

Process Integration and Performance of Chilled Ammonia CO₂ Capture Technology

Post combustion technology in a novel aluminium manufacturing process

Master of Science Thesis in the Master Degree Programme, Sustainable Energy Systems

JESPER ARONSSON
HENRIC BJÖRK

Department of Energy and Environment
Division of Energy Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden, 2011
Report No. T2011-355

REPORT NO. T2011-355

Process Integration and Performance of Chilled Ammonia CO₂ Capture Technology

Post combustion technology in a novel aluminium manufacturing
process

JESPER ARONSSON
HENRIC BJÖRK

Supervisor:
Examiner:

M.Sc. Henrik Jilvero
Prof. Filip Johnsson

Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2011

Process Integration and Performance of Chilled
Ammonia CO₂ Capture Technology
Post combustion technology in a novel aluminium
manufacturing process

JESPER ARONSSON
HENRIC BJÖRK

© JESPER ARONSSON, HENRIC BJÖRK, 2011

Technical report no T2011-355
Department of Energy and Environment
Division of Energy Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Cover:

Schematic of the CAP, showing the CO₂ capture
process in the bottom cycle and the NH₃ scrubbing
process in the top cycle.

Reproservice
Gothenburg, Sweden 2011

Acknowledgements

This work has been performed with the much appreciated support and expertise from our supervisor M.Sc. Henrik Jilvero, who in an admirable way always seemed to have some extra time for our questions. Henrik has more than once saved us from falling helplessly from the winding road of despair called Aspen Plus.

We would also like to thank our supplementary supervisors Associate Professor Klas Andersson and Ph.D. Fredrik Normann for providing additional guidance during project definition and start-up and in the end of our thesis work for commenting on our report and helping us decide which results to present and how to best present them, without using our information overload graphs.

Many thanks also to Professor Filip Johnsson for providing us with this interesting project; we are grateful to have been given the opportunity of working with his team. When on the subject, we also thank the entire team at the Department of Energy and Environment for five inspiring months and we wish all of you the best in your respective work.

Big thanks also to Hydro in general and Gunn-Iren Müller in particular for being very supportive throughout our work, for inviting us to tour their state of the art aluminium manufacturing plant and for being very open with process related information vital for the success of our work. Our collaborating partner in Norway, Tel-Tek, also deserves our gratitude for good cooperation, we consider ourselves fortunate to have worked with them and been a part of this project at such an early stage.

Lastly, we wish all current and forthcoming participants good luck with the continuation of this project and we hope that at least we will live to see the day when CO₂ capture is applied at the Sunndalsøra aluminium manufacturing plant.

Sincerely,
Jesper Aronsson & Henric Björk

Abstract

Global environmental concern with possible near-term political policies to increase cost for greenhouse gas emissions and an inclusion of aluminium production in the European emissions trading system have sparked an interest for CO₂ capture within the aluminium industry.

The aluminium manufacturing process produces large quantities of CO₂ emissions through a non-combustion process, this limits the potential technologies for CO₂ capture to post combustion only. A commercially available post combustion technology utilizes a solvent that is degraded in an oxidising environment, as is the case in aluminium manufacturing. The CO₂ capture technology investigated in this study uses ammonia as solvent. Ammonia is not degraded by oxygen. The process integration of the chilled ammonia process CO₂ capture technology in a novel aluminium manufacturing plant was investigated from a required reboiler duty and available heat from an integration point of view. The process gas leaving the aluminium manufacturing process is characterised by low CO₂ concentration and high flow rates compared to applications such as coal-power plants and sour-gas removal from natural gas. The effects on performance and behaviour of the chilled ammonia process for these low CO₂ concentrations have not been fully established and have therefore been investigated.

The process integration was performed for a case with varying process gas flow rate and CO₂ concentration. Gas properties were obtained from Hydro, the company operating the Sunndalsøra aluminium manufacturing plant studied in this report. To isolate and investigate the effects of varying CO₂ concentration, a case with constant process gas flow rate was also studied. The CO₂ concentration was varied between 4, 7, 10 and 15 vol%. To determine the amount of surplus heat available for process integration, a model of the process gas treatment train was created using the process simulation software Ebsilon Professional. The model consists of the existing process gas treatment train with the addition of two heat extractions for the top and bottom cycle process integration.

The chilled ammonia process was described in two separate models in order to determine the required reboiler duties, one for CO₂ capture in the bottom cycle and another for ammonia recovery in the top cycle. The simulation software Aspen Plus, handling heat and mass transfer, chemical reactions and complex solutions, was used for modelling. All components, except the top and bottom cycle absorbers, were modelled using an equilibrium calculation approach that assumes infinitely fast mass transfer and reaction kinetics in reactors. The absorbers were modelled using a rate-based approach in which also kinetics is considered, creating limiting factors for the speed and performance of the process. The CO₂ capture rate was predetermined to 85% with a maximum ammonia slip of 10 ppmv.

Through simulations it was observed that CO₂ only has a moderate effect on the bottom cycle specific reboiler duty, in kJ/kg CO₂ captured, but that the absolute reboiler duty increases as CO₂ concentration and total CO₂ content increases. The opposite effect was observed for the top cycle; with the absolute reboiler duty remaining relatively unchanged and the specific reboiler duty decreasing with increasing CO₂ concentration. The reboiler temperatures were found to be 111°C for the top cycle and between 194-207°C for the bottom cycle.

Through simulations of the process gas treatment train, it was established that surplus heat is available at temperatures sufficient for integration with the chilled ammonia process. It was found that the total heat demand for the chilled ammonia process could be covered to 50% by process integration for the best case scenario. The highest share of heat demand covered through process integration was achieved for the 4 vol% CO₂ concentration case. The share then decreases with increasing CO₂ concentration to 32% heat demand covered through integration for the 15 vol% case.

The study concluded that increasing the CO₂ concentration not necessarily will be economically favourable. The lower process gas flow rate associated with the higher CO₂ concentration allows for the use of smaller process equipment, lowering investment costs. The lower share of heat demand covered through process integration will however increase operational costs meaning that the most economically feasible CO₂ concentration is a trade-off between investment costs and operational costs.

Keywords: *Process integration, chilled ammonia process, CAP, post combustion, CO₂ capture, CCS, carbon dioxide, aqueous ammonia, aluminium, Aspen Plus, process simulation, rate-based*

Sammanfattning

En växande global miljöhänsyn, förestående politiska styrmedel med målsättningen att höja kostnaderna för utsläpp av växthusgaser samt en inkludering av aluminiumproduktionen i det europeiska handelssystemet för utsläppsrätter har lett till ett ökat intresse för CO₂-infångning från aluminiumindustrin.

Aluminiumproduktion ger upphov till stora mängder CO₂-utsläpp genom en process där ingen förbränning förekommer. Detta begränsar de CO₂-infångningsmetoder som kan användas till de som avskiljer CO₂ efter själva processen. En i dagsläget kommersiell teknologi av denna typ använder ett absorptionsmedel som degraderas i en syrerik miljö, likt den som återfinns i aluminiumproduktion. Den CO₂-infångningsprocess som undersökts i denna avhandling använder ammoniak, som inte degraderas vid kontakt med syre, för att separera CO₂ från processen. Processintegrering av CO₂-infångning med kyld ammoniak som absorptionsmedel, i en innovativ aluminiumproduktionsprocess har undersökts utifrån ett perspektiv där värmebehov och tillgänglig spillvärme betraktats. Processgasen som bildas vid aluminiumproduktion karakteriseras av låg CO₂-koncentration och stort gasflöde jämfört med processer som kolkraftanläggningar och naturgasrening. Hur CO₂-infångningsprocessen med kyld ammoniak uppför sig vid låg CO₂-koncentration är inte helt känt och har därför undersökts.

Processintegreringen har utförts för ett fall där gasflöde och CO₂-koncentration varierats. Processdata har erhållits från Hydro som driver den studerade aluminiumanläggningen i Sunndalsøra. För att kunna isolera och undersöka effekterna av enbart varierande CO₂-koncentration undersöktes ytterligare ett fall där gas flödet behölls konstant. CO₂-koncentrationen varierades mellan 4, 7, 10 och 15 vol%. För att bestämma mängden spillvärme som kan utnyttjas för processintegrering skapades en modell av gasreningsanläggningen i programmet Ebsilon Professional. Modellen består av den befintliga gasreningsanläggningen samt två värmeväxlare för processintegrering av CO₂-infångningsprocessen.

CO₂-infångningsprocessen med kyld ammoniak beskrevs genom två separata modeller för att bestämma det totala värmebehovet. En modell där CO₂-infångning i botten-cykeln beskrevs och en annan modell för att beskriva infångningen av flyktig ammoniak i topp-cykeln. Modellerna skapades i Aspen Plus, ett program som behandlar mass- och värmebalans, kemiska reaktioner och komplexa lösningar för att beskriva processen. Samtliga komponenter utom absorptionskolonnerna i topp- och botten-cykeln modellerades utifrån ett jämviktsantagande där masstransport antas oändligt snabb och med reaktionsjämvikt i kolonnerna. De båda absorptionskolonnerna modellerades utifrån ett hastighetsbaserat antagande där också processens kinetik beaktas. Avskiljningsgraden av CO₂ och de högsta tillåtna ammoniakutsläppen var förutbestämda till 85% respektive 10 ppmv.

Genom simuleringar kunde det fastställas att CO₂-koncentrationen endast har en måttlig påverkan på det specifika värmebehovet i botten-cykeln, angett i kJ/kg infångad CO₂, men att det absoluta värmebehovet ökar med ökande CO₂-koncentration och total mängd CO₂. I topp-cykeln observerades den motsatta effekten, det absoluta värmebehovet förblir relativt oförändrad medan det specifika värmebehovet minskar med ökande CO₂-koncentration. Temperaturnivåerna som behövs för regenerering fastställdes till 111°C för topp-cykeln och mellan 194-207°C för botten-cykeln. Genom simuleringar av gasreningsanläggningen konstaterades att spillvärme finns tillgänglig vid tillräckligt höga temperaturer för processintegrering av CO₂-infångningsprocessen. Vidare fastställdes det att CO₂-infångningsprocessens värmebehov kunde tillgodoses till 50% genom processintegrering av det fall med lägst totalt värmebehov. Den högsta andelen värmebehov som kunde tillgodoses genom processintegrering uppnåddes för en CO₂-koncentration på 4 vol%. Andelen av tillgodosett värmebehov minskar därefter med ökande CO₂-koncentration till 32% för en CO₂-koncentration på 15 vol%.

En av avhandlingens slutsatser var att en ökad CO₂-koncentration inte nödvändigtvis är ekonomiskt fördelaktigt. Det lägre gasflödet förknippat med högre CO₂-koncentration gör det möjligt att använda mindre CO₂-infångningsutrustning vilket ger lägre investeringskostnader. Den lägre andelen av tillgodosett värmebehov genom processintegrering ger dock upphov till ökade driftskostnader. Detta betyder att den CO₂-koncentration som är fördelaktig utifrån ett ekonomiskt perspektiv blir en avvägning mellan investeringskostnad och driftskostnad.

Contents

Acknowledgements.....	i
Abstract.....	iii
Sammanfattning	v
Abbreviations and Symbols	ix
List of Figures	xi
List of Tables	xiii
1. Introduction	1
1.1. Aim and Scope.....	2
2. Hydro Sunndalsøra	3
2.1. Process Gas Treatment	5
3. The Chilled Ammonia Process	7
3.1. CO ₂ Capture Cycle.....	8
3.2. NH ₃ Scrubbing Cycle	10
4. Method	11
4.1. Process Data	11
4.2. Modelling Tools.....	12
4.3. Process Integration.....	13
5. Modelling	15
5.1. Process Gas Treatment Model	15
5.2. CAP CO ₂ Capture Model.....	18
5.2.1. Input Data.....	18
5.2.2. Absorber Modelling.....	19
5.2.3. CO ₂ Capture Cycle.....	20
5.2.4. NH ₃ Scrubbing Cycle	23
5.2.5. Auxiliary Equipment	25
6. Results	27
6.1. CO ₂ Capture Cycle.....	27
6.2. Process Integration of the CAP	34
7. Conclusions	37
8. References	39
Appendix A – CO ₂ Concentration Properties Extrapolation	I
Appendix B – Dimensioning of Packed Columns	III

Abbreviations and Symbols

Abbreviations

CCS	Carbon Capture and Storage
IEA	The International Energy Agency
EU	The European Union
EU ETS	European Union Emissions Trading System
MEA	Monoethanolamine
CAP	The Chilled Ammonia Process
PM	Particulate Matter
VLE	Vapour-Liquid Equilibrium

Symbols

Greek Symbols

Symbol	Meaning	Unit
δ_g	Gas phase film thickness	m
δ_l	Liquid phase film thickness	m

Latin Symbols

C_A	Film concentration of species A	mol/m^3
C_{Ab}	Bulk concentration of species A	mol/m^3
C_{Bb}	Bulk concentration of species B	mol/m^3
ΔH_{Rx}	Heat of reaction	J/kg
$\Delta H_{solution}$	Heat of solution	J/kg
P_A	Film partial pressure of species A	Pa
P_{Ab}	Bulk partial pressure of species A	Pa
Z	Coordinate axis z	-

List of Figures

Figure 1. Schematic overview of a post combustion CO ₂ capture process integrated with an aluminium production process. The treated process gas enters the post combustion process where it is separated and sent for storage.....	1
Figure 2. Cross sectional view of the current generation of cells using the Hall-Héroult process for aluminium production. The product gas mixes fully with the cooling air resulting in a process gas with low CO ₂ concentration (0.9-1 vol%). Source: Hydro	3
Figure 3. Cross sectional view of a HAL Ultra cell with separate collector for product gas, lowering the volumetric flow of total process gas and increasing the CO ₂ concentration up to 4 vol%. Source: Hydro	4
Figure 4. Process gas treatment flow sheet at section 3 of the SU4. The process gas (yellow) is cleaned and scrubbed free from various contaminants throughout the gas treatment train. A heat exchanger supplies the local district heating network with hot water.....	5
Figure 5. Flowchart describing the CAP. CO ₂ is absorbed and stripped in the bottom cycle leaving pure CO ₂ and ammonia contaminated off-gas as the two outgoing streams. Off-gas is treated in the top cycle where ammonia is absorbed, stripped reintroduced to the CO ₂ absorption process. (15).....	7
Figure 6. Bubble point pressures of a 28 wt% ammonia solvent with a temperature of 8°C as a function of the CO ₂ loading for equilibrium simulations. (16)	9
Figure 7. Schematic overview of the aluminium manufacturing process and proposed heat source for process integration of the CAP.	13
Figure 8. Describes the model of the process gas treatment train. Grey boxes marks the different included sections. The green dashed line indicates the presently installed equipment at the existing SU4, section 3	15
Figure 9. Possible heat extraction for process integration of the CAP is modelled by a heat consumer connected to a heat exchanger. Both the bottom and top cycle process integration heat exchangers are modelled accordingly.	16
Figure 10. The dry scrubber is modelled by a selective splitter and a heat extraction block to simulate the ash and alumina separation and temperature drop of the actual process.....	16
Figure 11. A liquid-gas heat exchanger and a heat consumer are used to model the district heating heat exchanger.....	Fel! Bokmärket är inte definierat.
Figure 12. The wet scrubber is modelled in four steps, saturation, heat extraction, SO ₂ removal and excess sea water drainage.	17
Figure 13. Concentration profiles depending on chosen film theory.	19
Figure 14. Illustrative process flowchart describing the CO ₂ capture cycle model.....	20
Figure 15. The packed CO ₂ absorber column is modelled using Aspen RadFrac block.	20
Figure 16. The packed CO ₂ regenerator column is modelled using Aspen RadFrac block.	22
Figure 17. Illustrative process flow chart describing the NH ₃ scrubbing cycle model.....	23
Figure 18. The packed NH ₃ absorber column is modelled using Aspen RadFrac block.	23
Figure 19. The packed NH ₃ regenerator column is modelled using Aspen RadFrac block.	24

Figure 20. Reboiler duty per unit mass of captured CO ₂ shown for different lean stream loadings and grouped by total solvent flow. The data shown is for the 7% CO ₂ Hydro case.....	27
Figure 21. Reboiler duty averaged for different solvent flows, grouped by absorber CO ₂ loading, Hydro case.	28
Figure 22. Reboiler duty averaged for different solvent flows, grouped by absorber CO ₂ loading, constant flow case.	28
Figure 23. Mole fraction ammonia in the stream leaving the bottom cycle regenerator, Hydro case.	29
Figure 24. Ammonia slip from the absorber, Hydro case.....	29
Figure 25. Ammonia slip from the absorber, constant flow case.....	30
Figure 26. Ammonia slip from absorber with respect to lean stream CO ₂ loading, Hydro case.....	30
Figure 27. Top cycle reboiler duty and specific reboiler duty. Specific reboiler duty relates the reboiler duty to the amount of CO ₂ captured in the bottom cycle. Some values are missing due to non-convergent simulations.	31
Figure 28. Heat of evaporation for water in the regenerator related to the reboiler duty. Some values are missing due to non-convergent simulations.	32
Figure 29. Bottom cycle cooling need, Hydro case.	33
Figure 30. Top cycle cooling need, Hydro case. Some values are missing due to non-convergent simulations.	33
Figure 31. The required reboiler duty for different NH ₃ molality. A comparison between results from this study and studies made by Jilvero et al. (30) and Darde et al (16).	34
Figure 32. District heating, low and high temperature heat extraction available for process integration given different CO ₂ concentrations ranging from 4 to 15 vol%.....	35
Figure 33. Top and bottom cycle heat requirements compared to the available heat from process integration.....	35
Figure 34. Extrapolated values for temperatures and flow rates for 10 and 30% CO ₂ concentrations.	I
Figure 35. Describing the general design and layout of a packed column. The diffusion occurs at the phase interface between liquid and vapour in the packed bed. Source: Grén et al. (28)	III
Figure 36. Packed column flow rate correlation presented in a log-log graph. The ordinate (θ) and abscissa (FLV) are flow rate parameters used to determine the vapour flow velocity and subsequently the column diameter. Source: Grén et al. (28)	IV

List of Tables

Table 1. Measured and estimated emission data before gas treatment for a HAL Ultra cell (4).....	5
Table 2. Variables and values that make up the parametric study for the CO ₂ capture process	11
Table 3. The properties for process gas at various CO ₂ concentrations for the Hydro case. Temperature and pressure is 5°C and atmospheric respectively for each case when entering the CO ₂ capture process.....	12
Table 4. The properties for process gas at various CO ₂ concentrations, adjusted to constant flow rate. Temperature and pressure is 5°C and atmospheric respectively for each case when entering the CO ₂ capture process.	12
Table 5. Properties and composition of the process gas leaving the HAL Ultra potline for the 4 vol% CO ₂ concentration case.	15
Table 6. The properties of the process gas entering and exiting the CAP integration heat exchangers. The table presents the results for the 4 vol% CO ₂ concentration case.....	16
Table 7. The properties of the process gas entering the process gas cooler and the properties and composition of the process as leaving the cooler.....	18
Table 8. The properties for process gas at various CO ₂ concentrations leaving the aluminium plant gas treatment train. Temperature and pressure is 5°C and atmospheric respectively for each case.	18
Table 9. Simulation technical design specifications and properties of the CO ₂ absorber and its connecting streams for a 4 vol% CO ₂ concentration case with 6.59 mol NH ₃ /kg H ₂ O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be used as actual design parameters.	21
Table 10. Simulation technical design specifications and properties of the CO ₂ regenerator for a 4 vol% CO ₂ concentration case with 6.59 mol NH ₃ /kg H ₂ O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be used as actual design parameters.	22
Table 11. Simulation technical design specifications and properties of the CO ₂ absorber and its connecting streams for a 4 vol% CO ₂ concentration case with 6.59 mol NH ₃ /kg H ₂ O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be used as actual design parameters.	24
Table 12. Simulation technical design specifications and properties of the NH ₃ regenerator for a 4 vol% CO ₂ concentration case with 6.59 mol NH ₃ /kg H ₂ O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be used as actual design parameters.	25
Table 13. Top and bottom cycle reboiler temperature for different CO ₂ concentrations.	34
Table 14. Additional heat requirements and the share of required heat that is supplied by process integration.....	36
Table 15. Specified and calculated values for the bottom and top cycle absorbers using metal pall ring packing material.	V

1. Introduction

Global environmental concern with possible near-term political policies to increase cost for greenhouse gas emissions have made industrial applications for carbon capture and storage (CCS) interesting. The aluminium manufacturing industry utilizes a highly energy intensive process with direct emissions of CO₂. The international energy agency (IEA) estimates that for every tonne of aluminium produced, 1.52 tonnes of CO₂ is released to the atmosphere (1).

A directive (2) adopted by the European Union (EU) in April 2009 included aluminium production from alumina (primary) and aluminium production from recycled products (secondary) in the European Union Emissions Trading System (EU ETS) for the period 2013-2020 (3). During this period, the aluminium industry will receive a high share of needed allowances without extra cost in order to keep European aluminium production competitive on the global market. For the period following 2020, the emission targets will most likely be more stringent, resulting in higher costs coupled to direct greenhouse gas emissions from aluminium production. The inclusion of direct emissions from the aluminium industry into the EU ETS will with present technology result in higher production costs, giving incentives for investigation of CCS integration into the production process.

Present research about CCS is focused to a few technologies for CO₂ capture. The most prominent technologies are pre combustion, oxy-fuel combustion and post combustion. Post combustion, which is the technology in focus for this project, refers to CO₂ capture downstream of the main process (combustion, industrial manufacturing etc.), illustrated in Figure 1, making it suitable for retrofits at existing installations. In post combustion CO₂ capture technology, CO₂ is captured and separated from the flue gas stream by a solvent in an absorption reactor. The captured CO₂ is then transported to a regeneration reactor where CO₂ is released through heat addition, breaking the bonds formed in the absorber. The solvent is then recirculated back to the absorber for further CO₂ capture.

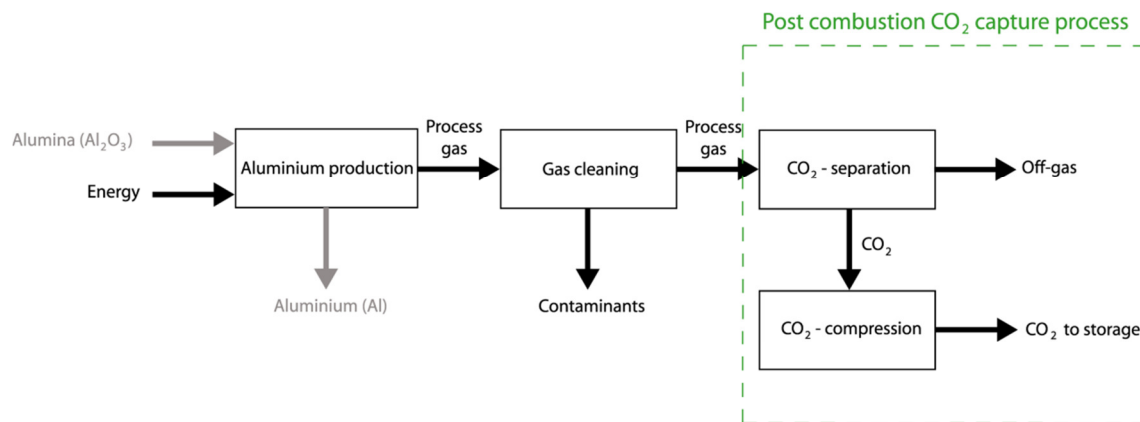


Figure 1. Schematic overview of a post combustion CO₂ capture process integrated with an aluminium production process. The treated process gas enters the post combustion process where it is separated and sent for storage.

There are several solvents suitable for CO₂ capture available, all with various advantages and disadvantages depending on the application considered. Two technologies considered when integrating CO₂ capture with aluminium production are the monoethanolamine process (MEA) and the chilled ammonia process (CAP) (4).

The selective removal of CO₂ at small and medium scale has been a commercial process for many years, for example for producing carbonated gas to be used in beverages. However, when considering CO₂ capture from power plants or other industrial processes, like the aluminium manufacturing process considered here, there are only few large scale commercial examples. (5)

Gas cleaning with MEA has been used in different industries since the 1930's (6), for example removal of acid gases like CO₂ from natural gas streams. MEA is an organic substance used because of its ability to form strong bonds with CO₂. This allows for low partial pressures of CO₂ in the flue gas. That is usually the case in power plants and, even more so, in the low CO₂

concentration aluminium manufacturing process (7). The CAP and MEA systems are rather similar in function and structure; both make use of nitrogen based compounds for absorption; both use an absorber, a stripper and heating and cooling systems. There are however some significant differences. The use of amines for CO₂ capture is a widely known technology. However, there are some inherent properties that make the use of MEA in certain processes unfavourable. Some of these properties are: high energy consumption for regeneration, degradation in an oxidising environment and corrosion of equipment due to salt formation (8).

The flue gas entering the absorber in the MEA process must first be treated in order to remove most of the SO₂ and NO₂. They otherwise react and form heat stable salts with MEA. The heat stable salts are not dissolved in the regenerator, resulting in lower solvent absorption capacity and decreased performance for the process (8). Salts are formed also in the CAP. These salts however, dissolve when heated and further affects the process by increasing the CO₂ absorption capacity of the solvent, decreasing the required solvent flow rate.

The pressure in the regenerator, and consequently that of the exiting CO₂ gas, is for the CAP about 30 bar. The high pressure results in lower energy requirement for compression compared to the MEA process in which the regenerator pressure is only slightly above atmospheric (1).

Arguably, the most important difference between the two solvents, considering the studied application, is the solvent degradation resistance. MEA is mainly degraded by carbamate polymerisation; thermal degradation above 205°C and oxidative degradation, of which the degradation by an oxidizing environment is the most prominent one considering the studied application (9). In a combustion process oxygen reacts with fuel in an exothermic reaction, producing heat and combustion products. In a power production process a fairly complete combustion can be achieved, resulting in a low concentration of oxygen in the flue gas. In the aluminium production process, air is used for cooling purposes and thus, no combustion takes place. Hence the process gas leaving the aluminium process has, except for higher CO₂ concentration and contaminants from the process, roughly the same composition as air and still contains roughly 21 vol% oxygen. Using MEA in such an oxidizing environment could result in severe degradation. Ammonia however, does not react with oxygen alone and is not degraded in an oxidizing environment like the one present in the aluminium production process. The CAP is therefore believed to have good potential when applied for CO₂ capture from the aluminium manufacturing process.

1.1. Aim and Scope

The overall aim of this work is to investigate how the performance of the CAP is affected by a low CO₂ concentration source and to design and integrate such a process for use at a novel aluminium manufacturing plant. The aim is to investigate different operating conditions affiliated with the HAL Ultra aluminium production process, and the specific effects of varying process gas CO₂ concentration, solvent flows and changes in solvent ammonia concentration from a heat duty requirement and ammonia emission restriction point of view.

This work focuses on the CAP for capture of CO₂ from the process gas produced in the aluminium manufacturing process. Many studies have been made regarding the CAP, including some with models and simulations similar in design to models in this study. However, most studies have been made with power production, combustion processes in mind. For the vast majority of coal, biomass and petroleum combustion processes, CO₂ constitutes about 20 wt% of the total flue gas flow. The CO₂ concentration expected from state-of-the-art aluminium cells is between 4-10 vol%, lower than the 20 wt% of the described combustion processes. It is therefore of interest to investigate how the required heat duty for the CAP is affected by the lower CO₂ concentration from the aluminium cells. Furthermore, post combustion CO₂ capture applications for industrial processes are not presently conventional and studies of such possible applications for the primary aluminium process are scarce. This study investigates if, where and how surplus heat is available for integration with the aluminium production.

2. Hydro Sunndalsøra

Primary aluminium is mainly produced in electrolytic cells through the Hall-Héroult process. In this process, alumina (Al_2O_3) is dissolved in a cryolitic solution (Na_3AlF_6). The base of the cell, in which the solution is contained, is insulated with refractory lining and floored with carbon blocks which act as process cathodes. To complete the electric circuit, carbon anodes are submerged in the solution. When an electric current is passed through the solution, via the carbon cathode and the carbon anode, alumina is reduced into aluminium. The carbon anode is consumed by the oxygen produced, which gives rise to emissions of CO_2 . Pure aluminium is deposited at the carbon cathode at the bottom of the cell where it is tapped off and cast. The Hall-Héroult process is continuous and alumina and pure aluminium are continuously added and removed at regular intervals. The melting point of the cryolitic solution, and therefore the temperature needed for the process, is close to $1\,000^\circ\text{C}$. To keep the temperature from rising and cause structural damage to the cell, the process is cooled by an air flow above the cryolitic solution. Process gas is formed when cooling air mixes with CO_2 , SO_2 and other compounds released from the cell. The process gas is transported from the cell for removal of SO_2 , particulate matter (PM), hydrogen fluorides (HF) and other pollutants before being released to the atmosphere (10).

A development of aluminium cell technology is needed to facilitate the integration of post combustion CO_2 capture with the aluminium production process. Aluminium smelting cells are generally using the Hall-Héroult process illustrated in Figure 2. In this process, CO_2 formed at the carbon anode is mixed fully with the cooling air. Due to the large volumetric air flows needed for cooling, the process gas leaving the cell contains a low concentration of CO_2 , in the range of 0.9-1 vol%.

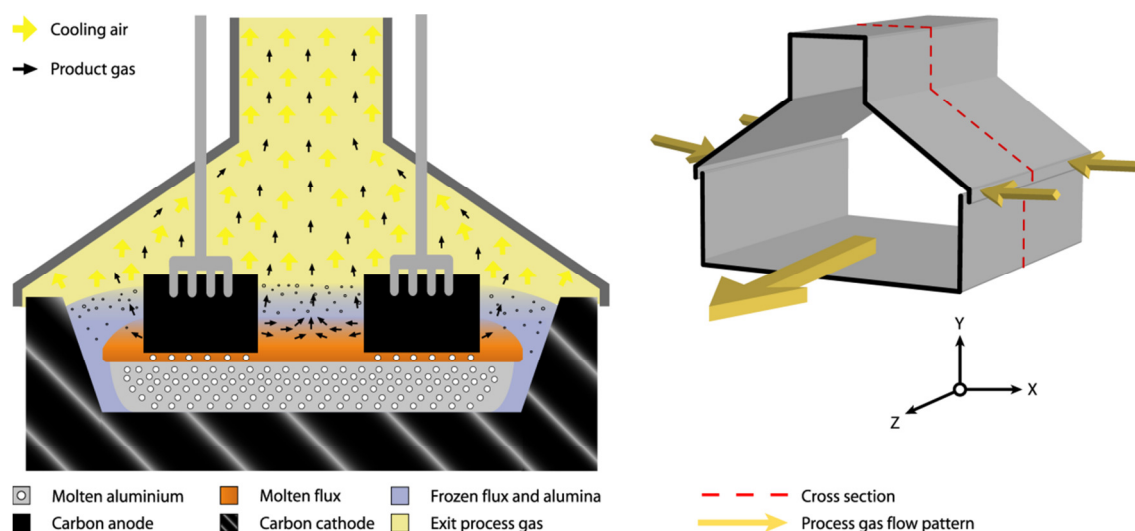


Figure 2. Cross sectional view of the current generation of cells using the Hall-Héroult process for aluminium production. The product gas mixes fully with the cooling air resulting in a process gas with low CO_2 concentration (0.9-1 vol%). Source: Hydro

Low CO_2 concentration and high volumetric gas flow rate requires large CO_2 capture and gas scrubbing equipment to achieve desired CO_2 capture rates. Large additional equipment means added investment cost and higher cost of operation. Additional costs that are not directly adding value to the final aluminium product results in an economically unfavourable investment with present costs associated with CO_2 emissions. (11)

To reduce cost and facilitate integration of CO_2 capture, Hydro's HAL Ultra cell, shown in Figure 3, is developed in such a way that most of the CO_2 is separated from the rest of the cooling air stream at the point where the CO_2 is released in the cell. This is achieved by introducing a new process gas collector in the cell and by reducing process gas flow rate, so that most gas released from the cryolitic solution can be collected and transported away for treatment. The novel design increases the CO_2 concentration to about 4 vol%. The higher CO_2 concentration and lower flow rate is believed to result in lower cost of both investment and operation, which enhances the possibility for introduction of CO_2 capture in the primary aluminium manufacturing process (4).

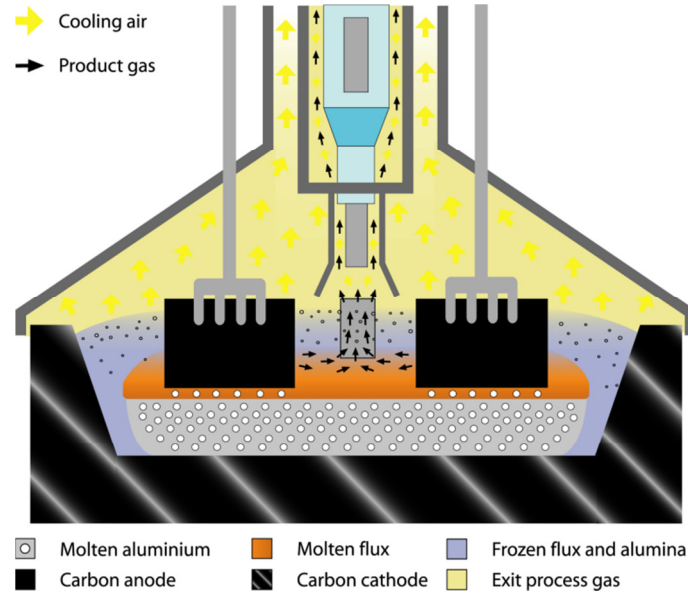


Figure 3. Cross sectional view of a HAL Ultra cell with separate collector for product gas, lowering the volumetric flow of total process gas and increasing the CO_2 concentration up to 4 vol%. Source: Hydro

The studied primary aluminium production facility is located in western Norway, in Møre og Romsdal County. The facility's location at the end of a fjord ensures reliable transportation routes by shipping and a large supply of cold sea water for process cooling.

After the completion of a major modernization in 2004, the Sunndalsøra aluminium manufacturing facility is considered to be one of Europe's most modern plants with an annual production capacity of 390 000 metric tonnes (3). The modernization included construction of a new line of aluminium cells called SU4, divided into three sections, in order to replace two lines of older cells.

Section 1 of SU4 consists of 108 cells and the other two, section 2 and 3, each contain 116 cells. The 340 cells, which together make up SU4, all use the Hall-Héroult process. The yearly total primary aluminium production capacity of SU4 is approximately 276 000 metric tonnes, more than 70% of the total production capacity of the Sunndalsøra facility. For this project, section 3 of the SU4 is chosen as reference when considering heat extraction for process integration and process gas stream data.

The pressure in the cells is kept at sub-atmospheric conditions in order to ensure that no process gas leaks from the cells into the atmosphere without gas treatment. The flow of cooling air and process gas from the cells during normal operation is 6 500 Nm^3/h . In order to keep the pressure difference at 0.5 mm H_2O even when cells are opened for anode exchange, additional suction is required. The anode exchange is limited to a few cells at a time with an increased air flow of 18 000 Nm^3/h for those cells (4). The process gas stream leaves the cell and is merged with the gas streams from the other cells in section 3. A potline with HAL Ultra cells has reduced cooling air flow rate in order to increase the concentration of CO_2 in the process gas. According to Hydro, achieving 4 vol% CO_2 concentration requires a reduction of the cooling air flow to 1 600 Nm^3/h for normal operation but remain at 18 000 Nm^3/h during anode exchange to ensure sufficient underpressure (4). The total process gas and cooling air flow rate using the HAL Ultra cell technology at section 3 is then:

$$(112 \cdot 1\,600 + 4 \cdot 18\,000)/3\,600 = 69.78 \text{ [Nm}^3/\text{s}] \quad (1.1)$$

The total process gas flow is reduced by a factor three compared to present operation. Emissions from a HAL Ultra cell with various cooling gas flow rates have been performed and measured or estimated by Hydro and the results are presented in Chapter 2.1.

Table 1. Measured and estimated emission data before gas treatment for a HAL Ultra cell (4).

Flow rate [Nm ³ /h]	Temperature [°C]	Concentration of gas [mg/ Nm ³]		Concentration of gas [vol%]	Concentration of total dust [mg/ Nm ³]
		HF	SO ₂	CO ₂	
7 000	130	155	235	0.6	500
4 000	185	235	411	0.9	500
2 000	265	400	822	3.0	500
1 600	290	500	1 027	4.0	500
1 000	345	780	1 800	7.0	500
800	365	1 060	2 055	10.0	500

Table 1 shows that in order to reach the desired 4 vol% of CO₂ in the product gas, the total flow rate need to be reduced to 1 600 Nm³/h. This will in turn affect the composition and properties of the process gas, resulting in higher temperatures and increased concentration of e.g. HF and SO₂ in comparison to present operation.

2.1. Process Gas Treatment

Due to contamination of mainly SO₂, PM and HF, the process gas needs treatment before released to atmosphere. The process gas treatment train at SU4 is shown in Figure 4 and consists of several stages to ensure sufficient removal of contaminants.

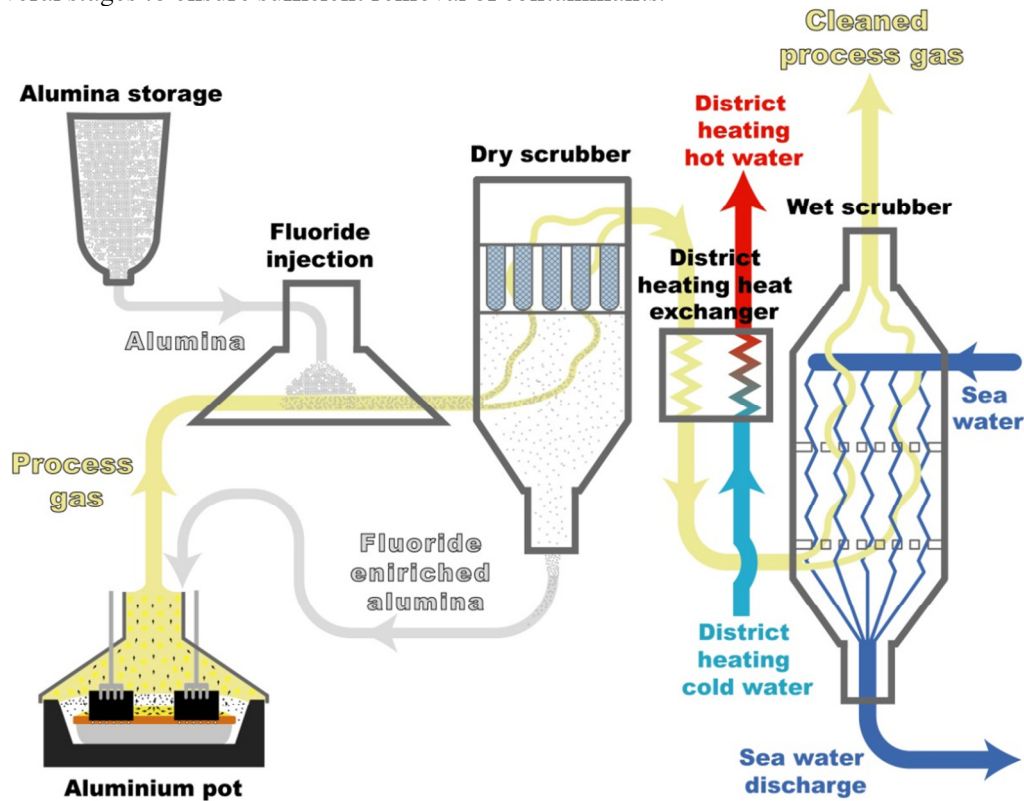


Figure 4. Process gas treatment flow sheet at section 3 of the SU4. The process gas (yellow) is cleaned and scrubbed free from various contaminants throughout the gas treatment train. A heat exchanger supplies the local district heating network with hot water.

When leaving the cells, the process gas stream is mixed with the ingoing alumina (Al₂O₃), which is then carried with the gas to the dry cleaning plant. Whilst mixed, the fluoride in the process gas will react with the alumina, forming fluoride enriched alumina. The fluoride injection reduces the amount of HF and other fluoride compounds released to the atmosphere. Fluoride is one of the components that make up the cryolitic solution in the cells, meaning that the recirculation of fluoride through alumina reduces the need of cryolite makeup. The dry scrubber consists of a cyclone and baghouse filtration system and is used to remove PM and to separate the fluoride

enriched alumina from the process gas stream. The process gas continues through the scrubber whilst the heavier alumina particles are collected at the bottom and distributed to the cell.

The section 3 process gas treatment train is connected to the Sunndalsøra district heating network by a heat exchanger. The heat exchanger is located between the dry and wet scrubbing plants, using heat that would otherwise be wasted. At present, the temperature of the process gas is about 100°C when entering and between 70-80°C when leaving the heat exchanger. The district heating water is heated from 60°C to 90°C in the heat exchanger and is then distributed to the Sunndalsøra district heating customers. (4)

Cold sea water is introduced at the top of the wet scrubber, countercurrent to the process gas. The main task for the wet scrubber is to remove SO₂ from the process gas. The wet scrubber also reduces the HF emissions but due to the high efficiency of the upstream dry scrubber, most HF is already removed (12). The sea water is discharged back into the sea after the wet scrubber at a slightly elevated temperature. The cleaned process gas is released to the atmosphere (4).

3. The Chilled Ammonia Process

CO₂ capture by the use of an aqueous ammonia solvent is a promising technology. Some expected advantages are: a comparatively inexpensive solvent; regeneration at pressure, minimizing solvent vaporization and pre-compressing the CO₂ for transport; a low heat of reaction and low regeneration energy consumption (13) (14). However, ammonia vaporization may be so great that a separate NH₃ capture cycle may be needed (15) and the need for cooling water is extensive.

A schematic of the CAP is given in Figure 5. Treated and cooled process gas containing CO₂ is passed through an absorption column where CO₂ reacts with the chilled aqueous ammonia solvent in which the CO₂ is absorbed. Typically 85-90% of the CO₂ is absorbed before discharge to the atmosphere. The solvent, now containing CO₂, is transported from the absorption column to a regenerator where the CO₂ is released through heat addition, breaking the chemical bonds. The released CO₂ stream, also containing water and residual ammonia, is first cleaned from water and ammonia then pressurized and sent for storage. The solvent is recycled back to the absorption column for further CO₂ absorption.

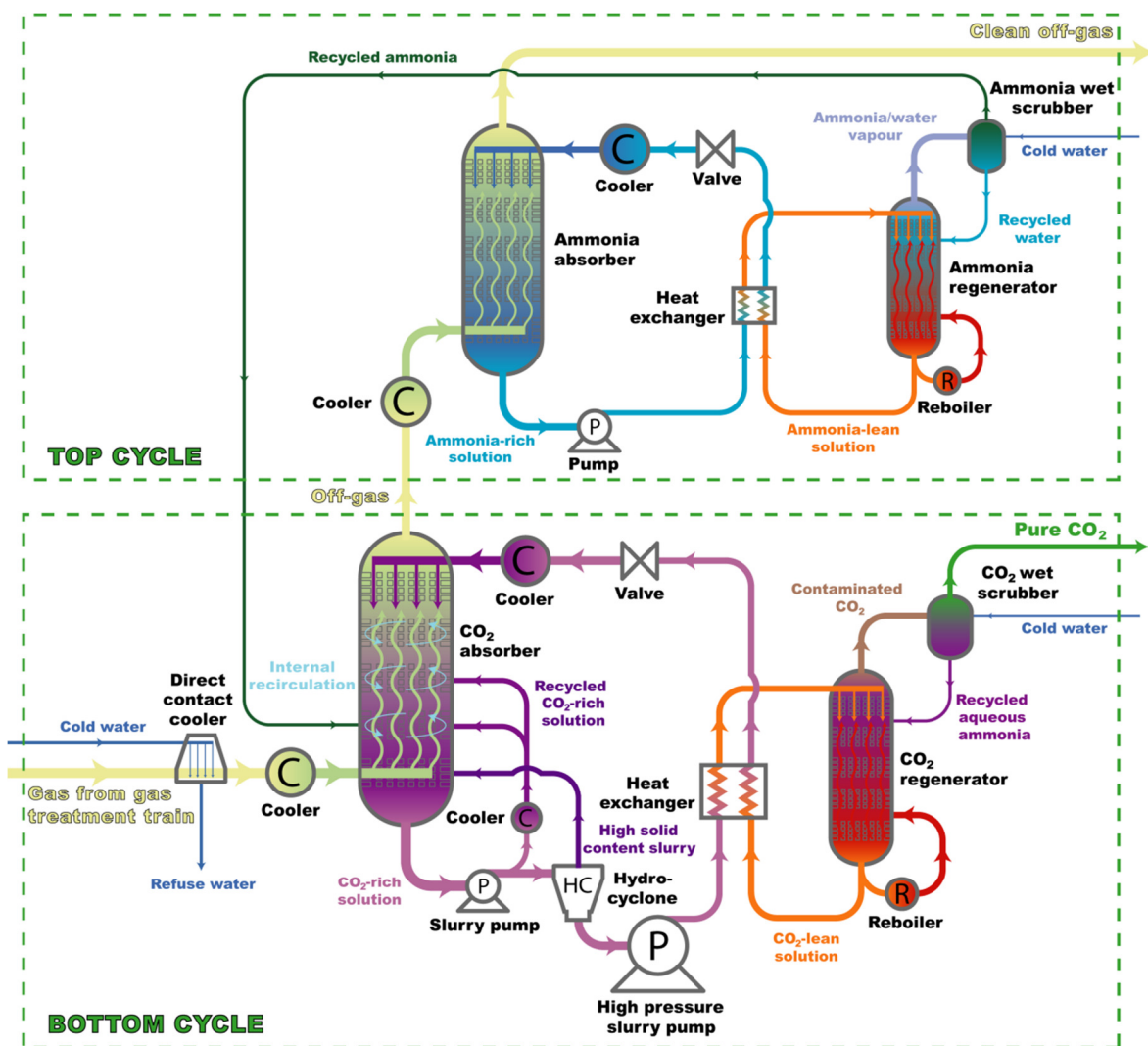


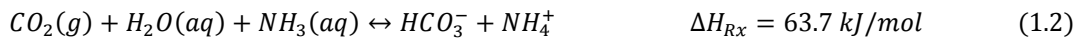
Figure 5. Flowchart describing the CAP. CO₂ is absorbed and stripped in the bottom cycle leaving pure CO₂ and ammonia contaminated off-gas as the two outgoing streams. Off-gas is treated in the top cycle where ammonia is absorbed, stripped reintroduced to the CO₂ absorption process. (15)

3.1. CO₂ Capture Cycle

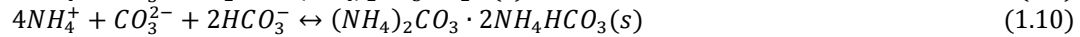
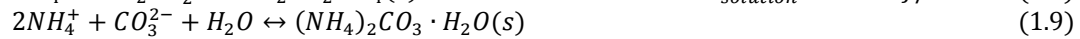
The absorber is of cross-flow type with the cooled CO₂-lean solution, coming from the regenerator, entering from the top and the cooled flue gas entering from the bottom at atmospheric pressure (16). In their response to critique by IEA GHG (1), Alstom claim to use a packed column of proprietary design, capable of handling solids. They also state that heat exchangers are used to remove heat from the exothermic absorption process. Alstom claim that the CAP is tolerant enough towards SO₂ to be fitted directly after conventional SO₂-cleaning systems and that it can capture residual SO₂, SO₃, HCl and PM (1).

According Gal (17), the optimal CO₂/NH₃ mole ratio (CO₂ loading) in the absorber should be 0.33-0.67 but values as low as 0.25 or as high as 1 are possible. According to Darde et al. the rich CO₂ loading should be in the range of 0.5-1 (16). Ratios in the higher end of the spectrum results in: a reduction of gaseous ammonia being released from the solution as a result of lower ammonia vapour pressure, an increase of undissolved solids and an increase in CO₂ vapour pressure, reducing capture efficiency (13). Ratios in the lower end of the spectrum have the opposite effect. Increasing temperature has great effect on the system: it gives an increased solubility of solids, it increases ammonia vapour pressure which increases ammonia vaporization and it increases CO₂ vapour pressure which reduces capture efficiency (13).

For the CAP, IEA (1) state the following main chemical reactions and standard heats of formation in the liquid phase:



And the following solid formation reactions and heat needed for dissolution:



Thus, the favoured reaction would be the formation of bicarbonate ions, a reaction which is prevalent below 15°C (1). At higher CO₂-loadings the solubility limit is reached and precipitation occurs. This implies that the CO₂-rich stream out of the absorber could be in slurry form (16). The stream flows through a high pressure pump, compressing it to 3.45-172.4 bar in order to avoid unwanted CO₂ vaporization (17). It should be noted that solids formation increases the total amount of heat needed for regeneration and that it demands use of equipment capable of handling solids (1). The solids formation however, allows for higher CO₂ loadings, resulting in lower flow rates.

The cold CO₂-rich stream is fed to the regenerator system where it is heated up by an auxiliary heater or heat exchanger to 50-200°C, with a preferable range of 100-150°C, and then fed into the regenerator column (16) (17). Due to the strong temperature dependence of the solubility of the solids (13), they dissolve when the slurry is heated enough (above 80°C according to Kozak et al. (14)).

The regenerator consists of a stripper column to which the rich, heated solution is fed at several different levels, according to Alstom in IEA GHG (1). The pressure in the column is elevated in order to demote water and ammonia vaporization while the solubility of CO₂ in water is greatly decreased. This allows for a more pure CO₂ stream to exit at the top of the column (16) (13). Alstom (1) state that they use a pressure of 30 bar at the bottom of the column. The reactions taking place are reversed compared to those presented as absorption reactions above.

Because of water and ammonia contamination of the CO₂ stream leaving the system, a cleaning system consisting of a wet scrubber is installed after the regenerator (16).

The stream of CO₂-lean solvent is cooled and reintroduced into the absorber (17) at a lean CO₂ loading of 0.25-0.67 (16). This range is suggested since CO₂ loadings below approximately 0.54 increases the ammonia bubble point pressure drastically, seen in Figure 6, thus increasing the amount of ammonia in the gas phase, contaminating the stream leaving the absorber (16).

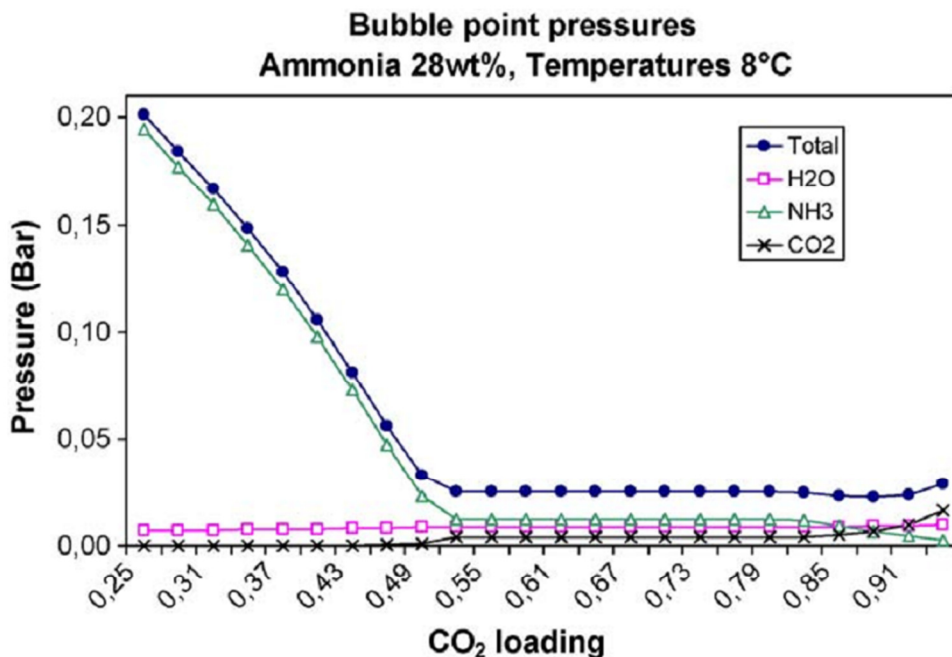


Figure 6. Bubble point pressures of a 28 wt% ammonia solvent with a temperature of 8°C as a function of the CO₂ loading for equilibrium simulations. (16)

Because of formation of solids in the absorber there is need for a pump capable of handling slurry. The type of pump usually used for this sort of application is a centrifugal pump with open impellers and large clearances (18). When handling slurry, lower pump efficiency and lower developed head can be expected compared to pumping water alone (19). Transporting slurry gives rise to wear on the equipment and may also promote corrosion attacks associated with erosion in chemical applications (19).

The heat exchanger transferring heat between the CO₂-rich stream coming from the absorber and the CO₂-lean stream coming from the regenerator needs to be able to handle slurry. Moretta (20) says that: “Spiral plate heat exchangers are ideal for cooling slurries and viscous fluids”. This is justified by that they are compact, have a decreased tendency of fouling, are easy to maintain and have increased heat transfer rates compared to other alternatives, opinions which are seconded by the heat exchanger manufacturing company Alfa Laval (21). Lee et al. (22) however use a tube-in-tube arrangement in their research, a setup which would allow for the use of a scraper if necessary to avoid fouling (18). Plate heat exchangers could be an alternative, as claimed in an advertisement in *Process Heating* (23). However, Couper et al. (18) claim that these are not suitable for use at pressures above 300 psig (20.68 bar).

There is also a possibility for adding a heat exchanger in series with the reboiler in the CO₂ regenerator. This would mean heat exchanging between the solution in the regenerator and with a gas stream coming directly from the potline. According to Hydro (4), this gas is contaminated, leading to fouling of the heat exchanger. Thus, the same kinds of heat exchangers could be used as the alternatives proposed for the rich/lean stream heat exchangers.

The CAP has need for cooling of several streams. The process gas feed, the rich recirculation stream and the lean return stream have to be cooled and there is also be need for intercooling in the absorber itself. The process gas stream is washed from SO₂ in a wet cleaning device which resembles a direct contact cooler, partially cooling it down. Because the preferred inlet temperature to the absorber is about 0-10°C, a supplementary cooler might be required to get sufficient cooling during the warmer parts of the. Examples of this sort of device are given by Couper et al. (18), as either absorption or compression refrigeration. Both of these types of

refrigeration can attain temperatures below 0°C. The two liquid streams in need of cooling can use the same kind of refrigeration cycles if needed, but should preferably be cooled by heat exchange with sea water. Hydro estimates that sea water will be available at a temperature of maximum 10°C all year round.

In order to increase the solids content in the slurry, IEA (1) states that Alstom uses a hydrocyclone in combination with a slurry retention tank. The slurry is concentrated from a solids content of 10-15 wt% to 30-50 wt%. This, according to IEA, allows for a reduction in sensible heat needed for heating the slurry.

3.2. NH₃ Scrubbing Cycle

There is a possibility of having high ammonia slip from the CO₂ capture cycle. Because of the ammonia slip there might be a need for a NH₃ capture cycle, as mentioned by Mathias et al. (15). In this cycle, ammonia is absorbed into water to create an aqueous solution. The solution is fed to a regenerator where the ammonia solubility is lower because of the higher temperature. The regenerator pressure can be kept at atmospheric levels to reduce solubility (24). However, a slightly raised pressure is recommended in order to reduce vaporization of water.

4. Method

To determine if the CAP can be integrated to the aluminium manufacturing process, two separate studies are carried out. The heat requirements for the CAP and how it is affected by low CO₂ concentration is determined through modelling and simulations of the process. How much heat that can be extracted from the process gas and used for process integration is determined through modelling and simulations of the existing process gas treatment train and the added heat extractions.

A model is created to investigate the effects of low CO₂ concentration process gas on the required heat duty for CO₂ capture. The outcome of the study is the reboiler duty and the specific reboiler duty¹ of the CAP, required to achieve a predetermined CO₂ capture rate and off-gas ammonia volumetric concentration. Knowledge of heat duty and temperature requirements is used to determine and propose available streams in the aluminium manufacturing process gas treatment train suitable for process integration of the CAP.

Given the properties of the CAP, the model is built to handle solvent slip, reducing the solvent discharge to the environment to the regulated levels of 10 ppmv. To satisfy a discharge of exactly 10 ppmv requires a smaller reboiler step size than is used during simulations. Thus, the use of an ammonia discharge span instead of a fixed concentration is made as a simulation technical solution to increase convergence in the model. The ammonia concentration is restricted to within the span of 5-15 ppmv of the outgoing process gas. Heat duty requirement for sufficient solvent abatement is taken into account when the process integration is investigated. Table 2 presents the parametric study carried out for the CO₂ capture cycle. In the study, CO₂ concentration, solvent flow rate and the absorber CO₂ loading is varied. The absorber CO₂ loading is an important reference measure and it is defined as the number of moles of CO₂ per moles of NH₃ in the absorber at simulation start-up. The solvent flow rate is defined as the molar flow rate of the aqueous ammonia solution at start-up. Another important parameter, not varied specifically here, used for comparison with previous studies is the solvent composition. This is defined as the ammonia molality and describes the amount of ammonia in relation to water in the solvent, mol NH₃/kg H₂O.

Table 2. Variables and values that make up the parametric study for the CO₂ capture process

Parameter	Unit	Low → High										
Concentration	[vol% CO ₂]	4			7			10			15	
Solvent flow rate	[kmol/s]	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	
Absorber CO ₂ loading	[mol CO ₂ /mol NH ₃]	0.25			0.3			0.35			0.4	

To identify available surplus heat at sufficient temperature and to determine process gas properties and flow rates, a heat and mass balance simulation model of the aluminium manufacturing process gas treatment train is created. The model is used to determine process gas properties used as input to the CO₂ capture model. Being the main heat source investigated for process integration, the process gas treatment train model is also used to determine where and how much heat that is available for heat integration of the CAP.

4.1. Process Data

The CO₂ capture cycle simulations are divided into two main cases. One case where the input values are obtained from Hydro, see Table 3, and another where the process gas flow rate is kept at a constant rate while the composition of CO₂ and N₂ is varied according to Table 4. They are referred to in the text as “Hydro case” and “constant flow case” respectively. The process data used for the Hydro case is based on measured and estimated results from the HAL Ultra process tests performed by Hydro. The provided data originates from different HAL Ultra operating conditions resulting in varying CO₂ concentrations and flow rates for investigation of heat duty and process integration requirements and possibilities. For the process integration study, using

¹ Defined as the energy needed to capture one unit mass of CO₂ [kJ/kg CO₂ captured]

input data provided by Hydro, varying the CO₂ concentration also means varying the process gas flow rate.

Table 3. The properties for process gas at various CO₂ concentrations for the Hydro case. Temperature and pressure is 5°C and atmospheric respectively for each case when entering the CO₂ capture process.

Process gas out from cells			Process gas entering the CO ₂ capture process				
			Composition [wt%]				
CO ₂ concentration [vol%]	Flow rate per cell [Nm ³ /h]	Temperature [°C]	Total mass flow [kg/s]	N ₂	O ₂	CO ₂	H ₂ O
4	1 600	290	82.43	71.2	22.4	5.9	0.528
7	1 000	345	60.40	67.2	22.0	10.2	0.520
10	800	365	53.07	63.4	21.7	14.4	0.512
15	487	379	41.59	57.4	21.1	21.0	0.498

Table 4. The properties for process gas at various CO₂ concentrations, adjusted to constant flow rate. Temperature and pressure is 5°C and atmospheric respectively for each case when entering the CO₂ capture process.

Process gas out from cells	Process gas entering the CO ₂ capture process				
	Composition [wt%]				
CO ₂ concentration [vol%]	Total mass flow [kg/s]	N ₂	O ₂	CO ₂	H ₂ O
4	60	72.6	21	5.9	0.5
7	60	68.3	21	10.2	0.5
10	60	64.1	21	14.4	0.5
15	60	57.4	21	21.0	0.5

4.2. Modelling Tools

Two modelling software are used in this study, Ebsilon Professional 7.0 and Aspen Plus 7.2. The data provided by Hydro is limited to properties of untreated process gas, requiring initial simulations to obtain the CAP inlet gas stream. The Ebsilon model is therefore used to simulate the aluminium plant gas treatment train to obtain the process gas outlet conditions. The Ebsilon model is furthermore used to identify the amount of heat available in the process gas and is the model used when determining the location and specifications for process integration.

The model used to simulate the CAP is built in Aspen which, except for mass and energy balance, also handles chemical reactions, complex solutions and the accompanying vapour-liquid equilibrium (VLE) calculations. The CAP model consists of two separate models. One model simulating the CO₂ capture cycle, referred to as the bottom cycle, and another simulating scrubbing and recovery of ammonia slip, referred to as the top cycle. Both models are used to investigate the required heat duty to achieve desired CO₂ capture and ammonia slip respectively. The absorbers and regenerators are modelled using the Aspen RadFrac component. The component is used for modelling of absorption and desorption. Two different calculation approaches can be used for RadFrac, equilibrium and rate-based calculation approach, more of which is described in 0.

4.3. Process Integration

As a result of low working temperature for the bottom cycle absorber in relation to the high temperatures required in the regenerator, both heating and cooling demand is required. The CAP' heating demand is the primary focus and it is determined for each of the different simulation cases. To investigate the possibility of process integration with the aluminium manufacturing process is therefore an important part of this report.

With constant working temperatures of around 1 000°C, the aluminium cells are interesting from a heat integration point of view. Integration directly with cells would pose some advantages, the foremost being the high temperature of the cell compared to the process gas leaving the cell. However, bringing water in close proximity to the cells is prohibited for safety reasons. Leakage of water from such a heat exchanger system could result in steam explosion, posing a threat to both equipment and personnel. The heat integration of the CAP is therefore focused to the process gas treatment train, utilizing heat from the process gas as shown in Figure 7.

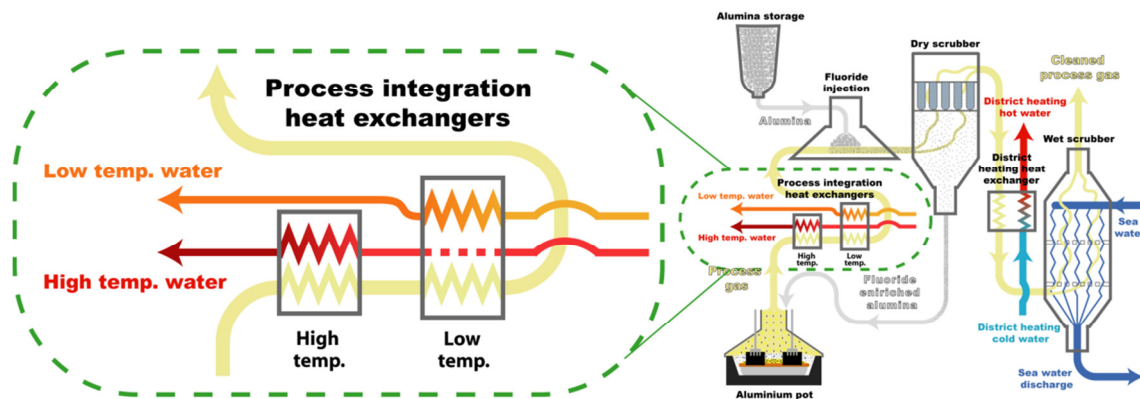


Figure 7. Schematic overview of the aluminium manufacturing process and proposed heat source for process integration of the CAP.

The heat consumers in the CAP are the bottom and top cycle reboilers and, while similar in principal and function, the working temperatures greatly differ between the two. The CO₂ capture simulations provide separate information about the minimum required temperature for both the bottom and top cycle reboilers, hence determining the minimum temperature of the process gas stream at which process integration of the two cycles can be considered. For the process integration study, the simulation cases with lowest total reboiler duty for the combined bottom and top cycle is considered. This is done for the different CO₂ concentrations and compared with the available heat from process integration with the aluminium process for the corresponding case.

Limiting conditions in the existing process gas treatment train together with the required reboiler temperature levels determine the most suitable location for process integration. The maximum allowed temperature in the process gas dry scrubber is specified to 110°C, meaning that enough heat needs to be extracted to lower the temperature to that specified level. If more heat is extracted from the process gas stream, lowering the temperature below 110°C, downstream equipment like the district heating heat exchanger will experience declining temperature driving force and efficiency. Given the nature of the technological measures planned by Hydro made to increase outlet CO₂ concentration, process gas flow rate is gradually decreased which in turn affects the potential for both process integration and district heating heat extraction. The district heating heat exchanger is not relocated or removed from its location in the existing process gas treatment train and output is optimized given the minimum required supply hot water temperature (90°C), return temperature (60°C) and the available heat in the process gas stream.

The high heat development from exothermic reactions in the bottom cycle absorber, together with hot gas and solvent streams in need of cooling, results in a significant total cooling demand for the CAP. In this particular case, the location of the primary aluminium facility is beneficial when cooling requirements are considered. The close proximity to the sea and hence to cold sea water at constant temperature, greatly reduces the potential costs for cooling. The sea water, assumed to have a temperature of between 5-10°C when utilized in the process, is used both in the

process gas treatment train and for cooling in the CAP. The actual integration of cooling is assumed with certainty to be of minor significance compared to the heat integration, consisting mostly of electricity for pumping. The cooling integration will consequently not be treated in the results.

5. Modelling

5.1. Process Gas Treatment Model

According to Hydro (4), the installed process gas treatment train would also be able to handle the decreased flow rate and higher concentration of contaminants expected from the future generation HAL Ultra cells considered in this report. The presented values and intermediate results in this model description are based on the HAL Ultra case with 4 vol% CO₂ concentration. All heat exchangers in the model are assumed to have a minimum temperature difference of 10°C.

The process modelling software Ebsilon Professional is used to acquire reliable properties and compositions for the process gas at the end of the process gas treatment train. The model can be divided into sections, shown in Figure 8, each describing a process in the gas treatment train.

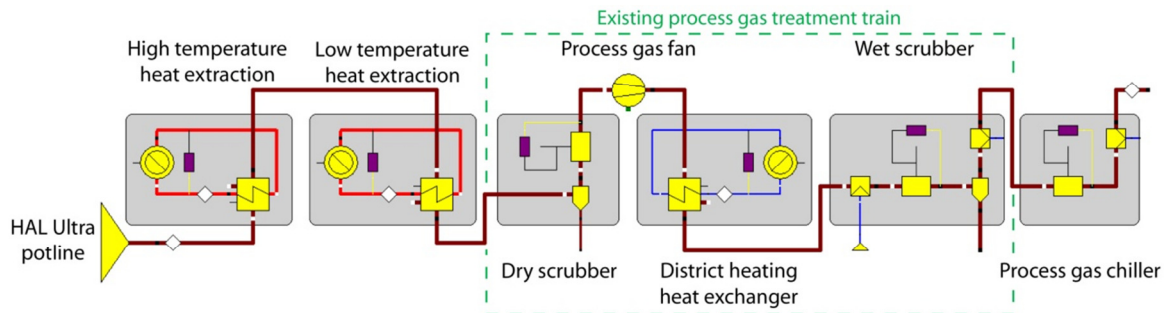


Figure 8. Describes the model of the process gas treatment train. Grey boxes mark the different included sections. The green dashed line indicates the presently installed equipment at the existing SU4, section 3

Knowledge about process gas properties and compositions at the cell outlet allows significant simplifications in the modelling. The process gas leaving the cells, presented earlier in Table 3 and Table 4 for all cases and in Table 5 for the 4 vol% CO₂ concentration case, is generated and constitutes the main inlet condition of the model.

Table 5. Properties and composition of the process gas leaving the HAL Ultra potline for the 4 vol% CO₂ concentration case.

HAL Ultra process gas		Temperature [°C]		Pressure [bar]	Mass flow rate [kg/s]	
Process gas inlet		290		1.013	84.36	
Composition [vol%]						
	N ₂	O ₂	CO ₂	SO ₂	Ash	
Process gas inlet	75.26	20.70	4.0	0.0287	0.0000833	

Process integration of the CAP reduces the need for supplementary heat addition. Heat exchangers, of which one is presented in Figure 9, are introduced at the beginning of the process gas treatment train. The heat extraction is modelled as two separate sections, one for heat integration of the bottom cycle reboiler, requiring high temperature heat, and another for the top cycle reboiler, working at lower temperature. Heat consumers connected to the heat exchangers simulate the reboilers in the CAP. The reboiler working temperature is assumed to be constant and the required heat exchanger temperatures are, with consideration to the minimum temperature difference, determined by the CO₂ capture model to 121°C for the top cycle reboiler and to vary between 204-217°C for the bottom cycle reboiler. The top and bottom cycle heat extractions are presented in Table 6. Process gas outlet conditions after bottom and top cycle heat extractions are determined by the maximum temperature allowed at the dry scrubber inlet (4).

The heat exchanger connected to the Sunndalsøra district heating network, shown in Figure 11, is modelled by a heat exchanger and a heat consumer. The heat consumer simulates the hot water usage in the town of Sunndalsøra, extracting heat in order to reach the heat exchanger outlet temperature. Hot water is supplied to the district heating system at 90°C and returned at 60°C.

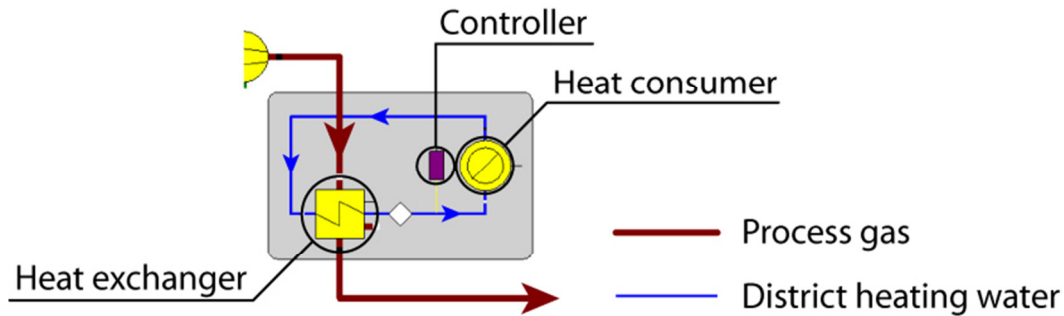


Figure 11. A liquid-gas heat exchanger and a heat consumer are used to model the district heating heat exchanger.

The wet scrubber, shown in Figure 12, is modelled in several steps in order to achieve a reliable simulation of the actual process. A wet scrubber resembles a direct contact cooler in that it introduces water directly into the process gas stream. The packed column wet scrubber is assumed to have an approach temperature of 1°C (13). Furthermore, sea water is assumed to be available at a maximum of 10°C throughout the year. (4) The introduction of sea water is simulated by saturating the process gas stream with water. Excess heat is extracted from the process gas stream in accordance to the maximum sea water temperature, lowering the process gas temperature to 11°C. To simulate SO₂ removal a splitter removes all SO₂ from the process gas. A drain is used to remove liquid water from the outlet process gas.

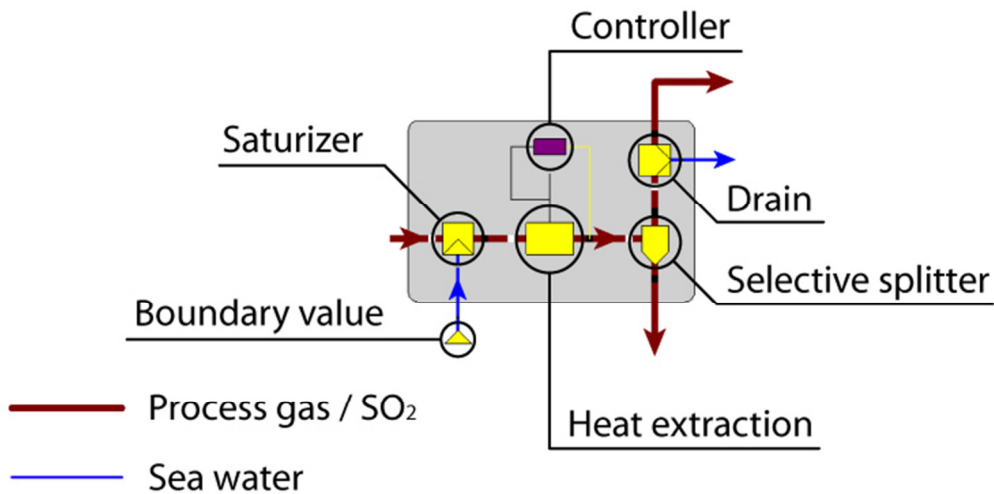


Figure 12. The wet scrubber is modelled in four steps, saturation, heat extraction, SO₂ removal and excess sea water drainage.

A cooler is used in order to reach desired temperature of the exiting process gas. The temperature of the process gas is lowered from 11°C to 5°C. A drain is used to remove condensed water from the process gas stream. The properties and composition of the process gas exiting the cooler, presented in Table 7, are used as input to the CAP investigated in this report.

Table 7. The properties of the process gas entering the process gas cooler and the properties and composition of the process as leaving the cooler.

Process gas cooler		Temperature [°C]		Pressure [bar]	Mass flow rate [kg/s]	
Process gas inlet		10.85		1.013	82.66	
Process gas outlet		5.0		1.013	82.43	
Cooling duty in process gas cooler			577 [kW]			
Composition						
Process gas outlet	N ₂	O ₂	CO ₂	H ₂ O	SO ₂	Ash
vol%	74.64	20.53	3.97	0.86	-	-
wt%	71.17	22.36	5.94	0.53	-	-

5.2. CAP CO₂ Capture Model

The simulations are carried out in two separate models, one describing CO₂ capture in the bottom cycle and another describing NH₃ abatement in the top cycle. The bottom cycle is illustrated in Figure 14 and the top cycle is illustrated in Figure 17.

5.2.1. Input Data

The treated process gas is introduced to the CO₂ capture process at 5°C and atmospheric pressure. The existing gas treatment is assumed to remove all contaminants like SO₂, PM and HF. The inlet condition of the process gas is presented in Table 8 for the examined CO₂ concentrations.

Table 8. The properties for process gas at various CO₂ concentrations leaving the aluminium plant gas treatment train. Temperature and pressure is 5°C and atmospheric respectively for each case.

	Process gas out from cells	Process gas entering the CO ₂ capture process				
	CO ₂ concentration [vol%]	Total mass flow [kg/s]	Composition [wt%]			
			N ₂	O ₂	CO ₂	H ₂ O
Measured / estimated ^b	4	82.43	71.17	22.36	5.94	0.53
	7	60.40	67.24	22.0	10.23	0.52
	10	53.07	63.44	21.66	14.39	0.51
Extrapolated ^c	15	41.59	57.36	21.11	21.04	0.50

b) Measurements and estimations performed by Hydro (4).

c) Extrapolated values from measurements and estimations performed by Hydro. Calculations further described in Appendix A – CO₂ Concentration Properties Extrapolation.

5.2.2. Absorber Modelling

The level of modelling complexity can be divided into five cases (25), the simplest being an equilibrium stage model with reaction equilibrium. Mass transfer is assumed to be infinitely fast within each stage and vapour and liquid phases are assumed to be at reaction equilibrium at the end of each stage (26). A more complex model is using a rate-based approach. The difference between equilibrium and rate-based calculations is that heat and mass transfer correlations are applied. A two-film model is used to describe heat and mass transfer in the gas-liquid interface, seen in Figure 13, as opposed to the two respective bulk phases. The two-film model assumes that there is no composition gradient in the bulk liquid due to high mixing and that all mass diffusion resistance is concentrated to the two film layers; where only steady state molecular diffusion occurs (27). In a reactive system such as CO_2 absorption, this model is however not sufficient. Therefore, several types of reaction characteristics have to be taken into account, some of which are shown in Figure 13. The figure shows the partial pressure and concentration profiles in the gas and liquid films, depending on input conditions and reaction speed.

The equilibrium stage model in Aspen Plus is equivalent to the simplest model with the addition of a bulk phase reaction kinetics assumption (8), increasing the accuracy of the model. According to Wang (8) equilibrium models are not sufficient when modelling amine absorption processes, why he suggests a rate-based approach being used instead. This is assumed to be the case for ammonia absorption processes as well and is why rate-based calculations with film and bulk phase reactions are applied. Onda et al. (1968) is used for mass transfer coefficient and interfacial area calculations and the Chilton and Colburn correlation is used for heat transfer coefficient calculations.

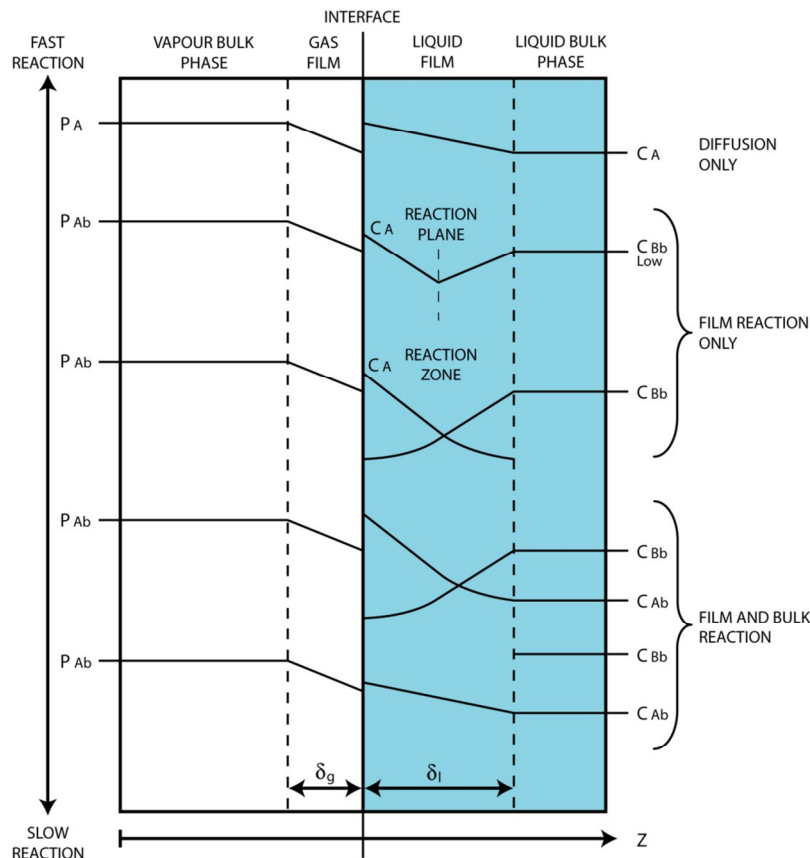


Figure 13. Concentration profiles depending on chosen film theory.

5.2.3. CO₂ Capture Cycle

The main components in the bottom cycle CO₂ capture model, shown in Figure 14, are the absorber and regenerator. Remaining components are described as auxiliary equipment at the end of this chapter.

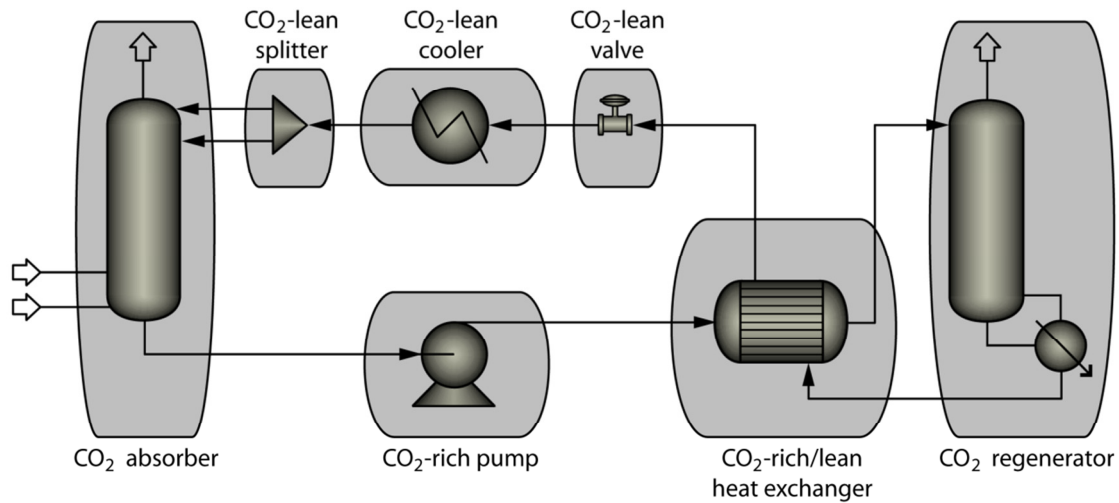


Figure 14. Illustrative process flowchart describing the CO₂ capture cycle model.

Simulations are performed through a set of cases with varying: process gas flow rate, containing individual CO₂ concentrations in accordance to Table 8; solvent flow rate and solvent composition. A fixed design specification varies the regenerator reboiler duty in order to achieve a total CO₂ capture rate of 85%. Reboiler duty, ammonia slip and reboiler temperature is generated as main results.

The bottom cycle CO₂ absorber, shown in Figure 15, is modelled with Aspen RadFrac packed column, using a rate-based approach. Rate-based modelling of the absorption column requires some additional specification of internal column design. The absorber diameter is calculated using a correlation by Grén et al. (28), this is further described in Appendix B – Dimensioning of Packed Column. The additional column design specifications; like height, number of stages, packing material and packing size, are all chosen for simulation technical reasons to achieve a stable model and should thus not be confused with actual absorber design specifications. The design parameters for one exemplified case with 4 vol% CO₂ concentration are presented in Table 9.

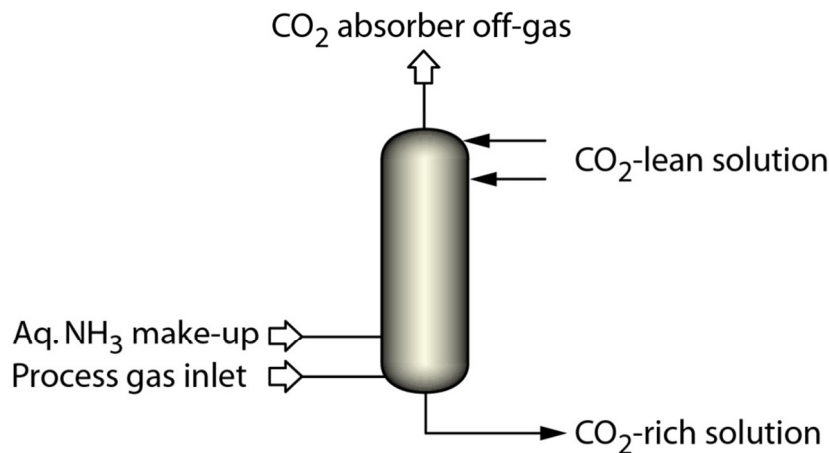


Figure 15. The packed CO₂ absorber column is modelled using Aspen RadFrac block.

Table 9. Simulation technical design specifications and properties of the CO₂ absorber and its connecting streams for a 4 vol% CO₂ concentration case with 6.59 mol NH₃/kg H₂O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be seen as actual design parameters.

Bottom cycle absorber design specifications					
CO ₂ absorber height		(120)		[m]	
CO ₂ absorber diameter		7.2		[m]	
Pressure		1.0132		[bar]	
Number of stages		(40)		[-]	
Packing type/material		(Pall ring/Metal)		[-]	
Packing size		(16)		[mm]	
CO ₂ absorber stream properties	Stage	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/s]	
Process gas inlet	40	5	1.0132	82.43	
CO ₂ absorber off-gas	1	6.85	1.0132	79.66	
CO ₂ -lean solution	1 / 5	5	1.0132	53.68	
Aqueous ammonia make-up	30	5	1.0132	2.93	
Total internal refrigeration duty in CO ₂ absorber			6.7	[MW]	
Composition					
CO ₂ absorber off-gas	N ₂	O ₂	CO ₂	H ₂ O	NH ₃
wt%	73.64	23.14	0.92	0.58	1.72

The process gas containing CO₂ is fed into the absorber at the bottom stage. The returning CO₂ lean solution, returning from the regenerator, is split into two equally sized streams and introduced to the absorber at stage 1 and 5. A make-up stream, introduced at stage 30, makes up for water and ammonia lost with the absorber and regenerator off-gas. Off-gas leaving the absorber at the top stage contains process gas, scrubbed free from most CO₂ but contaminated by ammonia slip, constituting the reason for the ammonia scrubbing top cycle. Internal circulation and refrigeration is needed to counter the exothermic reactions and keep the working temperature in the absorber between the desired 0-20°C. The refrigeration is supplied by using utility exchangers, drawing solvent from one stage in the absorber, cooling it to 8°C and returning it at a higher stage. In the CO₂ absorber model a total of 15 internal pumparounds, each with a flow rate of 1.5-2.5 kmol/s, are used to simulate the internal recirculation and to keep the temperature below 20°C at most times. The 15 internal pumparounds are chosen to achieve sufficient cooling and convergence in the model and does not necessarily reflect the reality in terms of amounts and placement. However, even in reality the CAP bottom cycle absorber is characterised by large internal recirculation (1).

The CO₂ regenerator is modelled as a packed column with the Aspen RadFrac block and the simulations are carried out at equilibrium, no internal column design is therefore specified. An equilibrium approach is a reasonable assumption since the temperature in the regenerator is very high, meaning high reaction speeds and lower impact from kinetics. The required reboiler duty and the temperature in the reboiler are determining factors when process integration is considered and hence of great interest for this study.

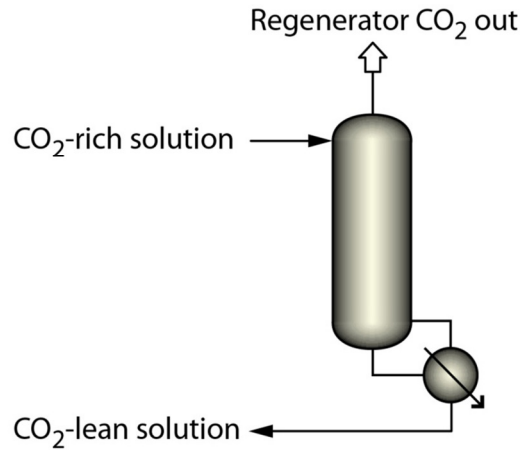


Figure 16. The packed CO₂ regenerator column is modelled using Aspen RadFrac block.

The regenerator has one inlet stream, the CO₂-rich stream from the bottom stage of the absorber. The CO₂-lean stream leaving the regenerator at the bottom is recycled back to the absorber for further absorption. The working pressure in the regenerator is 30 bar, allowing for desorption of CO₂ whilst preventing vaporization of water and ammonia. The CO₂ stream leaving the regenerator through the top contains a high percentage of CO₂ mixed with water and ammonia. The water and ammonia in the stream can then be removed using a flash tank. The design parameters for one exemplified case with 4 vol% CO₂ concentration are presented in Table 10.

Table 10. Simulation technical design specifications and properties of the CO₂ regenerator for a 4 vol% CO₂ concentration case with 6.59 mol NH₃/kg H₂O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be seen as actual design parameters.

Bottom cycle regenerator design specifications					
Pressure			30	[bar]	
Number of stages			(15)	[-]	
Regenerator stream properties	Stage	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/s]	
Regenerator CO ₂ out	1	182.9	30	5.70	
Reboiler temperature			212.7	[°C]	
Reboiler duty			13.9	[MW]	
Reboiler duty / kg of CO ₂ captured			3 337	[kJ/kg CO ₂ captured]	
Composition					
Regenerator CO ₂ out	N ₂	O ₂	CO ₂	H ₂ O	NH ₃
wt %	1.410 ⁻²	9.1·10 ⁻³	73.0	20.4	6.5

5.2.4. NH₃ Scrubbing Cycle

Much like the bottom cycle, the top cycle is modelled with an absorber and regenerator as main components. The top cycle, illustrated in Figure 17, is simulated with a stand-alone model but with the inlet stream specified to have properties and flow rates equal to the absorber off-gas stream in the bottom cycle.

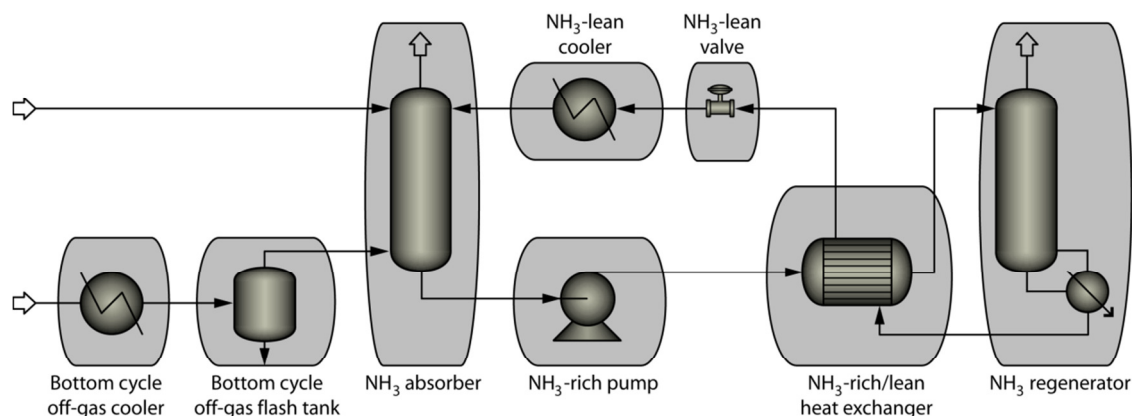


Figure 17. Illustrative process flow chart describing the NH₃ scrubbing cycle model.

The function of the top cycle is to clean the bottom cycle off-gas from ammonia slip, leaving the final off-gas free from harmful concentrations of ammonia. The NH₃ regenerator reboiler duty is varied to achieve a final ammonia slip of between 5-15 ppmv from the top cycle absorber, as suggested by Mathias, Paul M et al. (15).

The top cycle NH₃ absorber illustrated in Figure 18 is like its bottom cycle counterpart, modelled as a rate-based packed column. The internal column design parameters needed for rate-based calculations are presented for the same case as in the bottom cycle, with 4 vol% CO₂ concentration, in Table 11. The off-gas from the bottom cycle is cooled, flashed and introduced at the last stage of the NH₃ absorber. The NH₃-rich and lean streams leaves and enters the top cycle absorber in the top and bottom stage respectively. Water lost from the top cycle through the absorber and regenerator off-gas is balanced with a water make-up stream introduced directly at the top of the absorber.

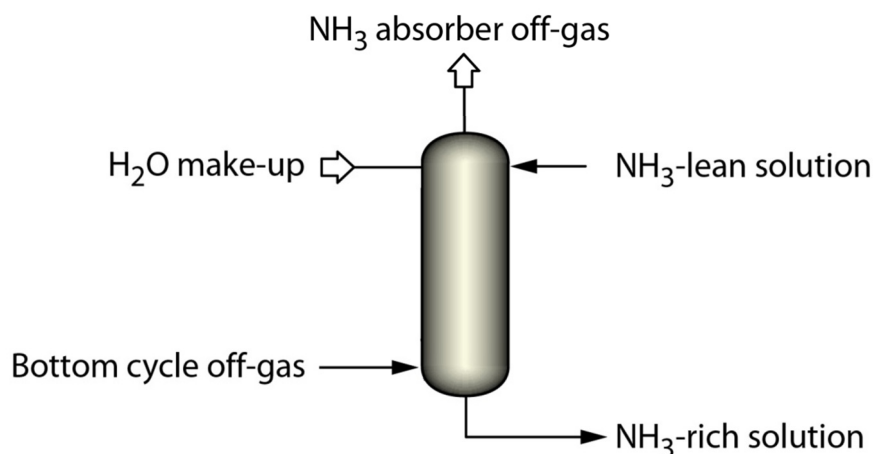


Figure 18. The packed NH₃ absorber column is modelled using Aspen RadFrac block.

Table 11. Simulation technical design specifications and properties of the CO₂ absorber and its connecting streams for a 4 vol% CO₂ concentration case with 6.59 mol NH₃/kg H₂O. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be seen as actual design parameters.

Top cycle absorber design specifications					
NH ₃ absorber height		(60)		[m]	
NH ₃ absorber diameter		6.5		[m]	
Pressure		1.0132		[bar]	
Number of stages		(30)		[-]	
Packing type/material		(Pall ring/Metal)		[-]	
Packing size		(16)		[mm]	
NH ₃ absorber stream properties	Stage	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/s]	
Bottom cycle off-gas inlet	30	5	1.0132	78.11	
NH ₃ absorber off-gas	1	5.01	1.0132	77.56	
H ₂ O make-up	1	5	1.0132	4.94	
Composition					
NH ₃ absorber off-gas	N ₂	O ₂	CO ₂	H ₂ O	NH ₃
wt%	75.63	23.76	$5.8 \cdot 10^{-2}$	0.55	$5.9 \cdot 10^{-4}$

The top cycle regenerator, illustrated in Figure 19, is an Aspen RadFrac equilibrium model of a packed column. Together with the bottom cycle reboiler, the required top cycle reboiler duty and temperature are of interest when considering process integration. The off-gas leaving the NH₃ regenerator consists of mainly water and ammonia. No further treatment is considered in the model and it is assumed that the off-gas stream is flashed and the resulting ammonia stream is return back into the system, reducing need for and ammonia make-up. The properties of the top cycle regenerator are presented in Table 12.

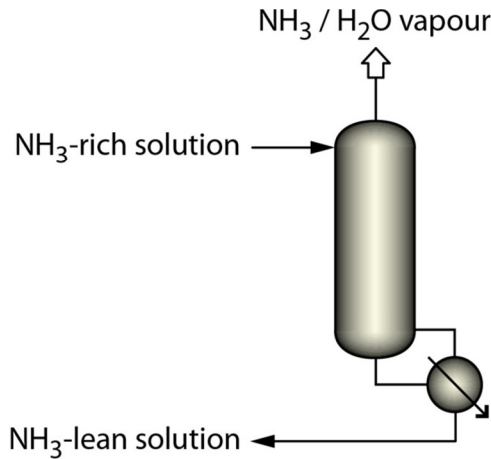


Figure 19. The packed NH₃ regenerator column is modelled using Aspen RadFrac block.

Table 12. Simulation technical design specifications and properties of the NH_3 regenerator for a 4 vol% CO_2 concentration case with 6.59 mol $\text{NH}_3/\text{kg H}_2\text{O}$. Numbers in brackets indicate parameters chosen for model stability and convergence and should not be seen as actual design parameters.

Top cycle regenerator design specifications		
Pressure	1.5	[bar]
Number of stages	(15)	[-]
NH_3 regenerator reboiler properties		
Reboiler temperature	111.3	[°C]
Reboiler duty	16.2	[MW]
NH_3 reboiler duty / kg of CO_2 captured in bottom cycle	3 891	[kJ/kg CO_2]

5.2.5. Auxiliary Equipment

The auxiliary equipment includes the supporting equipment not directly coupled with the CO_2 absorption/desorption and NH_3 abatement. The components for the bottom and top cycles are in general modelled in the same way, sharing most of the settings.

- Rich solvent pumps**
 The pump is modelled as a pressure changer, increasing the pressure from the atmospheric pressure of the bottom and top cycle absorbers to the 30 and 1.5 bar respectively, the working pressures of the regenerators. No losses or efficiencies are considered when modelling the pump.
- Rich/lean solvent heat exchangers**
 The process internal heat exchangers are modelled with the Aspen HeatX heat exchanger block. The stream flow direction is set to countercurrent flow and the minimum hot outlet temperature approach is specified to 10°C as suggested by Kothandaraman, A (29) and Mathias, Paul M et al. (15). The model uses the shortcut calculation method and therefore no internal heat exchanger design specifications are needed.
- Lean valves**
 The lean valves are pressure changers, decreasing the pressure in the bottom and top cycles from 30 and 1.5 bar respectively back to atmospheric pressure. Adiabatic flash calculation is used for the specified outlet pressures.
- Coolers**
 Coolers are used to cool the CO_2 -lean and NH_3 -lean streams down to the desired absorber inlet temperature of 5°C, applicable for both the bottom and top absorber. Another cooler is used to cool the bottom cycle off-gas to 5°C. The bottom cycle off-gas cooler helps keeping the temperature in the top cycle absorber down and increases the effect of the bottom cycle off-gas flash tank by facilitating for more water vapour to be flashed to liquid. The coolers are modelled with the Aspen heater/cooler block, assuming no pressure loss and a specified outlet pressure of 5°C.
- CO_2 -lean splitter**
 The CO_2 -lean splitter is needed to enable the returning lean stream to be introduced to different stages in the bottom cycle absorber, helping with the convergence and improving the absorber temperature profile. The CO_2 -lean splitter splits the CO_2 -lean stream into two equally large flows and introduces them to the absorber at stages 1 and 5.
- Bottom cycle off-gas flash tank**
 The bottom cycle off-gas is flashed before it is introduced into the top cycle absorber. The concentration of ammonia in the off-gas stream is reduced by flashing water vapour into liquid and draining it, also removing the ammonia dissolved in the water. The stream is flashed at 5°C and atmospheric pressure.

6. Results

6.1. CO₂ Capture Cycle

It is rather complex to present how reboiler duty is affected by CO₂ concentration only, since several other variables also come into play. Total solvent flow and CO₂ loading in the absorber are also investigated in order to explain what parameters affect reboiler duty except from CO₂ concentration. Ammonia slip is also of interest, as it affects the total system reboiler duty.

The effects of absorber CO₂ loading and solvent mole flow are shown in Figure 20. There is a tendency for reboiler duty to increase with increased absorber CO₂ loading. Because there is less free ammonia available with higher absorber CO₂ loading, the CO₂ loading in the lean stream entering the absorber has to be lower. The driving force for the absorption reaction will otherwise decrease due to decreased difference in concentration between CO₂ and NH₃, causing less CO₂ to be absorbed if other parameters are kept constant. The difference in reboiler duty is rather small, generally within 500 kW for a given solvent flow. It can also be noted that there for most cases is a slight increase in reboiler duty with increased solvent flow. The mole flow of ammonia is constant throughout each absorber CO₂ loading case, why the concentration decreases with increased total solvent mole flow; leading back to the same reasoning about driving force. Because the total solvent flow is increased, there is also more liquid to heat in the reboiler.

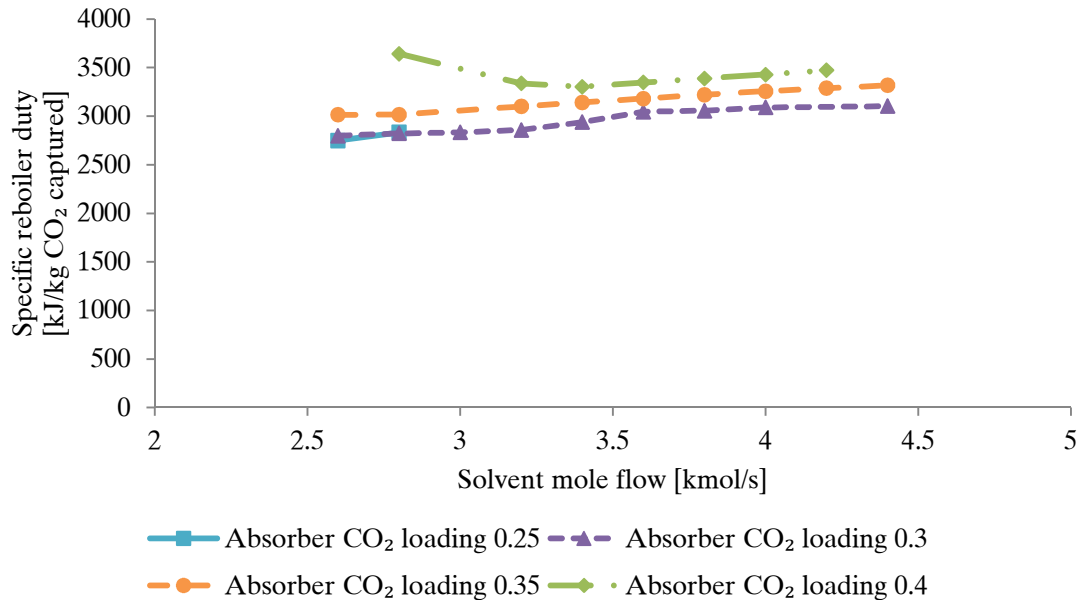


Figure 20. Reboiler duty per unit mass of captured CO₂ shown for different lean stream loadings and grouped by total solvent flow. The data shown is for the 7% CO₂ Hydro case.

The simulations show that, for a given absorber CO₂ loading, specific reboiler duty generally decreases with increased CO₂ concentration. It is however possible that there might be a concentration where the reboiler duty is at a minimum as the simulation results, shown in Figure 21 and Figure 22, hint that reboiler duty might increase for the 15% CO₂ case compared to the 10% CO₂ case. The explanation to this could be that the residence time in the absorber is not sufficient in the 15% case. The absorption reaction is known to be slow, why this could be the limiting factor, forcing the CO₂ loading in the lean stream to be lower and thereby increasing the amount of free ammonia in the 15% case compared to 10% case. Alas, this theory has to be rejected based on the simulation results as the lean stream CO₂ loading on an average is higher in the 15% case than in the 10% case. Instead, the reason is believed to be that the concentration of ammonia in the CO₂ out stream is unproportionally high in the case of 15% CO₂ concentration compared to the lower ones, see Figure 23. Closer examination of the cases makes it possible to deduct where the required reboiler duty originates from. The major contribution is the sensible heat needed to heat the water in the reboiler, followed by the heat of reaction for the absorption reactions. When looking at the required heat per kg CO₂ captured, it was found that the sensible heat decreases more than what the heat of reaction increases, with the exception of the 15% case.

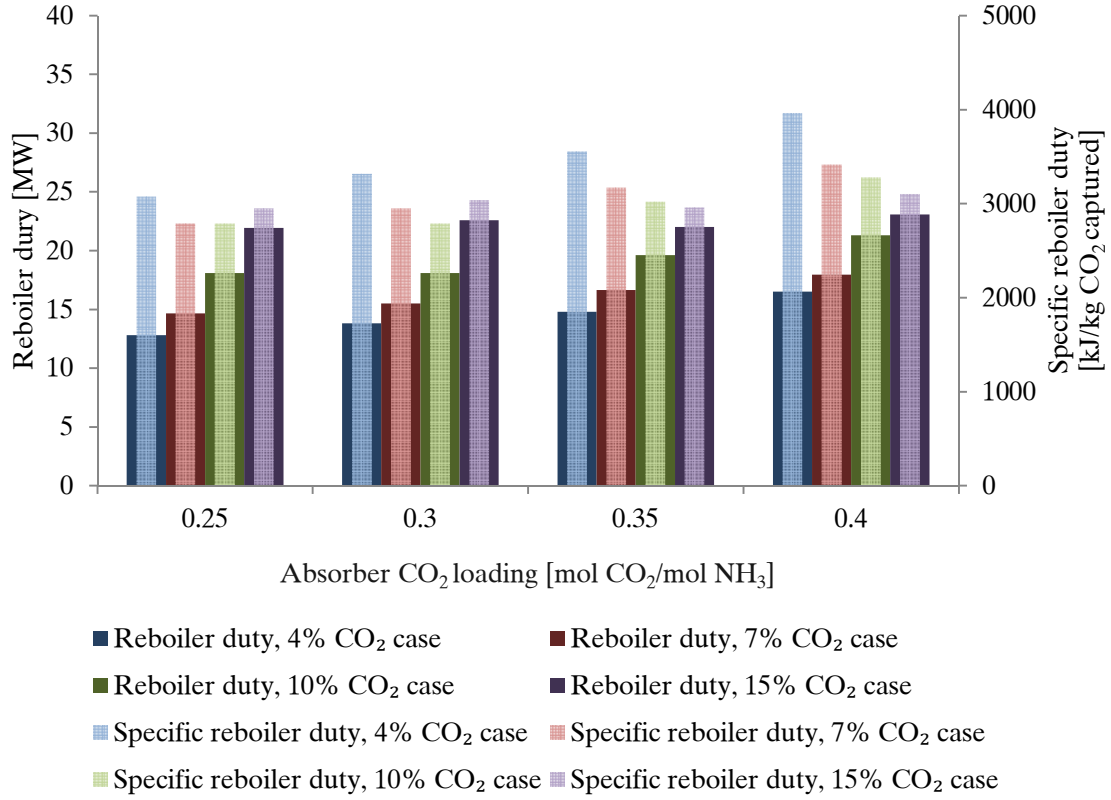


Figure 21. Reboiler duty averaged for different solvent flows, grouped by absorber CO₂ loading, Hydro case.

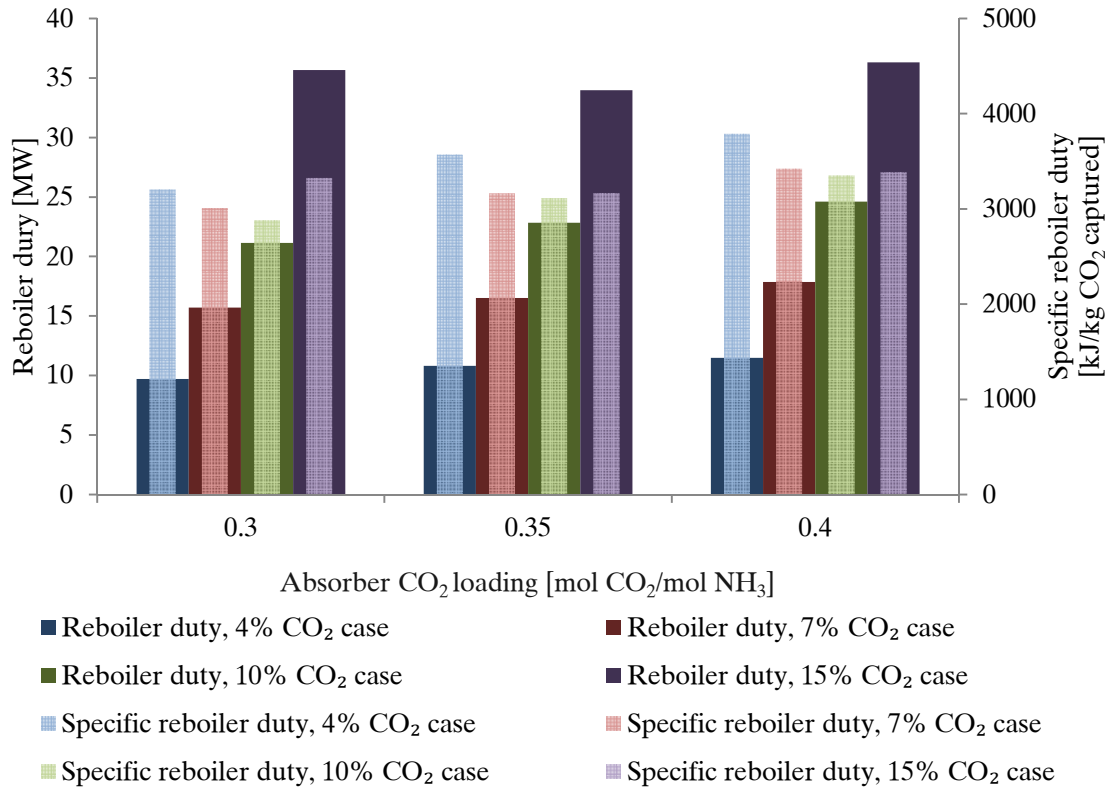


Figure 22. Reboiler duty averaged for different solvent flows, grouped by absorber CO₂ loading, constant flow case.

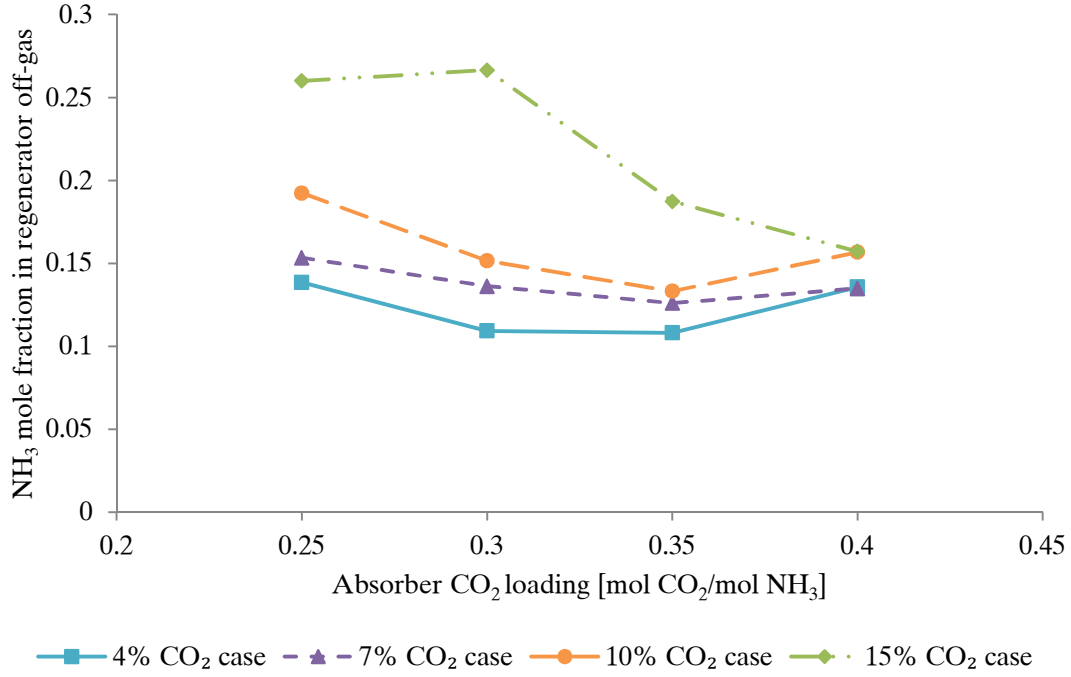


Figure 23. Mole fraction ammonia in the stream leaving the bottom cycle regenerator, Hydro case.

Slip from the absorber is of great significance due to legislation limiting the allowed ammonia concentration out from the system. The configuration also encompasses a separate top cycle designed to reduce ammonia slip to within legal limits. Figure 24 and Figure 25 show that absorber slip increases significantly with increasing NH_3 molality, and thus with increasing CO_2 concentration. This is believed to be because of the higher ammonia vapour pressure due to increased concentration.

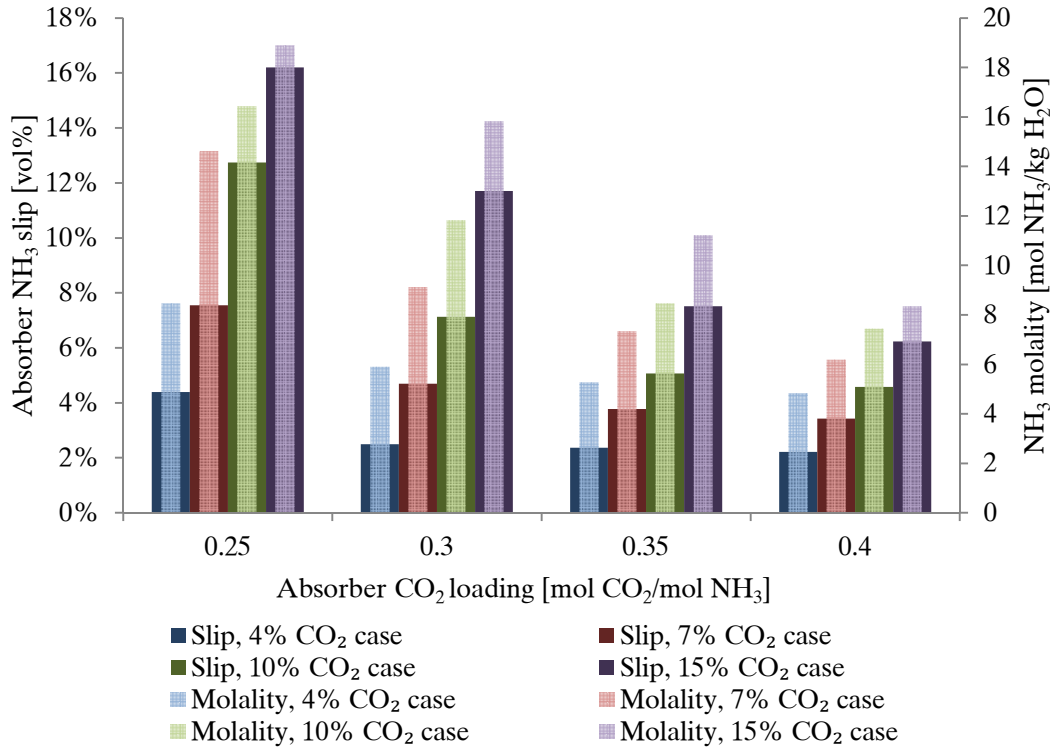


Figure 24. Ammonia slip from the absorber, Hydro case.

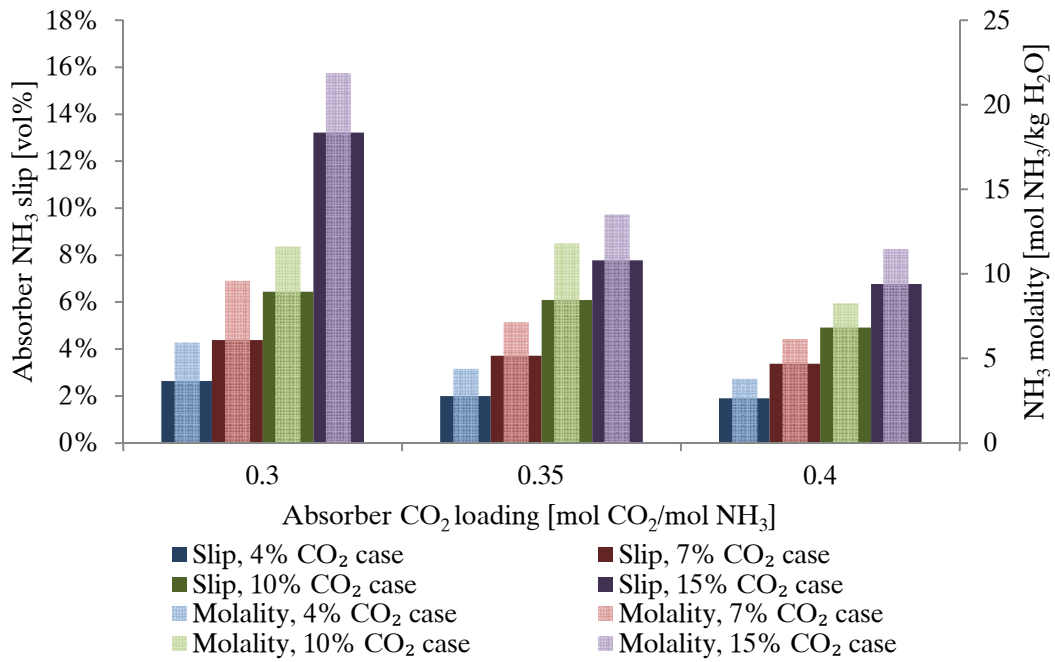


Figure 25. Ammonia slip from the absorber, constant flow case.

An important parameter when looking at ammonia slip is the lean stream CO_2 loading, shown in Figure 26. The results clearly show a decrease of slip with increased lean stream loading in the higher absorbent CO_2 loading cases, as could be expected. When absorber CO_2 loading decreases, the effect is more unclear. It could be expected due to the large increase of solvent NH_3 molality as seen in Figure 24 and Figure 25, causing higher ammonia partial pressure and counteracting the effect.

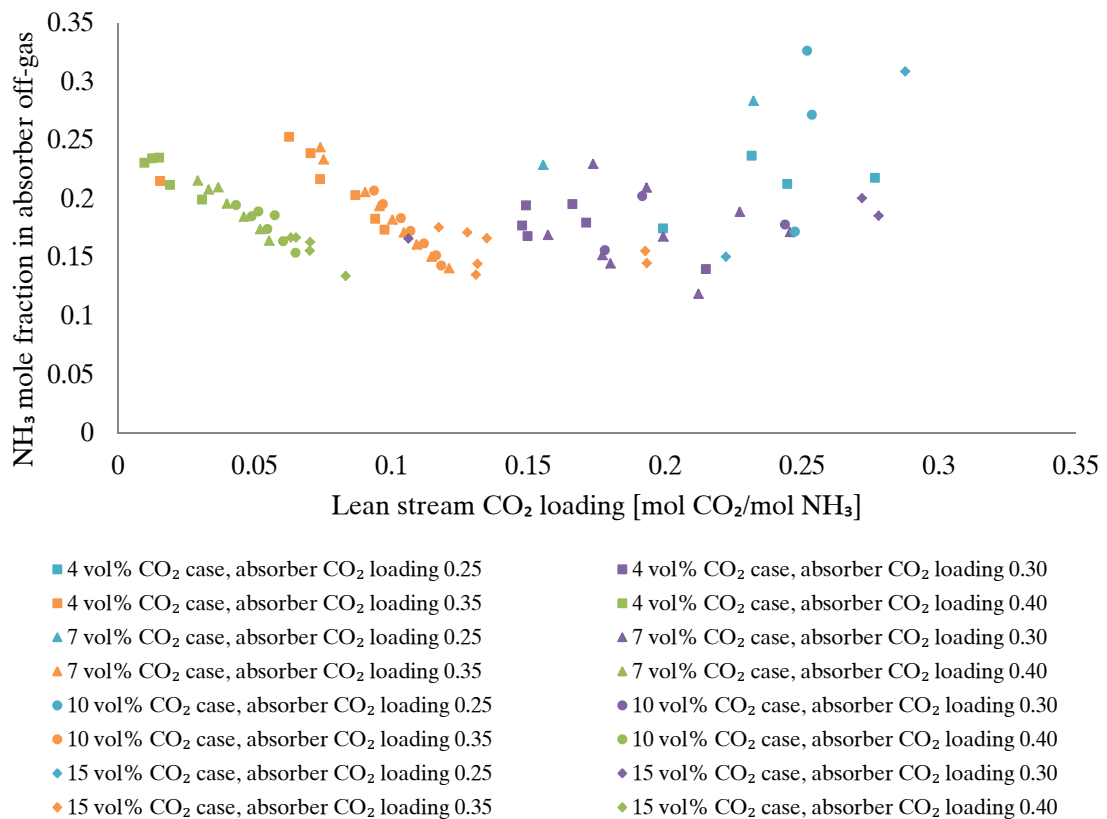


Figure 26. Ammonia slip from absorber with respect to lean stream CO_2 loading, Hydro case.

The temperature in the absorber is to be held below 20°C for good performance and preferably under 10°C for optimal performance. These figures are unfortunately not always achieved, and absorber temperature can reach values close to 35°C in some cases, in despite of solvent intercooling.

Results from the simulations show no correlation between high or low discharge within the span in terms of reboiler duty. A small change in reboiler duty resulted in the ammonia concentration moving outside the chosen discharge span, which also explains the convergence problems experienced with fixed discharge concentration. A high or low ammonia discharge concentration within the chosen span was found to have an insignificant effect on the top cycle reboiler duty in relation to effects caused by other parameters.

One case has been studied more in detail to determine the purity of the CO₂ stream leaving the system. The stream out of the regenerator contains about 42.5% H₂O, 10.8% NH₃ and 46.7% CO₂ along with traces of other species. After being flashed the vapour stream contains 99.9% CO₂ and the other species follow the liquid stream back into the system.

The performance of the top cycle is dependent on the characteristics of the bottom cycle. Figure 27 shows a slight trend of increasing total top cycle reboiler duty with increasing CO₂ concentration. The increased reboiler duty is caused by the increased ammonia slip from the bottom cycle at higher CO₂ concentrations. This requires more vaporization of ammonia in the regenerator in order to reach the specified discharge level. Increasing vaporization of ammonia also leads to increased vaporization of water which, as seen in Figure 28, is the main contributor to the required reboiler duty.

Figure 27 also shows a slight decrease in reboiler duty with increasing bottom cycle absorber CO₂ loading. This is to be expected since, as described previously, higher absorber CO₂ loading results in lower ammonia slip. Some values in Figure 27 are missing due to that those cases did not converge when running the simulations.

The specific reboiler duty relates the top cycle reboiler duty to the amount of CO₂ captured in the bottom cycle. As shown in Figure 27, the top cycle specific reboiler duty decreases with increasing CO₂ concentration, this is most apparent for the 0.35 mol CO₂/mol NH₃ cases. The result indicates that the increased CO₂ capture in the bottom cycle outweighs the effect of increased slip caused by the increasing CO₂ concentration. Higher CO₂ concentration will consequently result in lower top cycle reboiler duty per unit of CO₂ that is captured.

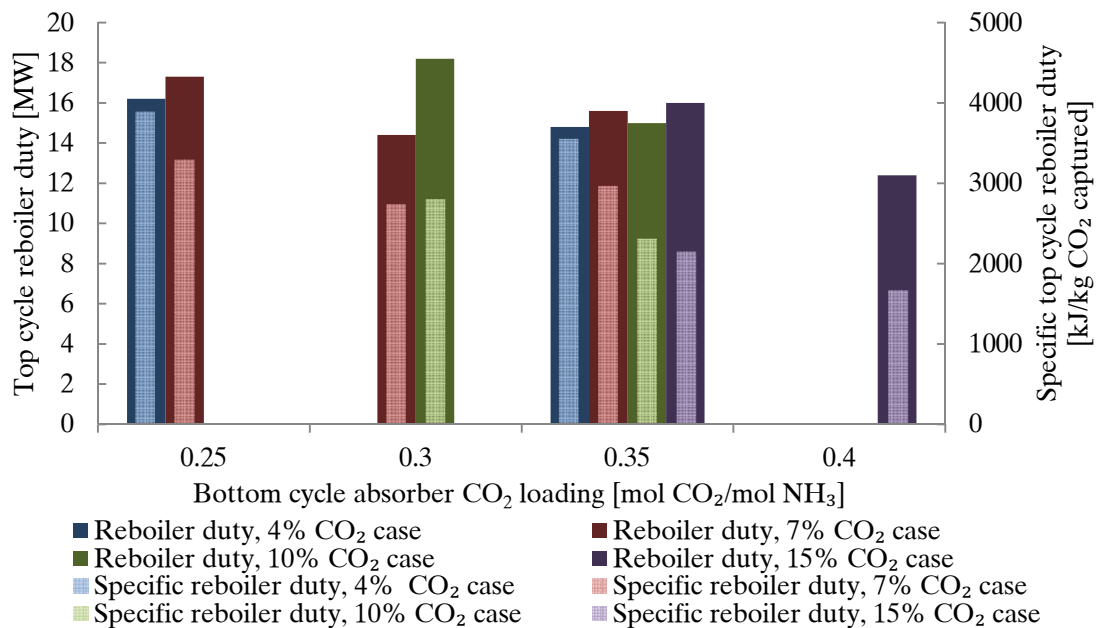


Figure 27. Top cycle reboiler duty and specific reboiler duty. Specific reboiler duty relates the reboiler duty to the amount of CO₂ captured in the bottom cycle. Some values are missing due to non-convergent simulations.

In Figure 28, it is studied where the required reboiler duty originates from. The main contribution to the top cycle reboiler duty is the vaporization of water with 65% on average of the total reboiler duty. Part of the difference in reboiler duty between the various cases can be explained by the amount of heat that is recovered in the rich/lean heat exchanger. The heat recovered depends on the NH_3 -lean stream flow rate leaving the regenerator and the temperature and flow rate of the rich stream.

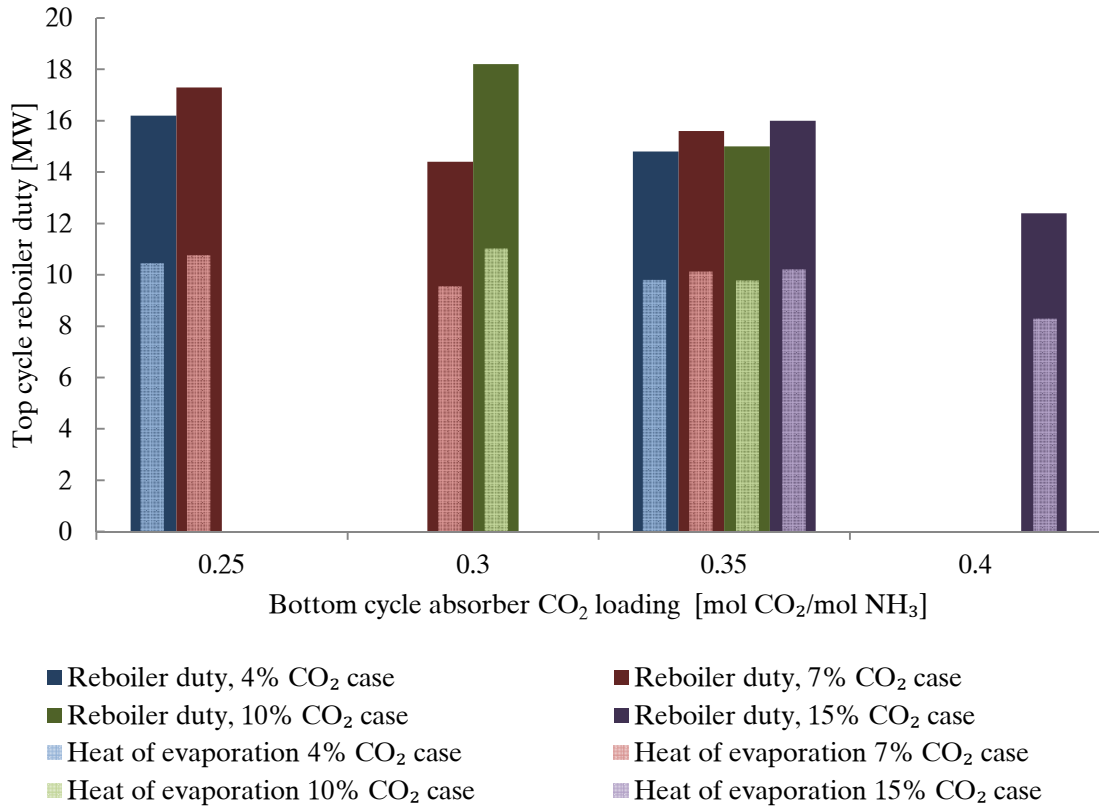


Figure 28. Heat of evaporation for water in the regenerator related to the reboiler duty. Some values are missing due to non-convergent simulations.

There is need for cooling in both top and bottom cycles. Cold water has to be supplied to the CO_2 absorber, the bottom cycle lean stream cooler, the top cycle process gas cooler and the top cycle lean stream cooler. The total cooling needs for bottom and top cycle are presented in Figure 29 and Figure 30 respectively. It is clear that the need for cooling in the bottom cycle increases with increasing CO_2 concentration and decreases with increased absorber CO_2 loading. This is logical since the absolute amount of CO_2 is increasing with concentration, meaning that more exothermic reactions are occurring when more CO_2 is captured in the system. When looking at the cooling duty per unit mass of CO_2 captured, it can be seen that it only varies slightly. The cooling requirement in the top cycle also increases with increasing CO_2 concentration. This can be related to that ammonia slip is generally higher at higher CO_2 concentrations. Since dissolution of ammonia in water is exothermic, the ammonia rich stream out from the absorber will be of a higher temperature the higher the amount of ammonia. It can then not be heated as much in the process internal heat exchanger, resulting in less heat extraction from the ammonia lean stream coming from the regenerator. Thus, the ammonia lean stream will have to be cooled further. When looking at the specific top cycle cooling requirement in Figure 30, it is unclear how it varies with CO_2 concentration.

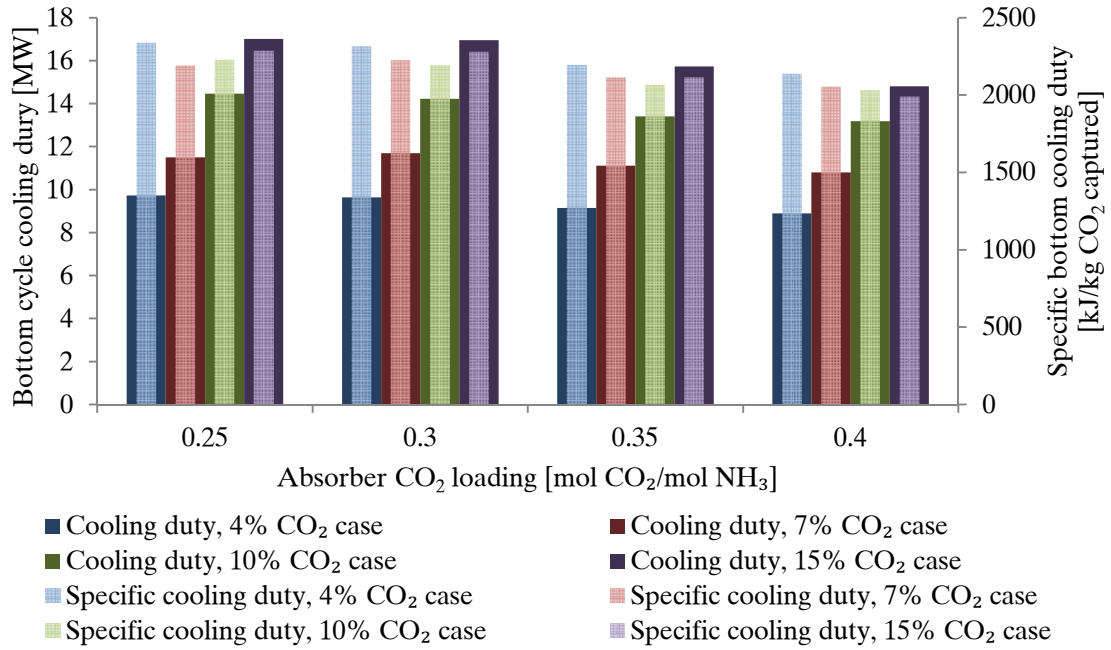


Figure 29. Bottom cycle cooling need, Hydro case.

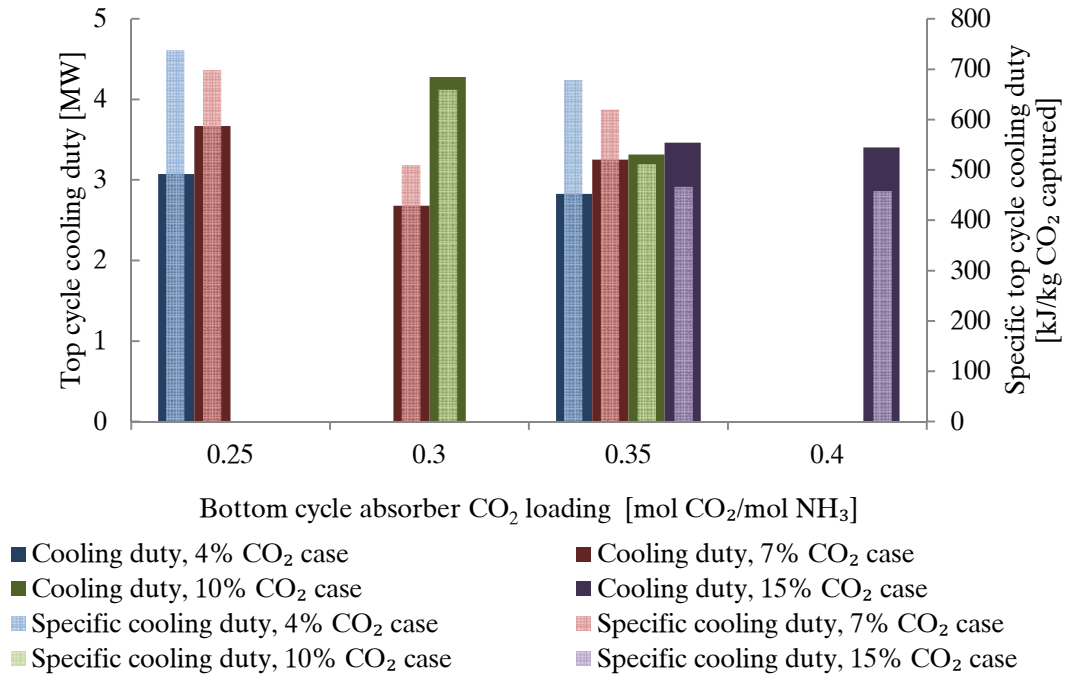


Figure 30. Top cycle cooling need, Hydro case. Some values are missing due to non-convergent simulations.

The CO₂ capture model is compared with similar studies made of the CAP. In Figure 31, results for the reboiler duty required to capture 1 kg of CO₂ is plotted and compared with results from Jilvero et al. (30) and Darde et al. (16). It should be noted that the results presented in Figure 31 only considers the bottom cycle and represent studies made with great differences in input data compared to this study. Jilvero et al. studies a coal combustion process with 19.9% CO₂ concentration whiles this study is made considering significantly lower concentrations. Both compared studies also use the Aspen Plus software to model the CO₂-NH₃-H₂O system. However, both Jilvero et al. and Darde et al. assume vapour-liquid-solid equilibrium for their models. This study applies rate-based calculation, described in Chapter 0, for the absorber which is an effort towards more accurately describing the actual process. However, it is apparent that the model follows the same overall trend as the compared results, with decreasing reboiler duty for higher NH₃ molality of the solvent.

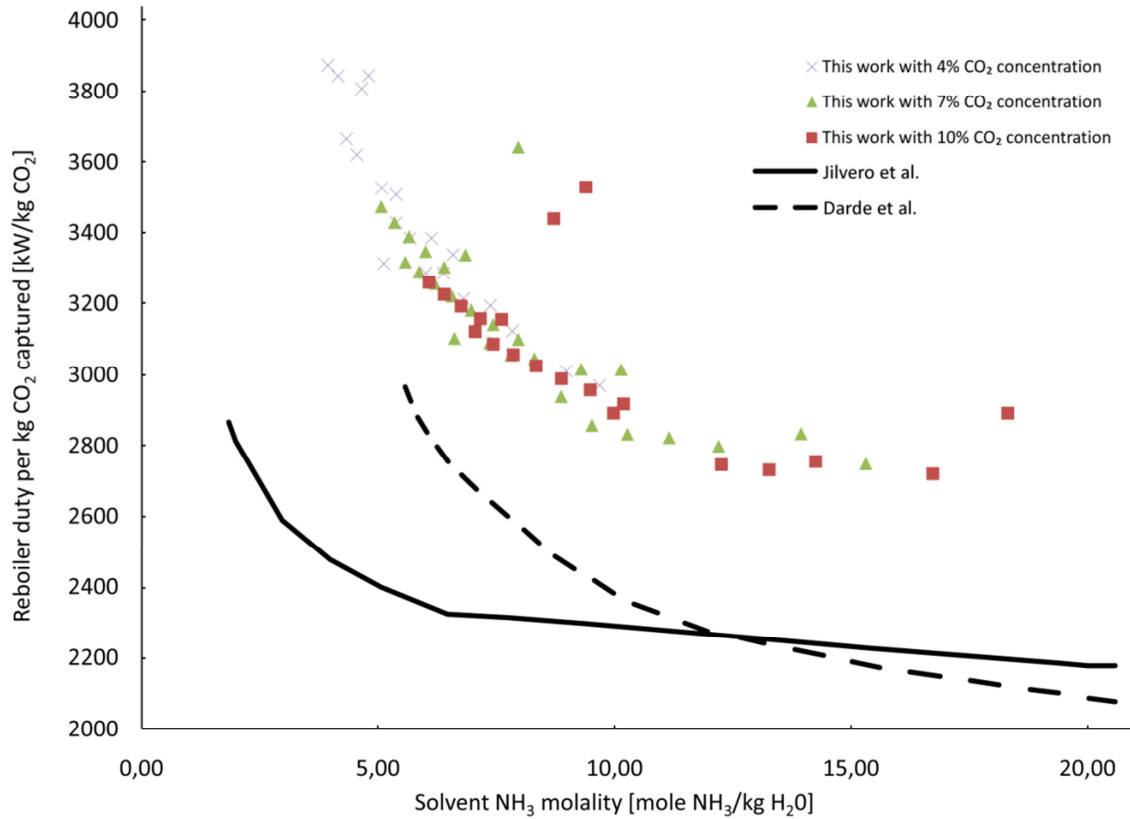


Figure 31. The required reboiler duty for different NH_3 molality. A comparison between results from this study and studies made by Jilvero et al. (30) and Darde et al (16).

6.2. Process Integration of the CAP

The proposed heat integration is made with heat exchangers in the beginning of the gas treatment train. The temperature of the process gas is highest directly after the cells, providing good conditions for making sufficient temperature heat available for process integration. The high and low temperature water is circulated between the process integration heat exchangers and the CO_2 capture cycle reboilers, supplying heat to the process.

The process gas flow rate varies with the CO_2 concentration, hence affecting the amount of heat that can be extracted for process integration and district heating. The working temperatures for the top and bottom cycle reboilers are given by the CO_2 capture simulations. The minimum required temperatures are by the simulations determined for each of the chosen cases for the top and bottom cycle respectively. The reboilers operate at constant temperature, resulting in a required process gas temperature of at least the reboiler operating temperature to be useful for integration. The top cycle reboiler working temperature is 111°C , the boiling point of water at 1.5 bar, for all the considered cases. The bottom cycle reboiler working temperature is found to vary significantly in between the different cases. The bottom cycle reboiler temperature for the cases chosen for process integration is presented in Table 13.

Table 13. Top and bottom cycle reboiler temperature for different CO_2 concentrations.

CO_2 concentration [vol% CO_2]	4 vol%	7 vol%	10 vol%	15 vol%
Bottom cycle reboiler temperature [$^\circ\text{C}$]	196.5	194.4	204.7	207.5
Top cycle reboiler temperature [$^\circ\text{C}$]	111.4	111.4	111.4	111.4

Results from the process gas treatment train simulations are presented in Figure 32 and Figure 33 for the different investigated CO_2 concentrations. Low CO_2 concentration is associated with lower process gas temperature and higher flow rate, section 0. If the 4 vol% CO_2 concentration case is considered, roughly 7.4 MW of low temperature heat is available for integration of the top cycle whilst the bottom cycle is supplied with 7.3 MW of high temperature heat. With increasing CO_2 concentration, more high temperature heat is made available due to higher process gas

temperature out from the cells. However, the lower process gas flow results in decreasing low temperature heat available for process integration. The total of amount of useful heat for process integration is decreased with increasing CO₂ concentration, Figure 32. This however, does not take into account the quality of the heat. Heat at higher temperature is of higher grade, requiring more energy and is more costly to produce, than heat at the temperature required in the top cycle reboiler.

The change in flow rate has the same effect on amount of heat that can be extracted for district heating, a total reduction from 2.5 to 1.2 MW with CO₂ concentration increasing from 4 to 15 vol%.

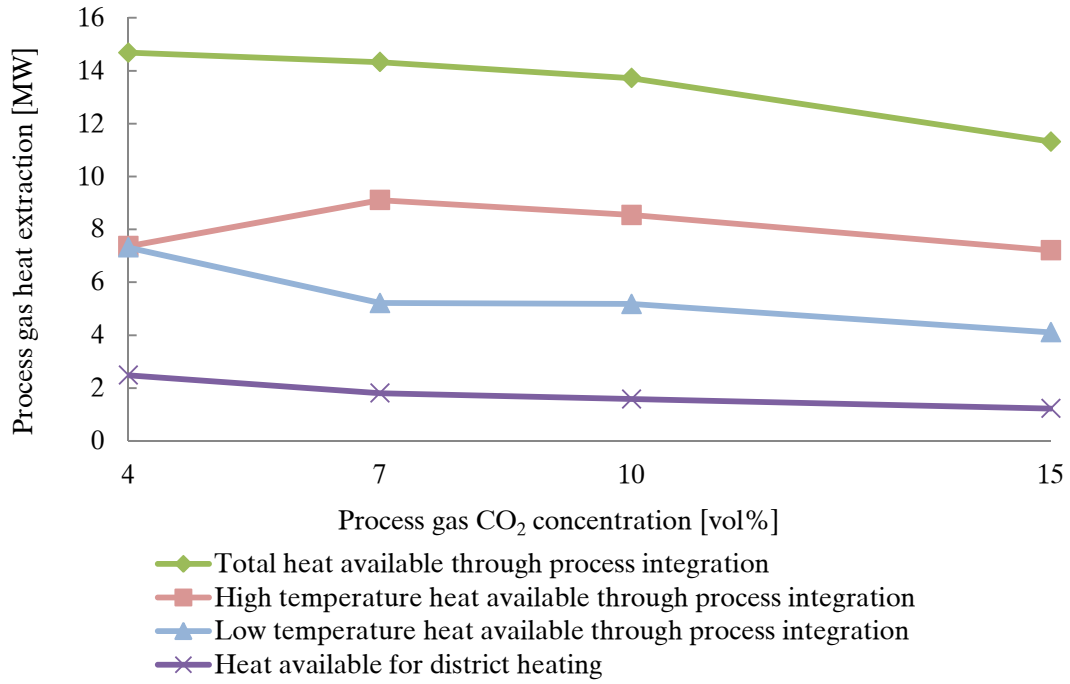


Figure 32. District heating, low and high temperature heat extraction available for process integration given different CO₂ concentrations ranging from 4 to 15 vol%.

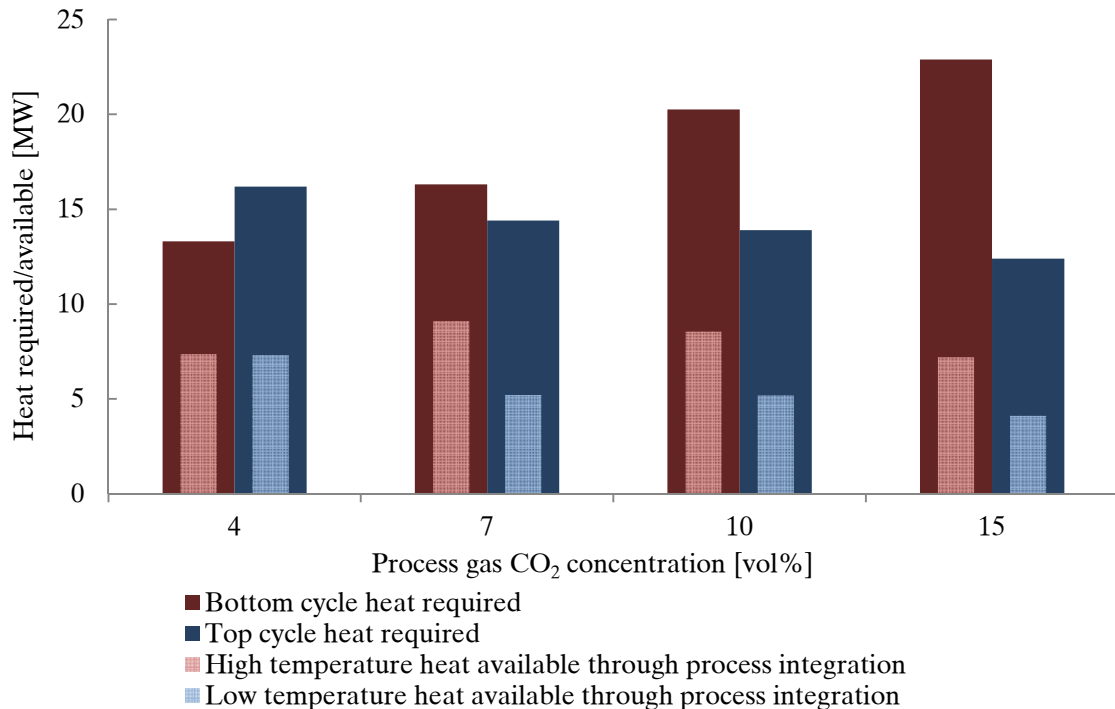


Figure 33. Top and bottom cycle heat requirements compared to the available heat from process integration.

Figure 33 presents the required heat for the top and bottom cycle, compared to the available heat from process integration. The increase in bottom cycle reboiler duty is expected since the CO₂ content in absolute terms increases with CO₂ concentration and thus, more CO₂ is captured. When the cases with lowest required reboiler duty for the total process are considered, the top cycle reboiler duty decreases with increasing CO₂ concentration. This is surprising since the general trend is an increasing ammonia slip with increasing CO₂ concentration. The decrease in the top cycle reboiler duty is however not as prominent as the increase in the bottom cycle, resulting in an overall increase of total cycle reboiler duty. The available heat from process integration will, according to Figure 33, not be enough to supply the top or bottom cycle with sufficient heat to fully integrate the CO₂ capture process. In order for the process to reach 85% CO₂ capture, additional heat, presented in Table 14, from external heat sources or further process integration is needed. Table 14 also shows that the largest share of heat integration is achieved for the 4 vol% case and then declining as the CO₂ concentration is increasing. For HAL Ultra design with 4 vol% CO₂ concentration, roughly 50% of the total heat requirements are satisfied by process integration. About 45% of the additional heat required is high grade heat needed for the bottom cycle.

Table 14. Additional heat requirements and the share of required heat that is supplied by process integration.

CO ₂ concentration [vol% CO ₂]		4 vol%	7 vol%	10 vol%	15 vol%
Bottom cycle	Additional heat required [MW]	5.93	7.19	11.72	15.68
	Share of heat integration	0.55	0.56	0.42	0.31
Top cycle	Additional heat required [MW]	8.89	9.19	8.72	8.29
	Share of heat integration	0.45	0.36	0.37	0.33
Total process	Additional heat required [MW]	14.82	16.38	20.44	23.97
	Share of total heat integration	0.50	0.47	0.40	0.32

Higher process gas temperature pose problems for existing downstream equipment. Investments in new equipment capable of handling higher temperatures can be made. Alternatively, heat from the process gas stream can be cooled away to meet temperature requirements. However, the proposed process integration allow for further use of existing equipment, displacing the cost of process gas treatment investments.

7. Conclusions

In this work, the process integration of CO₂ capture in a novel aluminium manufacturing plant, using the CAP, has been studied. Heat extractions for process integration could be proposed and studied through combining simulations made of both the CAP and the process gas treatment train. It was found that the process gas contains sufficient heat for partial process integration of the CAP for the specified CO₂ capture rate. It was also examined how reboiler duty is affected by CO₂ concentration alone.

The CO₂ capture process was simulated using Aspen Plus with a rate-based approach to the absorption reactions and an equilibrium approach for the regeneration. Because ammonia slip from the absorber is very high, more than 100 000 ppmv in some cases, an ammonia absorption cycle had to be implemented. The results from top and bottom cycle simulations were used as basis for process integration. The amount of heat that can be extracted from the HAL Ultra process was calculated using Epsilon Professional. The amount of heat that can be extracted was divided into two temperature levels for the two absorption cycles respectively.

The results from the process integration study showed that only a partial integration of the CAP can be achieved for all investigated CO₂ concentration cases. The highest share of heat demand covered through process integration, providing 50% of the required heat, was achieved for the 4 vol% CO₂ concentration case which was the lowest CO₂ concentration studied. Lower process gas flow rate for the higher CO₂ concentrations had negative effects on the amount of heat that could be extracted, offsetting the extra heat gained from increasing temperatures. This, combined with a large increase of bottom cycle specific reboiler duty, lead to the conclusion that the share of heat demand that can be covered by process integration decreases with increasing CO₂ concentration.

The result of the analysis of the CAP was that specific reboiler duty is lowered with increased CO₂ concentration, which was expected. What was not as expected is that the effect might not be so great that it, from a heat integration point of view, is profitable to increase the CO₂ concentration in the HAL Ultra process. The increased amount of CO₂ and reduced mass flow rate of process gas increases the reboiler duty and decreases the heat available from process integration respectively. It was also found that reduced solvent flow rate in the CO₂ capture cycle reduces reboiler duty. However, reduced solvent flow rate means increased NH₃ molality, which leads to higher ammonia slip. Higher ammonia slip in its turn, leads only to moderate change in reboiler duty in the NH₃ capture. The reboiler duty requirement was in the range of 2 800-4 000 kJ/(kg CO₂ captured) for the bottom cycle and 1 700-3 900 kJ/(kg CO₂ captured) for the top cycle.

The recommendation based on the results presented in this work is that the CO₂ capture process as a whole should be looked into more in depth before designing the final HAL Ultra process. The heat requirement for capturing CO₂ is not as obvious as could be expected. A high CO₂ concentration and low process gas flow rate means that smaller CO₂ capture equipment can be used, resulting in a lower total cost of investment. The higher share of heat integration, and thus lower operational costs, achieved for low CO₂ concentrations might however compensate for some or all of the increased investment cost due to large process gas flow rates and low CO₂ concentration. The key to achieving a low total cost is to find an optimal CO₂ concentration and solvent flow rate-based on equipment cost as well as reboiler duty in the CO₂ and NH₃ capture cycles together. Even if the required heat demand is optimized for the CO₂ capture cycle, it might not be low enough to be completely supplied by surplus heat. A recommendation with regard to this is to either integrate with waste heat from other parts of the aluminium manufacturing process. Directing the process gas through a gas turbine after cleaning it from ashes would increase the CO₂ concentration as well as supply heat for the CO₂ capture process and electricity for the aluminium production units.

The decrease in heat available for the local district heating network could, if replaced by fossil fuels, potentially off-set some of the captured CO₂. The decrease in available district heating is however not affected by the process integration itself, but the lower process gas flow rate required for achieving the higher CO₂ concentrations. There are potential locations for extracting heat at sufficient temperatures to increase the heat supplied for district heating, the CO₂ stream out from the bottom cycle regenerator being one. Additional gas treatment trains can also be fitted with heat exchangers to make up for the lost district heating supply, only one is presently used. It must

however be considered that the demand for district heating in Sunndalsøra is limited to the population of 4 000-5 000 currently residing in the village and thereby no significant off-set of greenhouse gas emissions from decreased use of district heating can be expected from integration of CO₂ capture at the plant.

In addition to varying CO₂ concentration, solvent flow rate, ammonia concentration and CO₂ capture rate should also be investigated in order to ensure the most cost-effective solution. An increased CO₂ capture rate would lead to lower lean stream loading; increasing ammonia slip. It would however also result in more ammonia bound in chemical compounds in the absorber. The total top and bottom cycle reboiler duty would probably increase in absolute numbers but the duty per unit mass of CO₂ captured might decrease thanks to the increased amount of CO₂ captured in the cycle. Another factor is the cost of CO₂. If it is high enough, it would possibly be economically beneficial having a higher capture rate even though the capture system investment and running costs increase.

A possibility which should be researched further is to integrate the CO₂ capture process with capture of HF. The reaction between ammonia and HF forms ammonium hydrogen fluoride, a salt at room temperature. There is a possibility of cleaning the flue gas from HF with ammonia before it enters the CO₂ absorber, as ammonia contamination of the flue gas would not matter. Another side effect which should be looked into further is the capture of SO₂ with ammonia, either before the CO₂ capture cycle or in it. Ammonia and SO₂ can form diammonium sulphide or ammonium bisulphide, possibly eliminating the need for other SO₂ cleaning equipment.

8. References

1. **IEA Greenhouse Gas R&D Programme (IEA GHG).** *Evaluation of post-combustion CO₂ capture solvent concepts*. 2009. 2009/14.
2. **Directive 2009/29/EC. European Union (EU).** 140, s.l. : European Union, 2009, Vol. L.
3. **Hydro.** *Annual Report – 2009*. s.l. : Hydro, 2009.
4. **Müller, Gunn Iren.** *Hydro*. Sunndalsøra, December 2010.
5. **IEA Greenhouse Gas R&D Programme (IEA GHG).** *Improvement in Power Generation with Post-Combustion Capture of CO₂*. 2004. PH4/33.
6. **Thomsen, Kaj.** Current status of R&D in post combustion CO₂ capture. s.l. : Center for Energy Resources Engineering, Technical University of Denmark, 2011.
7. **Sherif, Ahmed.** *Integration of a Carbon Capture Process in a Chemical Industry*. Gothenburg : Department of Energy and Environment, 2010.
8. **Wang, M., et al., et al.** Post-Combustion CO₂ capture with chemical absorption: A state-of-the-art review. *Chemical Engineering Research and Design*. 2010. DOI: 10.1016/j.cherd.2010.11.005.
9. **Davidson, Robert M.** *Post-combustion Carbon Capture from Coal Fired Plants - Solvent Scrubbing*. s.l. : IEA Clean Coal Centre, 2007. ISBN 92-9029-444-2.
10. **IEA Greenhouse Gas R&D Programme (IEA GHG).** *Greenhouse Gas Emissions from the Aluminum Industry*. Cheltenham : ICF Consulting, 2000.
11. **Telemark Teknisk Industrielle Utviklingssenter.** *CO₂ fangst av utslipp fra industrianlegg*. s.l. : Telemark Teknisk Industrielle Utviklingssenter, 2009.
12. **U.S Environmental Protection Agency.** *Primary Aluminum Industry: Technical Support Document for Proposed MACT Standards*. 1996.
13. **EPRI.** *Chilled-ammonia Post Combustion CO₂ Capture System–Laboratory and Economic Evaluation Results*. Palo Alto, CA : EPRI, 2006. 1012797.
14. *Chilled Ammonia Process for CO₂ Capture*. **Kozak, Fred, et al., et al.** 1, s.l. : Elsevier, 2009, Energy Procedia, Vol. 1, pp. 1419-1426. 1876-6102.
15. *Quantitative evaluation of the chilled-ammonia process for CO₂ capture using thermodynamic analysis and process simulation*. **Mathias, Paul M, Reddy, Satish and O'Connell, John P.** 2010, International Journal of Greenhouse Gas Control, Vol. 4, pp. 174-179. 1750-5836.
16. *Chilled Ammonia process for CO₂ capture*. **Darde, Victor, et al., et al.** 2010, International Journal of Greenhouse Gas Control, Vol. 4, pp. 131-136.
17. **Gal, Eli.** *Ultra Cleaning of Combustion Gas Including the Removal of CO₂*. WO 2006/022885 AI United States of America, 2 March 2006.
18. **Couper, James R., et al., et al.** *Chemical Process Equipment - Selection and Design*. s.l. : Elsevier, 2010. 978-0-12-372506-6.
19. **Wilson, K.C., et al., et al.** *Slurry transport using centrifugal pumps*. s.l. : Springer, 2006.
20. **Moretta, Angelo A.** Spiral Plate Heat Exchangers: Sizing Units for Cooling Non-Newtonian Slurries. *Chemical Engineering*. 2010, Vol. 117, 5.
21. **Alfa Laval.** Alfa Laval - spiral heat exchangers. *Alfa Laval*. [Online] 01 10 2007. [Cited: 08 03 2011.] http://www.alfalaval.com/solution-finder/products/the_high_pressure_spiral_heat_exchanger/Documents/Product_brochure_spiral_heatexchanger.pdf.
22. **Lee, Dong Won and Sharma, Atul.** Melting of ice slurry in a tube-in-tube heat exchanger. *International Journal of Energy Research*. 2006, Vol. 30, pp. 1013-1021.
23. **Paul Mueller Co.** Heat Exchangers. *Process Heating*. 2006, Vol. 13, 7, p. 30.
24. **Appl, Max.** Ammonia. *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim : Wiley-VCH, 2006. DOI: 10.1002/14356007.a02_143.pub2.
25. **Kenig, E. Y., Schneider, R. and Górak, A.** Reactive absorption: Optimal process design via optimal modelling. *Chemical Engineering Science*. 2001, 56.
26. **Noeres, C., Kenig, E.Y. and Górak, A.** Modelling of reactive separation processes: reactive absorption and reactive distillation. *Chemical Engineering and Processing*. 2003, 42, pp. 157-178.
27. **Taylor, Ross and Krishna, R.** *Multicomponent mass transfer*. s.l. : John Wiley & Sons, inc., 1993. 0-471-57417-4.
28. **Grén, Urban and Theliander, Hans.** *Grundläggande Kemisk Apparatteknik*. Göteborg : Chalmers Tekniska Högskola, 1998.
29. **Kothandaraman, Anusha.** *Carbon Dioxide Capture by Chemical Absorption: A Solvent Comparison Study*. s.l. : Massachusetts Institute of Technology, 2010.

30. **Jilvero, Henrik, et al., et al.** *Thermal Integration and Modelling of the Chilled Ammonia Process*. Gothenborg : Division of Energy Technology, Department of Energy and Environment, Chalmers University of Technology, 2010.

Appendix A – CO₂ Concentration Properties Extrapolation

Data supplied by Hydro (4) is limited to CO₂ concentrations up to 10%. To increase the accuracy of the results and for validation of the constructed model with previously made models, process gas data with higher CO₂ concentrations is needed. Figure 34 illustrates how values for 10 to 30% CO₂ concentrations are fitted to the curve of measured and estimated values supplied by Hydro.

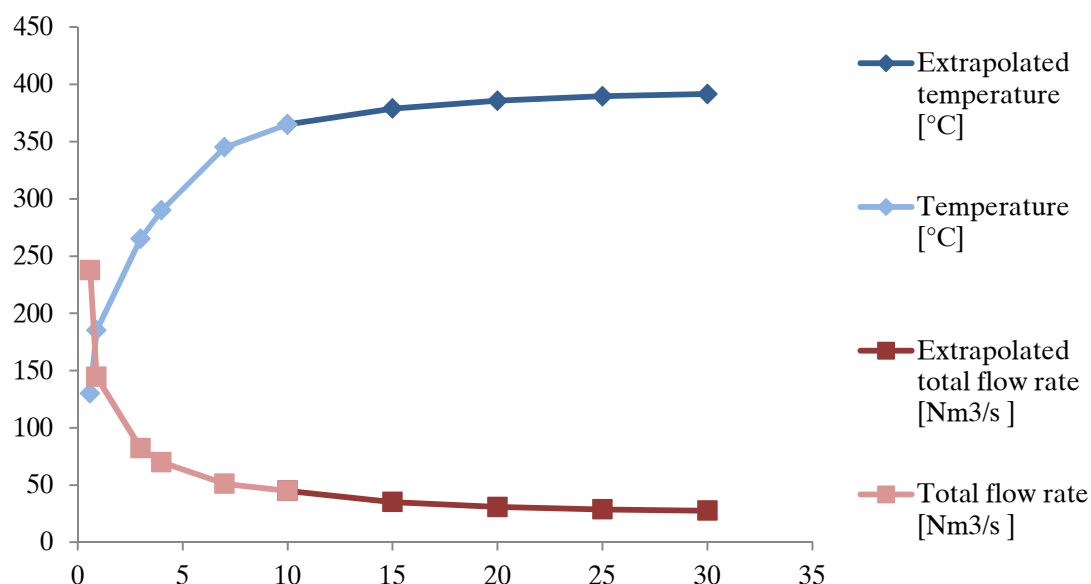


Figure 34. Extrapolated values for temperatures and flow rates for 10 and 30% CO₂ concentrations.

Appendix B – Dimensioning of Packed Columns

The main task for a column in any separation process is to transfer matter from one phase to another, e.g. liquid and gas. The most common way of doing this is through diffusion of matter over a phase interface. To ensure sufficient (high) exchange of mass between phases, three major properties should be considered. (28)

- The driving force over the gas-liquid interface
- The total available surface area
- The mass transfer rate

In packed columns, different kinds of packing material are used to increase the surface area between the phases at which the diffusion takes place.

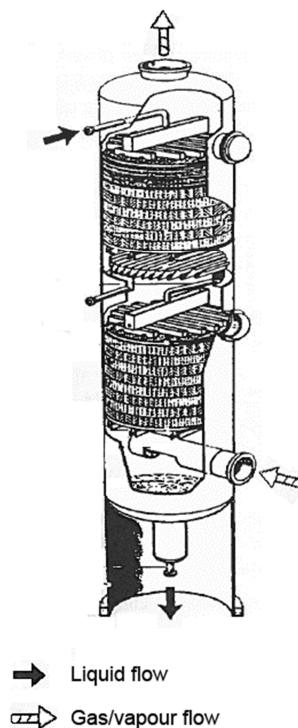


Figure 35. Describing the general design and layout of a packed column. The diffusion occurs at the phase interface between liquid and vapour in the packed bed. Source: Grén et al. (28)

The general design and layout of a packed column with counter current flow is described in Figure 35, showing the introduction of liquid flow in the top of the column and G/L flow in the bottom. The liquid is distributed throughout the column cross section and as it flows downwards it meets with the rising gas/vapour, contact between the phases takes place which enables gas separation.

The use of rate-based simulations for packed columns in Aspen requires specification of certain column specifications, e.g. column dimensions and packing parameters. The packed columns used in the CO₂ capture model are dimensioned using correlations from *Grundläggande kemisk apparatteknik* (28) by Grén et al. The correlation was developed to simplify design of packed columns and will not give an exact design. The correlation will however provide a good enough estimation for the modelling of the packed columns in this thesis.

The column diameter (\emptyset) is calculated using the flow rate correlation in Figure 36, knowledge about the total volumetric vapour flow rate in the column and the type of packing used. The ordinate (Θ) and abscissa (FLV) are dimensionless flow rate parameters used in Figure 36:

$$\theta = \frac{u_{Gf}^2 \cdot S_b}{g \cdot e^3} \cdot \frac{\rho_G}{\rho_L} \cdot \left(\frac{\mu_L}{\mu_W} \right)^{0.2} \quad (1.11)$$

$$FLV = \frac{L'}{G'} \cdot \left(\frac{\rho_G}{\rho_L} \right)^{0.5} \quad (1.12)$$

Where:

u_{Gf}	flow velocity of vapour in column	$[m/s]$
S_b	specific packing area	$[m^2/m^3]$
g	gravity	$[m/s^2]$
e	packing porosity	$[-]$
ρ_L	liquid density	$[kg/m^3]$
ρ_G	vapour density	$[kg/m^3]$
μ_L	liquid dynamic viscosity	$[mPa \cdot s]$
μ_W	water dynamic viscosity at 20°C	$[mPa \cdot s]$
L'	liquid mass flow	$[kg/s]$
G'	vapour mass flow	$[kg/s]$

The FLV flow rate parameter is calculated with known flow rates of liquid and vapour using Equation X. Figure 36 is used to find the ordinate that correlates to the calculated FLV value.

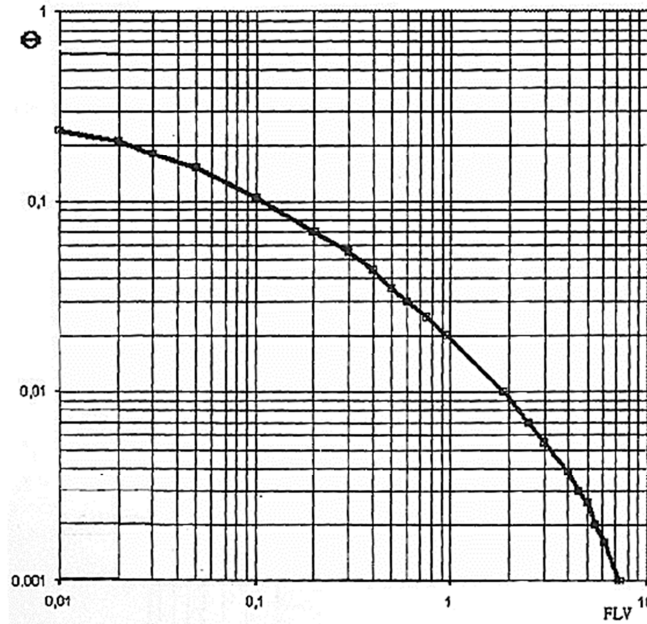


Figure 36. Packed column flow rate correlation presented in a log-log graph. The ordinate (θ) and abscissa (FLV) are flow rate parameters used to determine the vapour flow velocity and subsequently the column diameter. Source: Grén et al. (28)

The vapour flow velocity in the column is derived from Equation X:

$$u_{Gf} = \sqrt{\frac{\left(\frac{\theta \cdot g \cdot e^3 \cdot \rho_L}{S_b \cdot \rho_G} \right)}{\left(\frac{\mu_L}{\mu_W} \right)^{0.2}}} \quad (1.13)$$

The diameter of the packed column can be calculated using the calculated vapour flow velocity and the known volumetric flow rate of vapour, V_G , in the column.

$$\emptyset = \sqrt{\frac{4 \cdot V_G}{\pi \cdot u_{Gf}}} \quad (1.14)$$

The absorbers are modelled as packed columns, requiring further specifications of e.g. choice of packing material and size. Table 15 presents the results from a general case with 4 vol% CO₂ concentration, meaning high process gas flow rate. The column diameter calculated for the high flow rate 4 vol% CO₂ concentration case is also used for the other cases, all of which have lower flow rates. The same packing material and packing specifications is chosen for both the bottom and top cycle absorbers. The flow rates, densities and viscosities are results generated in the model.

Table 15. Specified and calculated values for the bottom and top cycle absorbers using metal pall ring packing material.

		Bottom cycle CO ₂ absorber	Top cycle NH ₃ absorber	
Packing material		Pall ring, metal 16 [mm]	Pall ring, metal 16 [mm]	
Liquid mass flow	L'	85.124	72.5	[kg/s]
Gas mass flow	G'	81.449	77.56	[kg/s]
Liquid density	ρ_L	944.06	998.7	[kg/m ³]
Vapour density	ρ_G	1.213	1.258	[kg/m ³]
Liquid dynamic viscosity	μ_L	0.862	1.088	[mPa s]
Water dynamic viscosity at 20°C	μ_w	1.002	1.002	[mPa s]
Gravity	g	9.81	9.81	[m/s ²]
Specific packing area	S _b	341	341	[m ² /m ³]
Packing porosity	e	0.93	0.93	[-]
Gas flow in column	V _G	67.205	61.65	[m ³ /s]
Figure 36 abscissa (<i>dimensionless flow rate parameter</i>)	FLW	0.037	0.033	[-]
Figure 36 ordinate (<i>dimensionless flow rate parameter</i>)	θ	0.175	0.18	[-]
Flow velocity of vapour in column	u _{Gf}	1.802	1.803	[m/s]
Column cross sectional area	A	37.295	34.185	[m ²]
Column diameter	\emptyset	6.891	6.597	[m]