass balances). However, it is strongly recommended (see Recommendations paragraph 13.2) that further research is performed about these emissions and the prevention of ammonia emissions in the above mentioned equipment.

9.1.2 Legislation on the gaseous waste stream

Ammonia exhaust is a big issue in Dutch and European legislation, due to the severe environmental impact and the stench. Legislation has become more stringent in the past years, and will become even more stringent. The emission ceiling for ammonia in 2010 is 128 kton. The emission target is at 100 kton in 2010, of which 9 kton is reserved for the industrial sector (and 86 kton for the agricultural sector and 5 kton for the transport sector), which is a reduction of about 20% of the total emissions in the Netherlands in 2000 [VROM, 2004].

Off course, given the fact that the amount of ammonia within the process can not be ignored, an environmental permit has to be applied for. However, compared to other industries, the total release is small.

10 Process Safety

The recycling of magnesium is not a process that is without risk. In this design the design team looked for a process that reduced the safety risks towards the operating personnel as much as possible. To quantify those risks, two important tools were used, the Hazard and Operability study (HAZOP) and the Fire and Explosion Index (FEI) assessment. Knowing the different hazards and risks of the process helps to design a safe process and probably a better understanding of the different process steps that were chosen.

In figure 10.1 a rough plan is sketched of the plant as it is currently in use. Remag is planning to install the crushing and sieving installation to the left of the slag storage. In this design the aim is to install the dissolving reactor on the right side of the slag storage, far away from the work floor, which must be kept free of water, since the molten magnesium reacts violently with water. With this in mind, a HAZOP study is done for the most critical piece of equipment.

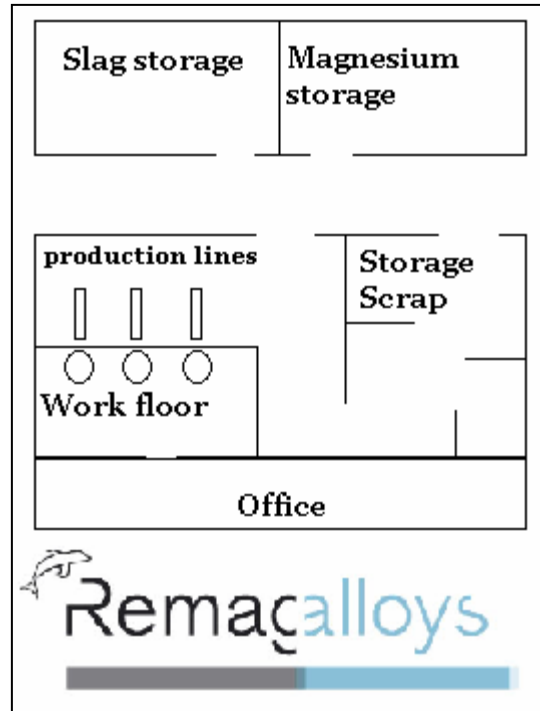


Figure 10.1: Plan of Remag, Delfzijl

10.1 Hazop analysis

The Hazard and Operability study is carried out for the most critical piece of equipment in the conceptual process design. Assumed here is that the dissolving reactor is the most critical step in the process, due to the fact that dissolving the slag involves two highly exothermic reactions. If finely distributed magnesium slag particles are dissolved in water there is a rapid temperature rise and also a release of ammonia gas. It is important to have control over the reaction, so the reactor is cooled. The ammonia is transported with an extractor fan to a scrubber and kept in solution.

A formal operability study is the systematic study of design, using “guide words” to help generate thought about the way deviations from the intended operating conditions can cause hazardous situations. Some guide words are: Intention, Deviation, Causes,

Consequences and Actions. With the help of these guidewords the process was assessed. The results of the assessment can be found in appendix 10-1, Hazop analysis of the process.

Keep in mind that streams <19>, <28> and <29> are back up streams and are only turned on if the quality of the salt solution is different from desired.

The recommendations for process safety from the Hazop analysis are summarized below.

- Low level alarm for the dissolving tank (V04), which controls the valve of the stream number 4.
- Low flow pressure alarm for the dissolving tank (V04), which controls the emission of ammonia
- High temperature alarm for the dissolving tank (V04), which controls the temperature in the reaction and so the rate of reaction
- Non return valve for the compressor (C01), which controls the ammonia emission from the dissolving tank running only in one direction
- Quality control alarm for the eutectic freezer (EF01), which controls the outgoing streams <16> and <25>

The success or failure of the Hazop depends on several factors:

- The completeness and accuracy of drawings and other data used as a basis for the study.
- The technical skills and insights of the team.
- The ability of the team to use the approach as an aid to their imagination in visualizing deviations, causes, and consequences.
- The ability of the team to concentrate on the more serious hazards that are identified.

The start up procedure for the process is not very complex. First vessels (V01), (V02), (V03) and (V04) are filled with water. Next the extractor fan is switched on. The pH control is switched on which will ensure that any ammonia that is formed after the slag stream is opened is scrubbed out of the off gas. Finally the slag stream feed is switched on. After this the rest of the process automatically falls in line.

The shut down procedure is even easier. If something goes wrong stream <1> closes first of all. No reaction will occur anymore. After this streams <7> and <19> are automatically closed, if the flow controllers do their work.

10.2 Dow Fire & Explosion Index

The National Fire Protection Association (NFPA) has developed a system for indicating the health, flammability and reactivity hazards of chemicals. The NFPA hazard diamond is used world wide in labelling containers of chemical substances. The NFPA methodology is also used in the Dow Fire & Explosion Index. The combination of the fire rating (NF) and the reactivity rating (NR), both of which can vary from 0 (no hazard) to 4 (maximum hazard), determines the Material Factor (MF). The Material Factor can vary from 0 to 40, is a measure of the fire and explosion hazard of a given chemical. The Material Factor is determined in appendix 10-2, Determination of the material factor. The hazardous components are metallic magnesium, magnesium oxide, hydrochloric acid (in solution), manganese oxide (in small amount available) and the gasses ammonia and hydrogen. The ratings of magnesium nitride are not available, but when Mg_3N_2 is heated to decomposition, it may emit toxic fumes.

The degree of hazard for the process at Remag, especially for the dissolving step, is judged as hazardous. The calculation made for the Dow Fire & Explosion Index [from Lemkowitz & Pasman, 2002] is filled in for the dissolving tank, as can be seen in appendix 10-3, DOW Fire and Explosion Index. The Dow Fire and Explosion Index is completed for the most hazardous component, this is for the dissolving tank the metallic magnesium. Hydrogen is present and has a larger material factor (21) but the concentration is too small for it to be considered the dominant material. Only for the equipment where hazardous components (in dangerous concentrations) are present a Dow Fire and Explosion index is set up.

The Dow Fire and Explosion Index can be regarded as a worst-case hazardous index, a small change in the applied material factor would result in significant changes of the overall index. The indexes can be seen in appendix 10-3. For the dissolving tank the degree of hazard is severe (Index = 269) and is far more risky than the processes in the mixing vessel (V05) and in the dryer (D01) which were respectively 100 and 124.

Table 10.1: Degree of Hazard, from Chemical Risk Management, 2002

Index Range	Degree of Hazard
1-6	Light
62-96	Moderate
97-127	Intermediate
128-158	Heavy
159-up	Severe

10.3 Explosion limits

The only dangerous gaseous components in the process are ammonia and hydrogen. From literature [gasdetection.com, 2004] the Lower Explosion Limit (LEL) and an Upper Explosion Limit (UEL) were obtained, see table 10.2.

Table 10.2: Lower and Upper Explosion Level

Material	LEL (% per Vol.)	UEL (% per Vol.)	TLV/TWA (ppm)	IDLH (ppm)	Density (Air = 1.0)
Ammonia	15.0	28.0	25	300	0.6
Hydrogen	4.0	75.0	A	A	0.1

LEL	Lower Explosive Limit	IDLH	Immediately Dangerous to Life or Health
UEL	Upper Explosive Limit	Density	< 1.0 = lighter than air and > 1.0 = heavier than air
PPM	Parts Per Million	A	Asphyxiant
TLV/TWA	Threshold Limit Value/Time Weighted Average		

The gaseous waste stream from the slag treatment process contains only 0.02 % by volume ammonia (244 m³ per year) and only 1.07% by volume hydrogen (15.600 m³ per year). The emitted gasses are far below the lower explosion limits so cause no extra hazard.

10.4 Spillage

It is thought by the design team that the possibility of spillage or leakage by one of the process streams should be considered. The possible risks depend of the leakage of the pipes. Dangerous pipes are the lines with hydrochloric acid, streams <7> and <29>, but also lines <2>, <4>, <21>, <9>, <23> and <24>.

The stream of slag particles is actually safe, but if the line is ruptured and the particles come in contact with water, a dangerous situation can occur. The dissolving tank (V04) is the most dangerous piece of equipment. Good and periodic inspection of the tank of possible crack formation or malfunctioning is desirable.

Another point of interest is the inspection of the out going streams <8>, <14>, <15>, <17> and <18>. If the composition of the streams is different it can point out that there is a spillage or leakage by one of the process streams or a malfunctioning of equipment.

11 Finance

11.1 Introduction

The following text is a description of the finance for Remag Alloys, Delfzijl. In this chapter the costs are discussed as they were explained to the design team by Remag [Elzinga,2004]. The opening of Remag Alloys took place in November 2003. The total investments to build the plant including the office facility are about 6.0 M€. At the moment of writing the plant has only been running for 7 months, so it is hard to say something concrete about its finance. The direct costs can roughly be determined. Variable process costs however are not easy to determine. We think that even Remag has problems to calculate these costs.

The fixed capital is the total cost of the plant ready for start-up. With the information from the board of Remag it is said that the fixed capital cost is about 6.0 M€. The process at Remag is a batch process containing per batch roughly 2200 kg of scrap with 50 kg flux, the salt Emgesal, to produce roughly 2000 kg of magnesium and 150 kg of slag per batch.

The costs of the raw material are not constant but the mean price is for the type I scrap, € 1.40 per kg, for the salt Emgesal € 0.90 per kg and for the argon gas € 0.70 per m³. The argon gas is used to loosen the slag at the bottom of the crucible. The slag floats to the top of the crucible and can be easily skimmed off from the magnesium batch.

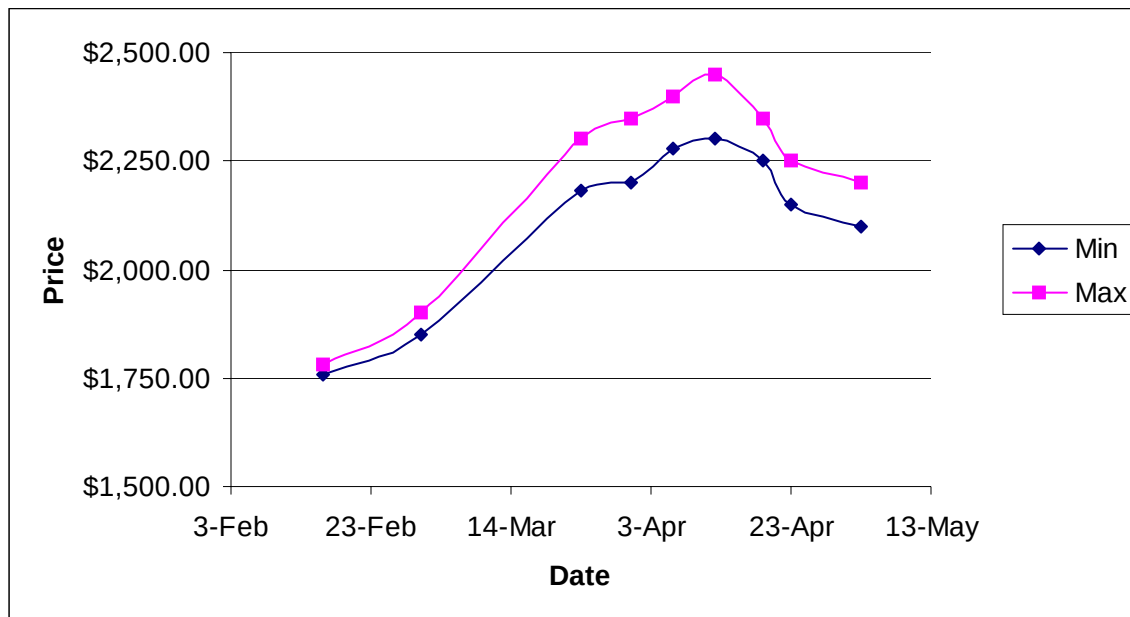


Figure 11.1: 99.8% Pure magnesium price on the Chinese market in \$/mt [magnesium.com,2004]

Remag is aiming for a production of about 10,000 tons of magnesium alloys per year for 2005, but is currently producing around a capacity of 5,000 tons per year. The magnesium ingots are 8 to 12 kg in weight and are sold in bundles from 700 to 1000 kg. The price of magnesium is strongly fluctuating due to the variation supply on the Chinese market [magnesium.com, 2004]. With about 25% of the total world production China is the largest magnesium producing country in the world. Figure 11.1 represents the price of 99.8% pure magnesium on the Chinese market in\$/metric ton over the period of February through May in 2004.

The current price of magnesium is about \$2.10 - \$2.20 per kilogram. With information from the board of Remag, we may consider the market price in Europe to be about 2.25 €/kg for the magnesium ingots produced at Remag, we may assume that the gross returns on the selling of magnesium for the aimed production for 2003 is around 11.25 M€/a. The costs are determined below (paragraph 11.2 through 11.4).

11.2 Equipment

The plant was designed to incorporate three production lines. In the near future, probably already in June 2004, the third line will be put into use. There are now two production lines working including two induction ovens to heat up the two crucibles, two vessels to temporarily store the magnesium product and two production bands, to produce the magnesium ingots. The total investment cost of one production line is about 1.0 M€.

Table 11.1: Assumption total investment costs

Equipment costs	Million €
Production lines	3.0
Office facility	2.4
Deposit and storage	0.6
Total	6.0

The cost of one crucible is about 20 k€ and has only a lifetime of 6 months, due to the high temperatures and the accompanying metal fatigue. These extra costs are taken with the plant overhead costs, which are determined as 50% of the operating labour. The total costs for the second hand crushing and sieving Remag is planning to install in 2004 is about 250 k€ which is seen as an extra investment in 2004.

The new equipment as can be seen in the process flow sheet in figure 5.1 is calculated in appendix 11-1, New equipment costs in 2005, and appendix 11-2, Cost factors for major equipment. The costs are determined over the major equipment and are the bare module

costs, also known as the PCE. The costs determined in mid 1998 and 2003 are in US dollars, so with a exchange rate to euros (times 0.83) and an assumed inflation factor of 4% the prices for 2005 can be determined. The total new equipment cost for 2005 are 116.9 k€

The total physical plant costs (PPC) and the fixed capita for the new equipment are calculated in appendix 11-2 with specific cost factors and formula. With this the fixed capital for the new equipment can be calculated, see table 11.2. Since the new equipment is installed in the already existing building for the storage of the slag, no new building has to be built or money has to be invested for site preparation.

Table 11.2: Total new equipment costs 2005

Item	k€
Total new equipment cost (PCE)	115.9
Total physical plant costs (PPC)	278.2
Fixed capital new equipment	403.3

11.3 Operating costs

The operating costs can be divided into direct and indirect costs. The direct costs can be further split into the fixed costs and variable operating costs. The maintenance costs is determined as 10% of the total fixed capital (i.e. 600 k€). The variable operating costs are calculated according to Coulson & Richardson's [Sinnott, 1999].

Current assumptions for the total processing of scrap per year are about 5200 tons, with a total cost of 7.9 M€. Further assumptions for the total flux used to be about 125 ton and 7100 m³ of Argon gas used with a total costs of respectively € 112,500.- and € 5000.-

Table 11.3: Variable operating costs

Variable costs	Price per unit (€)	Unit per year 2003	Total costs (k€/a)	Total costs (€/ton product)
Raw material				
Argon gas (m ³)	€ 0.70	7100	4.97	0.99
Salt Emgesal (ton)	€ 0.90	125	112.50	22.50
Scrap type I (ton)	€ 1.40	5214	7,299.60	1,459.92
Miscellaneous materials	10% of the Maintenance		60.00	12.00
Utilities				
Electricity (kWh)	€ 0.08	5214000	417.12	83.42
Shipping and packaging	5% of the Maintenance		30.00	6.00
			7,924.19	1,584.84

In table 11.3 the variable operating costs are determined for 2005, when Remag is planning to double the production to 11.000 ton of magnesium.

The fixed operating costs can also be determined with Coulson & Richardson [Sinnott, 1999]. The operating labour is assumed for the current situation at Remag having 4 shifts of 7 people working. The personnel costs are divided into the costs for the office personnel and the personnel at the work floor. There are in total 4 people working in the office at Remag, 40 hours a week.

At Remag the magnesium production process is becoming a 24 hours job for 7 days a week. Remag expects in mid 2004 to process every day of the week containing 5 shifts of 7 people working 8 hours a day. Nowadays due to the start up problems of the factory sometimes one crucible is down or there is no work in the weekends. Currently they have only 4 shifts circulating for 24 hours a day. In appendix 11-4 the personnel cost are estimated for 2003 and 2005, when Remag is planning to double the production and more people are needed on the work floor.

The total assumption for the personnel costs in 2003 is 742,1 k€. With this information we can calculate the fixed operating costs in table 11.4. In appendix 11-5 the total costs for 2005 are calculated and compared with those in 2003.

Table 11.4: Fixed operating costs

Fixed costs	For 2003	Total costs (k€/a)	Total costs (€/ton product)
Maintenance	10% of the fixed capital	600.00	120.00
Operating labour	calculated in appendix 11-4	742.12	148.42
Laboratory costs	20% of the operating labour	148.42	29.68
Supervision	20% of the operating labour	148.42	29.68
Plant overhead	50% of the operating labour	371.06	74.21
Capital charges	15% of the fixed capital	900.00	180.00
Insurance	1% of the fixed capital	60.00	12.00
Local taxes	2% of the fixed capital	120.00	24.00
Royalties	1% of the fixed capital	60.00	12.00
		3,150.0	630.0

The total operating costs per annum can now be calculated, when adding up the variable costs and the fixed costs.

Table 11.5: Total production costs for 2003 and 2005

	Total costs (k€/a)	Total costs (€/ton product)	Total costs (k€/a)	Total costs (€/ton product)
	2003		2005	
Total production costs	11,074.2	2,214.8	19,193.1	1,919.3

In the near future Remag plans to transport the smallest slag fraction to a waste disposal plant for € 150 per ton. The total costs for this way of disposing of the waste stream will be about 45.8 k€ per year (305 ton of slag) for 2004 and for the future, something like 91.5 k€ per year (610 ton of slag). In this design the design team doesn't think that transporting the slag to the waste disposal is a good and sustainable solution. Processing the slag, as described in our report, and selling the products is a more sustainable solution.

11.4 Income

Remag can sell the magnesium for about 2,25 €/kg. They produce ingots weighing 8 to 12 kg, which are sold in bundles from 700 to 1000 kg. The price for a bundle is about €1575.- to €2250.- selling most back to the automotive industry. The net cash flow is calculated in table 11.6.

Table 11.6: Net cash flow for 2003 and 2005

	in 2003		in 2005	
	k€	€/ton product	k€	€/ton product
Total income	11,250	2,250	22,500	2,250
Total operating costs	11,074	2,215	19,193	1,919
Net cash flow	176	35	3,307	331

This profit is calculated with the expected amount of 5,000 ton of magnesium production in 2003. Since the plant is in its start-up phase it is doubtful if this amount is feasible. Remag is planning to double the production to 10,000 ton of magnesium already in 2005. The plant is build for this capacity.

The income of selling the waste products formed with the crushing and sieving process and the dissolving process is also taken into account. Currently Remag cannot give any information about the slag fractions for the desulphurisation and it is further no market is found yet for the oxides formed at the dissolving process. To give an example for the assumed extra incomes generated by the dissolving process, we assume the price of de-icing salt about € 0,20 per kg, with an production of 290 tpa in 2005 of salt, this gives an extra income of about 58 k€.

11.5 Discounted cash flow

To calculate the discounted cash flow rate of return (DCFRR), it is assumed that the present worth of the future earnings is sensitive to the interest rate. By calculating the NPW (net present worth) for the various interest rates, it is possible to find an interest rate at which the cumulative net present worth at the end of the project is zero. This is a measure of the maximum rate that the project could pay and still break even by the end of the project.

$$\text{DCFRR} = \sum_{n=1}^{n=t} \frac{\text{NFW}}{(1+r')^n} = 0 \quad (11-1)$$

With NFW is the future worth of the net cash flow in year n.

The DCFRR is found by the trial and error method, to find the discount rate that just pays off the project investment and still break even by the end of the project life.

The following assumptions were made to calculate the DCFRR. The total investments costs are 6 M€. The construction time of the plant is 2 years starting in 2001, so the investments made are divided over 2 years. The DCFRR is determined twice, one without investments done for the dissolving process and one with investments in 2005 for the dissolving process. The net cash flow before tax is 176 k€ per year in 2003 starting when the construction time is over until 2005 and then the net cash flow is 3,307 k€ until 2015.

The discounted cash flow is a percentage times the net cash flow and the interest percentage is 8%. With these assumptions the net cash flow table can be compiled. It is given in appendix 11-6 for a period of 15 years without the new investment of the dissolving process and one with the dissolving process. The undiscounted earnings would be with the investments for the crushing and sieving installation and the dissolving process is about 30.08 M€ in 15 years and the discounted earnings would be 12.60 M€.

With this we can calculate the discounted cash flow rate of return (DCFRR). We determine the interest rate at which the discounted earnings equal the total investments. The time is set to 15 years. The trail-and error method is used to determine the “correct” interest rate. We find a very high interest rate of 26,07% (normal interest rate is about 8%), this is due to the very high net cash flow from 2005 till 2015. The results are presented in table 11.7.

Table 11.7: Discounted cash flow rate of return

Years	Discounted percentage	Investment	Discounted cash flow	Cumulative discounted CF
2001	1.00	-€ 3,000,000		-€ 3,000,000
2002	0.79	-€ 2,379,630		-€ 5,379,630
2003	0.63		€ 110,736	-€ 5,268,894
2004	0.50	-€ 250,000	€ 87,837	-€ 5,431,057
2005	0.40	-€ 403,333.00	€ 1,309,143	-€ 4,525,247
2006	0.31		€ 1,038,426	-€ 3,486,821
2007	0.25		€ 823,690	-€ 2,663,132
2008	0.20		€ 653,359	-€ 2,009,772
2009	0.16		€ 518,251	-€ 1,491,521
2010	0.12		€ 411,082	-€ 1,080,439
2011	0.10		€ 326,074	-€ 754,365
2012	0.08		€ 258,645	-€ 495,720
2013	0.06		€ 205,160	-€ 290,559
2014	0.05		€ 162,735	-€ 127,824
2015	0.04		€ 129,083	€ 1,259
Total		€ 6,032,963	€ 6,034,222	€ 1,259

Still there is a little difference between the total investments and the total discounted cash flow, but that's negligible. The results can be made visible in a graph seen in appendix11-7. The break-even point (line which crosses the x-as) and the maximum investment (minimum of the curve) are clearly visible.

To calculate the Rate of Return (ROR), which is the ratio of annual profit to investment, the economical lifetime of the plant is assumed to be 15 years. The ROR is a simple index of the performance of the money invested; it is complicated by the fact that the annual profit (net cash flow) will not be constant over the life of the project and the original investment.

$$\text{Rate of Return} = \frac{\text{Cumulative net cash flow at end of project}}{\text{Life of project} \cdot \text{Original investment}} \cdot 100\% \quad (11-2)$$

Usually the ROR is estimated over one year, but since Remag is doubling the production in 2005, the net cash flow is changing so much that the estimation of the ROR over 1 year is not very representative. With this in mind the Rate of Return determined with a cumulative net cash flow of about 19.0 M€, the project life of 15 years and a original investment of 6.65 M€, the ROR becomes 20.4%.

The pay-back time is as the annual savings are constant:

$$\text{Pay-back time} = \frac{100}{\text{Rate of Return}} = 4.9 \text{ years} \quad (11-3)$$

These calculations are for the plant in total, if it is assumed that Remag installs the crushing and sieving installation in 2004 and the dissolving process in 2005, it is interesting to know when these specific investments costs are earned back. For this it a lot of assumptions have to be made.

Assumed is that Remag is producing 700 ton of slag per year in 2005. Remag can decide to do nothing with the slag and transport the slag to the waste disposal for 150 € per ton. If Remag decides to process the slag, 69 ton of slag per year is transported towards the desulphurisation process (profit/costs yet unknown) and 21.8 ton of the slag, mostly magnesium, is fed back to the crucible. Resulting in 609 ton per year for further processing. In the dissolving process 129 ton per year washing water and 130 ton per year of hydrochloric acid is needed to further process the remaining slag, resulting in a production of 502 ton per year oxide stream and a 289 ton per year salt stream. Roughly 77 ton per year of water and gas purge is leaving the process. Results can be seen in table 11.8.

Table 11.8: Streams going in and out in 2005

In 2005	Ton per year		Ton per year
Streams going in		Streams going out	
From C&S	609.2	Oxides	502.1
Water	129.0	Salts	289.3
Hydrochloric acid	130.2	Water & Gas purge	77.0
Total:	868.4	Total:	868.4

Further it is assumed that the price for process water is 0.08 € per m³ [Grievink, Luteijn, Swinkels, 2003] and for hydrochloric acid 0.19 € per kg [icheme.org, 2004]. The price of de-icing salt is about 0,20 € per kg and for oxides the profit are yet unknown. The utility costs, consist of electricity cost, are determined for the main equipment in the dissolving process. The total electricity needed is about 214. 103 kWh, so the costs are about 17.1 k€, results can be seen in table 11.9.

Table 11.9: Utility costs

Equipment	Type	Duty (kW)
Scrubber (V01)	Stirring	0.60
Dissolver (V04)	Stirring	1.00
Dryer (D01)	Heating	7.24
Dryer (D02)	Heating	3.59
Cooler (E02)	Cooling	0.29
Eutectic Freezer (EF01)	Cooling	14.04
Total		26.76
Yearly cost		214098 kWh
Cost		0.08 €/kWh
Total cost		17.1 k€

Further assumptions are that Remag has two different options. Option 1 is to crush and sieves the slag and transports it to the waste disposal. Option 2 is to crush and sieve and dissolve the remaining slag. Assumed is that no more personnel is needed if the dissolving process is running. The current personnel will be sufficient and that the shipping and packaging costs are negligible. The results can be seen in table 11.10.

Table 11.10: Results for the two different options

	Option 1		Option 2	
	Costs per year	Revenue per year	Costs per year	Revenue per year
From C&S	€ 91,382.64			
Desulphurisation		unknown		unknown
Water			€ 10.32	
Hydrochloric acid			€ 24,803.10	
Oxides				unknown
Salts				€ 57,860.00
Electricity			€ 17,128.00	
Total:	€ 91,382.64	€ 0.00	€ 41,941.42	€ 57,860.00

As can be seen in table 11.10, the costs of option 1 are about 91.4 k€, not taken into account the revenue for the desulphurisation. Option 2 yields a profit of about 15.9 k€, not taking into account the revenue for the desulphurisation and the oxides. If Remag decides to build the dissolving process it also saves the costs for the waste disposal, saving per year about 107 k€.

The calculations of for the total equipment costs as determined are 403 k€ (for a detailed overview see table 11.2 and appendix 11-2). The rate of return for the part of the plant that is designed is calculated with formula 11-2:

$$\text{Rate of Return} = \frac{1.59\text{M}}{15 \cdot 403\text{k}} \cdot 100\% = 26.3\%$$

This means the payback time is:

$$\text{Pay-back time} = \frac{100}{\text{Rate of Return}} = 3.8 \text{ years}$$

11.6 Cost review and reduction

The costs can be reviewed for the current processing at Remag and for the dissolving process in particular. The main costs for the current process is the purchase of scrap for processing. Remag is depended from the purchase price of the supplier of scrap and have to make the best deal. The cost reduction is largely dependent of the best purchase policy. The investment costs are seen as non-adjustable.

The main costs for the dissolving process are the reactor dissolving tank (V04), belt filter (BF01) and the Eutectic freezer (EF01), these are investments costs and have to be done by the company. The small amounts of operating costs are negligible compared to the current process. Uncertainty about the selling of the fractions for desulphurisation and the price of the oxides are left out of consideration, so higher revenues may be possible in the future. If the dissolving process becomes a success, Remag can think of processing more slag from other magnesium recycling companies.

11.7 Sensitivities

To make a good cost analysis, a sensitivity analyses has to be made. Costs factors can change and have effect of the profit and cash flow. The price of magnesium is strongly fluctuating as was mentioned in paragraph 11.1, so a good sensitivity analysis is very much desired. Sensitivity with respect to the operating cost, product prices are determined. The changes in income are analysed with the respect on the cumulative net cash flow, the rate of return value and the pay back time.

Table 11.11: Sensitivity analysis for a decrease and increase of 10% of the process

	10% decrease	10% increase
Cum net cash flow(M€)	20.94	17.13
Rate of Return (%)	22.5	18.4
Pay back time (years)	4.4	5.4

It is clear to see that the economic criteria change in a linear way with changes in the process.

12 Creativity and Group process tools

This chapter describes the methods with which the design team tried to be creative. Besides the application of methods and tools, a lot of attention was paid to good personal relationships among the group members. The daily work took place in a pleasant atmosphere that was achieved with a good organised study room with tea, coffee, filled refrigerator and laptop with printer. Among the team members there was attention for each other's interests, which improved communication and decreased hesitation for bringing up disagreement. This is good, because a negotiable atmosphere to a certain extent is required for being effective as a team.

12.1 Creativity

The decision making process can be controlled by assuming that there are six different levels of thinking. Edward de Bono describes this method in the book "Six thinking hats" [De Bono, 1993]. The aim of the theory is to be able to draw a "map" of all the possible thoughts before you draw any conclusions. This will increase the possible alternatives and will provide a complete overview of these alternatives and subsequently a path can be chosen and the decision will be taken.

De Bono describes in his theory the difference between active and reactive thinking. Most people react on things that happen in daily life, this is called background thinking. Another way of thinking is active thinking, also called conscious thinking. Although you might think that you know what you think and what your opinion is, when you deliberately try to sketch all the possibilities you might think in another way and change your decision.

The design team decided to use the method of the six thinking hats because it is an easy way to structure thoughts and it gives insight and overview. Perhaps, through using this method, progress was made in the way of thinking, and as a result insights and ideas were had that had otherwise never occurred.

The theory of the six thinking hats was used in creativity sessions. The theory is based on the principle that people can control their thoughts and decisions by categorizing them in six main ways. De Bono visualizes these categories with hats of different colours. Visualization helps to be aware of the use of a certain category of thinking; this jargon is also an easy way to communicate about this theory with others. The six categories with their corresponding colours are:

- | | |
|-------------------------------------|------------|
| 1. Thinking in facts or numbers | White hat |
| 2. Thinking in emotions | Red hat |
| 3. Thinking in a positive way | Yellow hat |
| 4. Thinking in a negative way | Black hat |
| 5. Thinking in a creative way | Green hat |
| 6. Thinking in a controlling manner | Blue hat |

These six thinking hats are explained more in depth in Appendix 12-1.

As students from the Delft University of Technology, the design team is mainly educated in analytical thinking. It is sometimes hard to consider more aspects of a problem instead of immediately trying to find solutions for a problem. Sometimes it is more useful and more creative to take a look in other directions that seem to have nothing to do with the actual problem, but could at a certain point give more insight into the possibilities and in that way could initiate new ideas.

In the group the principle “drawing” was also taken more literally by trying to sketch the block diagrams at an early stage and categorizing the brainstorm sessions on big flip-over paper and hanging them next to each other on the wall. This gave an easy way to review the previous creativity sessions and helped to structure the thoughts. This wallpaper remained during the design, which inspired the design team to keep up the good work near the end of the project, when the activities became more fixed on the technological aspects.

Apart from the six thinking hats theory, which was an excellent method to make the thinking process more efficient, also a few creativity tools were used to be able to generate thoughts. The tools that helped to generate thoughts were amongst others brain writing, brainstorming, wishful thinking, check-lists and morphological analysis [Thompson, 1998].

The design team gave high priority to contact and communication with specialists that could give their view on sections of the design. This helped reviewing the total design and gave fresh input to the design team and stimulation for out of the box thinking. Practical examples of this will be given in the third paragraph of this chapter where a more in depth description of the application of the six thinking hats related to the development of the design is given.

12.2 Group Process Tools

There are several group process tools such as tests and methods that can be used on the persons in the group you are working with. We made use of three well-known tests, the

Belbin test [Belbin, 1993], the Thomas-Killman [Thomas and Killmann] conflict mode instrument and the Meyer Briggs type indicator test (MBTI). With these tests the design team got insight in each others characters and in the strengths and weaknesses of the group as a whole. The teams intention was to pay extra attention to the group weaknesses in order to be a more effective design team.

12.2.1 Belbin test

The Belbin test is a role test. The functional role of the test is how each member of a team performs in terms of the specifically technical demands placed upon him. The team members are chosen for functional roles on the basis of their experience and without regard to any personal characteristics or aptitudes that fit them for additional tasks within the team. Also a pattern of characteristic behaviour can be discovered in the way that the different persons play their part in a team. Belbin discovered eight useful types of roles, these are: the chairman, a company worker, the complete finisher, the monitor evaluator, the plant, the resource investigator, the shaper and the team worker. The plant for instance is a person with interest for new ideas and strategies and naturally gives special attention to major issues and looks for possible breaks in approach to the problem with which the group is confronted.

We did this test individually and the results are presented in appendix 12-2.

12.2.2 The Thomas-Killman conflict mode test

The Thomas-Killman conflict mode test is an instrument that describes a person's behaviour in a conflict situation in terms of two dimensions: assertiveness and cooperativeness. These two basic dimensions of behaviour can be used to define the five modes of dealing with the conflicts. The five modes are: competing, collaborating, compromising, avoiding and accommodating. The results of the test are presented in appendix 12-2.

12.2.3 The Meyer Briggs Type Indicator

In order to determine the composition of our group and get a feel for the type of people in our group we decided to do a Meyer Briggs Type Indicator (MBTI) test. This test is used all over the world to assess the different personality types within the group. The test examines a person on four factors: introversion vs. extroversion, sensing vs. intuition, thinking vs. feeling, judging vs. perceiving.

Each member of the design team individually took the test. The results of the test results are given in Appendix 12-2.

12.2.4 *Group Strengths and Weaknesses*

The test results in the appendices point out the following strengths and weaknesses for the group:

Group Strengths:

- All are company workers
- Everyone is collaborating
- All different personality contrasts are represented within the team

Group Weaknesses:

- Not very inclined to be plants
- Not very inclined to be complete finishers
- Not very inclined to be competing

According to these strengths and weaknesses the team paid extra attention to the weaknesses by:

- Applying the six thinking hats in weekly brainstorm sessions in order to improve the plant ability of the team
- Following a strict schedule in order to become complete finishers
- Generation of some competition between the team members by working separately on different process alternatives of the same process step with the agreement to present each other the outcomes of the different alternatives. This way of working generated competition between the team members to a certain extent. Competition has a somewhat negative undertone, nevertheless it could contribute to high performances when in good balance with the other aspects of the Thomas-Killman test such as collaboration, compromising and accommodation.

12.3 Development of a creative plan, the drawing of the map

In this paragraph a brief overview is given of the creative development of the design during the three months preparation time. Not all creative developments could be covered and monitored since this is a continuous process, but it is tried to outline here the most important highlights. A list of contacts performing review can be found in appendix 12-3.

12.3.1 *First period up to the BOD*

In the first few weeks up to the BOD every day brainstorm sessions were held in order to try to “sketch” and define the problem and generating alternatives without having any in depth knowledge or specifications on the current process and materials.

The brainstorm sessions were not only focused on alternatives for slag processing, but a state of out of the box thinking (green hat thinking) was reached by for instance:

- Taking the core business of Remag into account and see if in that area also changes are possible in order to get around the waste problem that Remag has in alternative ways.
- Optimisation/changes of the current process
- Possible destination for the waste stream
- Optimisations for the crucible in the current process
- Focussing on a different market
- Supply of different scrap types
- Scrap pre-treatment in order to minimize waste production in a later stage of the process.
- Considering the problem from industries point of view rather than just from the point of view of Remag.

In the first few weeks this brainstorming was not very structured because of a lack of knowledge about the current process and the properties of the materials and as a result not yet defined problem descriptions and battery limits. This disordered brainstorming was rather an advantage than a disadvantage because creativity could flourish since the team was not influenced by prejudice (yellow hat thinking), although it felt sometimes uncomfortable because a solution within a certain period of time was required. In this stage of the process the most alternatives for process optimisation were generated.

On march 19th at 9:30 pm, the first brainstorm session was held in the presence of the creativity coach Ir. G. Mul. The coach was enthusiastic about the first generated alternatives for the process optimizations and encouraged the team to focus more on separation techniques for the slag processing.

On March 24th one week before the deadline of the BOD the team visited Remag together with the project principal Dr. R. van der Weijden. The design team had prepared a questionnaire for the managing director of Remag in order to get more insight in the process and the materials.

Two days later (March 26th, 9:30 pm) another brainstorm session in the presence of the creativity coach was held and the team decided that with the knowledge that was gained on the current process during the visit at Remag it was logical to focus the process design on slag treatment, nevertheless the design team and the coach took possible process optimizations concerning the consolidator in the current process into account.

The results of the brainstorm sessions of the first period can be found in appendix 2-1 process alternatives.

12.3.2 Period up to the interim report

This period is characterised by the Go/ No Go decision for the separation technique of water and salts.

The way in which the design team decided to choose between eutectic freezing and evaporating as a way of separating water from the salts is a good example of active thinking (see chapter 2, decision making). A matrix was made of the available solutions for solving the problem versus the criteria on which the design team wanted to base the decision (see also table 2.1: Description of factors for comparison of separation techniques). The table was filled in through assigning each cell in the table a value of 0, 1 or 2. This was done independently of the other group members. In this way the design team assessed each solution on all the criteria we feel are important in making a design.

The two techniques turned out to have the almost the same score when all the values of the different criteria were added up. A more in depth discussion and comparison of the different criteria showed that robustness and costs were criteria that were the main reasons for choosing eutectic freezing above evaporation.

In this way the team tried to unravel decision criteria and tried to draw a path based on reasoning with facts and numbers (white hat thinking) a final decision was taken based on a very negative aspect that came out of this reasoning for the evaporator followed by rejection of this technique (black hat thinking).

12.3.3 Period up to the final report

In the last period more insight was gained into the particle distribution and the slag composition because of experiments and analysis that were done (appendix 14-1), that improved the quality of the equipment design and strengthened recommendations.

The last period of the design was characterised as working out the process flow scheme in detail. In this period also alternatives were generated in order to optimise the design and to aim for a simple and clear process flow scheme. In this period for instance simplification within the process flow scheme was made by replacing an advanced multiple stage scrubber that was preceded by a buffer tank together by one stirred tank in which the same scrubbing process could take place (green hat thinking).

12.3.4 *The hats*

When the hats were used successively in different orders it helped for each individual personally and it helped the team members help each other in generating a huge amount of alternative ideas. In the first steps for drawing a map mainly the white, yellow and green hats were used. This is done in order to create all the different paths and not to exclude any possibilities in an early stage. The black hat and the red hat are more useful in the deciding stage, when paths have to be chosen. If for instance the black hat was applied too soon this would have severely limited the paths to a solution, on the other hand if the black hat was applied at too late a stage the design team would have been very inefficient with the available time, because a huge amount of ideas would have been generated but there would not have been enough time to give the most promising ones the attention they deserve. For the final path to choose the criteria were that it must be a realistic path to be a solution to the problem definition (see chapter 1, Introduction) that is economically and practically feasible.

13 Conclusions and Recommendations

Several key conclusions can be drawn from the design as it was reported. The first main objective is to process the slag stream that was produced as a waste product by the magnesium recycling process in an environmentally safe and economically feasible way. In this particular objective the design team is succeeded, although some comments must be made on this, since some parts of the design need further research. The magnesium melting process itself, as it is applied at Remag, was also examined to see if any innovations could be implemented. For this particular objective also conclusions are drawn.

In the second paragraph of this chapter the reader is provided with recommendations for future research and points of focus in both this design and in this area of industry. The recommendations are divided in two sections, namely the ones that are about the magnesium process itself, which was not described extensively in this report, but was looked at during the project, and the ones that concern the slag treatment process.

13.1 Conclusions

The conclusions from the experiments on the magnesium nitrides analyses from the slag are very clear. The consolidator has a negative effect, in terms of magnesium nitride formation. However, this effect can be justified by the fact that the total magnesium yield is increased. If the same yield can be achieved by recycling the stream of the large fraction of crushed slag the choice should be made to remove the consolidator from the process. If this is not possible a consideration should be made between a higher magnesium yield and a lower ammonia content in downstream processing. Cooling the slag in presence of air also facilitates the formation of magnesium nitrides and should therefore be avoided. This can be done by sealing the slag with a hood and creating an argon atmosphere under the hood. A reduction of about 50% of the magnesium nitrides can be achieved in this matter.

One of the strengths of this design is that it produces a minimal amount of waste. Under given assumptions the ammonia emission to the atmosphere is about 0.2 ton per annum. Furthermore 1.4 ton of hydrogen is released, which is diluted in air under the lower explosion limit. No liquid waste streams are produced. However, further research should be performed on the sealing of the equipment to prevent ammonia from escaping the process.

A weakness in the design is that the eutectic freeze crystalliser is not yet commercially applied. Research on this particular type of equipment is in a very advanced state and

very good results have been obtained in a pilot plant scale setup with similar capacity at the process equipment section department of the Delft University of Technology. Therefore it seems promising to perform research on the exact behaviour of the salt solution in this unit.

The safety analysis points out that dissolving the slag is a risky process. The Hazop study indicates that especially the dissolver needs extra attention. The quality control of the different in-going and out-going stream deserve full attention. From the Fire and Explosion Index almost the same results were received. With this extra attention and a good control system, a safer process can be obtained.

From an economical point of view this design is very attractive. Both the fixed and variable costs, respectively k€ 403 and k€ 41.9 per annum, are low compared to the magnesium recycling process. Furthermore, the salt stream is saleable at a price of € 0.20 per kg. The metal oxides stream is also saleable, but no price has been determined. In contrast to dumping of the slag as waste, which would cost € 150 per ton, the by-product streams generate a positive cash flow. This decreases the rate of return on investment of the slag treatment process to roughly 3.8 years.

13.2 Recommendations

13.2.1 Recommendations on the magnesium process

Recycle of the large slag fraction

In paragraph 3.2 is stated that the large slag fraction will be recycled to the crucible. This is the process that will be installed at Remag. After discussion with professor Boin [Boin, 2004] the design team has decided to recommend doing further research at this for the following reason that there is the possibility of pollution of the melt with other metals. The large slag fraction comes from several batches, thus carries several magnesium alloys. In contrast to the aluminium recycling industry, the family of magnesium alloys is rather small. Magnesium alloy has very specific restrictions regarding the presence of alloying metals. A batch can easily be ruined by small amounts of undesired metals.

The use of the consolidator

From the ammonia content analysis (See appendix 14-1) it can be concluded that the consolidator has a negative effect on the magnesium nitride content of the slag, which leads to the formation of ammonia, as is stated in paragraph 4.1, reaction 4-2. If it is possible to recycle the large fraction of the crushed slag (See paragraph 1.2.1 on crushing and sieving of the slag) to the crucible, there seems no need for the consolidator anymore. Off course, an analysis will have to be made to determine the exact yields of the magnesium content this large fraction stream.

If it is not possible to recycle the large slag fraction another evaluation has to be done. In that case, a consideration has to be made between the profit gained by the yield of the consolidator and the loss in extra process costs for the precautions that have to be taken to keep ammonia emissions under control (Especially in the slag crushing and sieving process, vessels (V01) and (V04) and compressor (C01)). These are taken along in this process design, but can maybe be decreased, if the magnesium nitride content in the slag is lowered. However, measures on ammonia will always have to be taken, since the formation of magnesium nitride in the crucible seems inevitable [Boin, 2004].

Research on the usage of other types of salt

Another option for possibilities on process improvement that came up during the project was the use of other types of salt [Boin, 2004]. Although this idea was not elaborated, the design team feels that innovations for the melting process can be found in this direction. Advantages of other, lighter types of salt are that they protect the melt better from oxidation and nitrification, and that they can be skimmed of easier, without the use of argon agitation (See paragraph 3.1 on general information).

13.2.2 Recommendations on the slag treatment process

Slag cooling conditions

After the slag has been removed from the crucible (and either treated by the crucible or not) it has to cool down. From the ammonia content analysis (See paragraph 4.4 on ammonia experiment) it can be concluded that magnesium nitrification takes also place during cooling by air. Changing the conditions under which the slag cools down, by sealing it from air, can easily put an end to this. A patent was found that deals with this kind of problem [US Patent 4.842.255, 1989], however newer solutions might be more suitable.

The basic idea is that the slag is covered with a hood that seals the slag completely from the air. This can be done in many ways, e.g. by rubber strips or liquid seals. In the hood there can be an argon in- and outlet to remove all present air from the sealed compartment. When the slag is cooled down the hood can be removed. Nitrification of the magnesium does not take place at ambient conditions.

This solution is very simple and very cheap and can save roughly 50% of the presence of magnesium nitride in the slag (See paragraph 4.4 on experiments). Therefore it is strongly recommended to implement a similar solution.

Dissolving

It was considered to combine dissolving with filtration in one step. This could be done for example by taking a belt filter on which at the same time two processes take place dissolving of the salts and reaction of the nitrides and magnesium. In this way a minimum amount of water could be used for both dissolving and reaction. The biggest

disadvantage of this method is the formation of gasses during the reaction, what will cause fluidisation in the slag layer on the belt and axial dispersion will make prediction and calculations too difficult to control. Nevertheless this could be an interesting process innovation when there is more knowledge on the slag composition and particle size and distribution. By not combining the dissolving and filtration steps, the process will be better controllable with the current knowledge, what will contribute to the safety of the process.

Eutectic freeze temperature analysis

Before the eutectic freezing process can be implemented more research needs to be done about the behaviour of the salt solution in the eutectic freezer. To begin with, the eutectic temperature of the solution should be known. Further research on a pilot plant scale process should be performed to determine the actual amount of work that is needed for crystallisation.

Combined drying of salt and metal oxides

In the process flow sheet (see figure 5.1) two separate driers (D01) and (D02) are used for the drying of respectively the metal oxides <15> and the salts <18>. It might be possible to lead both streams separately through one (bigger) drying unit. An economical evaluation has to be performed to point out what the investment and process costs are and whether this process improvement is feasible.

Analysis on ammonia emission from process units

As was stated in paragraph 9.1 on the gaseous waste stream, the ammonia emission from other process units than the scrubber (V01) was ignored. In practice this will not be the case; i.e. ammonia fumes will escape from the other equipment. Special care and precautions have to be taken in the design of the equipment to minimise these emissions, since ammonia fumes form both health hazards for employees and environmental damage. A solution to this problem could be found in the sealing of equipment to prevent the emission and/or the installation of extractor fans.

Furthermore, if the ammonia emission from the gas purge <8> appears to be too large, it must be considered to build a wastewater treatment system, with which the ammonia can be removed.

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