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### Investigation into optimal $CO_2$ concentration for $CO_2$ capture from aluminium production

Anette Mathisen<sup>a</sup>\*, Henriette Sørensen<sup>a</sup>, Morten Melaaen<sup>b</sup>, Gunn-Iren Müller<sup>c</sup>

<sup>a</sup>Tel-Tek, Kjølnes Ring 30, 3918 Porsgrunn, Norway <sup>b</sup>Telemark University College, Kjølnes Ring 56, 3918 Porsgrunn, Norway <sup>c</sup>Hydro Aluminium, Hydrovegen 67, 3905 Porsgrunn, Norway

#### Abstract

Capture of  $CO_2$  from aluminum production has been simulated using Aspen Plus and Aspen Hysys. The technology used for aluminum production is the Hall-Héroult and the current cell design necessitates that large amounts of false air is supplied to the cells. This results in a  $CO_2$  concentration in the process gas at around 1 vol%, which is considered uneconomical for  $CO_2$  capture. Therefore, the aim of this investigation is to evaluate the  $CO_2$  capture from aluminum production when the process gas  $CO_2$  concentration is increased to 4, 7 and 10 vol%. Generic MEA based  $CO_2$  capture models have been built-up in Aspen Plus and Aspen Hysys. Based on the results from the simulations with the current assumptions, the overall recommendation is to increase the  $CO_2$  concentration to 4 vol%.

Keywords: Aluminum production; CO2; MEA; Aspen Plus, Aspen Hysys

#### 1. Introduction

In order to combat man-made climate change, process industry as well as the power production sector can expect to be submitted to  $CO_2$  emission constraints. Aluminium is a light-weight metal and the most widely used non-ferrous metal, with a wide variety of uses. The raw material of aluminium is bauxite from which alumina (aluminium oxide) is extracted. Alumina has a high smelting point (about 2000°C), and therefore electrolysis is used. This process is called the Hall-Héroult. Here, alumina is dissolved in molten cryolite (the electrolyte) and reacted with carbon at a temperature between 950 – 980°C. The carbon acts as an anode (negatively charged) and is continuously depleted. The aluminum is deposited in pots that are also lined with carbon. These acts as cathodes and are positively charged. The reaction equation for the reduction is given in Eq. 1.

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

(1)

According to the equation, the process gas from aluminum production should mainly consist of  $CO_2$ , however this is not the case. The current cell design necessitates that large amounts of false air is added to the cell as temperature control, and as a consequence the process gas typically has a  $CO_2$  concentration of about 1 vol%. This concentration is considered to be too low for economically viable  $CO_2$  capture. Therefore, the main aim of this investigation is to explore the optimal  $CO_2$  concentration, i.e. the lowest  $CO_2$  concentration that could make  $CO_2$  capture from aluminum production more economically interesting. The investigation will involve process simulations with both Aspen Plus and Aspen Hysys.

Changing the electrolysis cells, i.e. the design and materials used, can reduce the amount of false air which is needed and increase the  $CO_2$  concentration in the process gas.  $CO_2$  capture plant simulations of process gases with varying  $CO_2$  concentrations, 4, 7 and 10 vol%, are performed. It is assumed that any

<sup>\*</sup> Corresponding author. Tel.: +47-93637730

E-mail address: anette.mathisen@tel-tek.no.

modifications to the cell design will not affect the formation of  $CO_2$  in the production process. Therefore, the flow rate of  $CO_2$  is the same in all cases. The results are evaluated according to specific reboiler duty, and to an extent the size of main process equipment, the absorber column in particular.

In addition to the higher  $CO_2$  concentration, an increase in process gas temperature can also be expected. This excess energy can be utilised in the regeneration of MEA in the  $CO_2$  capture plant. The current investigation also includes utilisation of the excess energy from the process gas. Here, the amount of  $CO_2$  that can be captured using this energy alone will be quantified. As a consequence of this investigation, the term optimal  $CO_2$  capture rate will be discussed. Capturing  $CO_2$  from industrial processes will in many cases involve an external energy plant to provide the energy. This will increase the cost of  $CO_2$  capture and utilising excess energy from the production plant is favorable.

A model of a generic  $CO_2$  capture plant, where monoethanolamine (MEA) is used as the solvent is used as the basis for the simulations in both Aspen Plus and Aspen Hysys.

#### 2. CO<sub>2</sub> capture and aluminum production

Aluminium production is a highly energy intensive process. Much effort is being put into reducing the energy consumption. And while a lot of progress has been made, it is likely that also  $CO_2$  capture will be a part of the solution to reduce green house gas emissions. In this investigation a modified aluminum plant located in Norway is coupled with a generic MEA based post-combustion  $CO_2$  capture plant.

#### 2.1. CO<sub>2</sub> capture

The  $CO_2$  capture from the aluminum plant takes place in a generic MEA based plant. The process gas enters at the bottom of an absorption tower where it flows countercurrent with the absorbent, 30 weight% MEA in a solution (lean solvent), fed to the absorber at the top. The  $CO_2$  reacts with the absorbent and leaves the absorber at the bottom in the liquid flow (rich solvent). The cleaned process gas is vented to the atmosphere at the top of the absorber. The rich solvent is heat exchanged with the lean solvent returning to the absorber after regeneration. After heating, the rich solvent enters the desorption column at the top and flows countercurrent with steam from the reboiler. The heat reverses the reactions and  $CO_2$  exits the desorber at the top, while the lean solvent exists at the bottom and recycled back to the absorber. A sketch of a MEA based  $CO_2$  capture plant is shown in Figure 1.

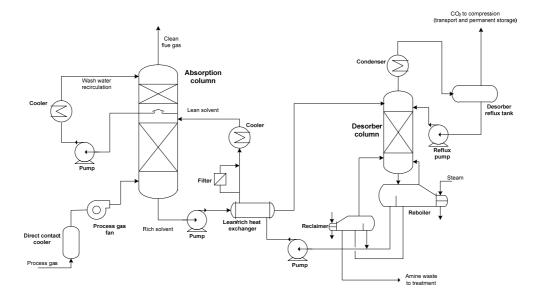


Fig. 1. Sketch of a MEA based CO<sub>2</sub> capture plant.

Generally, it can be said that the two single most cost demanding equipment units associated with  $CO_2$  capture is due to the packing height in the columns, especially the absorber, and the rich lean solvent heat exchanger. The operational cost is mainly due to the energy demand in the reboiler of the desorber, and also compression of  $CO_2$  to some extent, however this is not taken into further consideration in this investigation.

#### 2.2. Aluminum production

The current aluminium production technology, the Hall-Héroult process, results in a  $CO_2$  process gas concentration of approximately 1 vol%. The process gas goes through a post-treatment process (dry and wet scrubbing) after exiting from the cells, both to recover valuable materials for reuse in the process and to adhere to current emission limitations. No additional treatments before the  $CO_2$  capture plant have been considered in this investigation. What is distinctive with the aluminum production in Norway is the cold water used in the wet scrubber system. This wash water cools the process gas down to 9.5 °C. The low process gas temperature makes the need for additional cooling before absorption unnecessary. Nor is it necessary with a lean solvent cooler in the solvent recycle loop.

The current  $CO_2$  concentration is considered to be too low for effective and consequently, economically sound  $CO_2$  capture. The focus of this investigation is therefore to consider the effect on  $CO_2$  capture efficiency when the  $CO_2$  concentration is increased from 1 vol% to 4, 7 and 10 vol%. One way of increasing the concentration of  $CO_2$  in the process gas is to modify the aluminum production technology in order to reduce the amount of air needed for cooling. This means that the process gas in addition to the higher  $CO_2$  concentration will have a higher temperature, but smaller process gas flow rates. The energy that can theoretically be extracted from the process gas should be utilised in the capture plant. For maximum utilisation of this energy, the extraction should be implemented before further treatment of the process gas. In Figure 2, a sketch of an aluminum plant integrated with heat recovery, post-treatment and  $CO_2$  capture is shown. In Table 1, the most important parameters of the process gas are given.

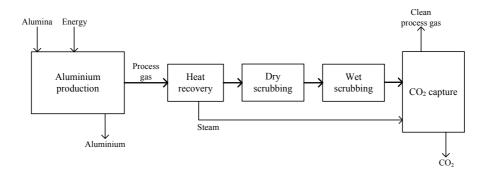


Fig. 2. Sketch of aluminum production with heat recovery and CO<sub>2</sub> capture.

Table 1. The most important parameters of the process gas.

CO <sub>2</sub> concentration (vol%)*	Process gas flow rate (kg/s)	Temperature before heat extraction (C)	Energy that can be extracted (MW)	Temperature before CO <sub>2</sub>
				capture (C)**
4	85	265	10.2	9.5
7	49	330	9.3	9.5
10	35	365	7.9	9.5

\*The rest of the process gas is assumed to contain water vapour, nitrogen and oxygen.

\*\*Due to the low temperature of sea water used in the wet scrubber.

#### 3. Simulations

The simulations are performed on the basis that capture of  $CO_2$  from a process gas becomes economically feasible when the concentration is around 4 vol%  $CO_2$  (typical concentration in a CCGT plant). Currently, the  $CO_2$  concentration in a process gas from aluminum production plants is approximately 1 vol%. The effect of increasing the  $CO_2$  concentration to 4 vol% and then further for 7 and 10 vol% is therefore investigated. Information about the process gas flow rate and temperature is given in Table 1. The total amount of  $CO_2$  entering the capture plant is the same for all cases. The evaluations are done by comparing the specific reboiler duty.

For this work a generic MEA  $CO_2$  capture plant is simulated in both Aspen Plus and Aspen Hysys. For the simulations in Aspen Hysys, the Peng-Robinson equation of state is used to calculate thermodynamic properties and the amine package Kent Eisenberg is used to predict the Murphree efficiency in columns. For more on Murphree efficiencies the reader is referred to  $\emptyset$  [1]. In Aspen Plus, the absorber and desorber columns are simulated using the RadFrac block for rate-based calculations with the Electrolyte NRTL property model, and the Reidlich-Kwong equation of state. Capture rates of 85 and 90%  $CO_2$  is sought. Extensive work has been done in the field, amongst others are Kothandaraman [2] and  $\emptyset$  i [1].

#### 3.1. Aspen Plus simulations

Both an open and closed loop simulation model of a MEA capture plant has been developed in Aspen Plus. The current investigation is based on the open loop model, however a selection of the simulations are verified in the closed loop. Two sets of simulations are performed, 1) where the absorber packing height is kept constant at 14 m and the amount of lean solvent is varied to achieve 85 and 90% capture rate, 2) where the amount of lean solvent is kept constant and the absorber packing height is varied to

achieve 85% capture rate. The reason for choosing these two approaches to the simulations is that these are the main factors that influence the cost of  $CO_2$  capture. The amount of MEA circulating in the capture plant very much dictates the duty of the desorber reboiler. The desorber packing height is kept constant in all simulations at 7 m. The packing material selected for the absorber and desorber is standard metal Mellapak 250Y. The  $\Delta T_{min}$  is set to 5 and 15°C for the cold and warm side, respectively, in the lean/rich heat exchanger. Generally, it can be said that a specific reboiler duty at around 4.2 MJ/kg  $CO_2$  captured is acceptable. In Figure 3, the results from the simulations are shown.

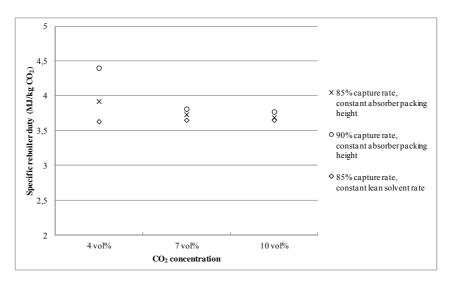


Fig. 3. Specific reboiler duty by CO<sub>2</sub> concentration and capture rate as simulated in Aspen Plus.

The figure shows how the specific reboiler duty varies with  $CO_2$  concentration and capture rate for constant absorber packing height and constant lean solvent rate. The figure shows that the specific reboiler duty decreases with increasing  $CO_2$  concentration when the absorber packing height is kept constant and the lean solvent rate is varied. A higher lean solvent rate is needed to achieve 85 and 90% capture rate for the 4 vol% simulations than for the 7 and 10 vol% cases. For the simulation with constant lean solvent rate, 4 vol%  $CO_2$  in the process gas gives a slightly lower specific reboiler duty than the rest. However, here the absorber packing height is increased to 25, 22 and 19.5 m, respectively for 4, 7 and 10 vol%  $CO_2$  in order to reach 85% capture rate. As expected, the figure also shows that the specific reboiler duty increases with increased capture rate as a higher capture rate increases the solvent flow rate.

#### 3.2. Aspen Hysys simulations

A closed loop generic MEA capture plant model has been developed in Aspen Hysys. Both the lean solvent flow and the absorber height are kept constant for all simulations. The results from the simulations are shown in Figure 4. It can be seen that at an 85% capture rate there are small differences between the  $CO_2$  concentrations, with the 4 vol% case giving a slightly higher reboiler duty. Increasing the capture rate to 90% gives a high, above 4.2 MJ/kg captured  $CO_2$ , specific reboiler duty for the 4 vol% case. No distinction can be made between 7 and 10 vol%. As seen in the Aspen Plus simulations, an increase in capture rate from 85 to 90% increases the specific reboiler duty.

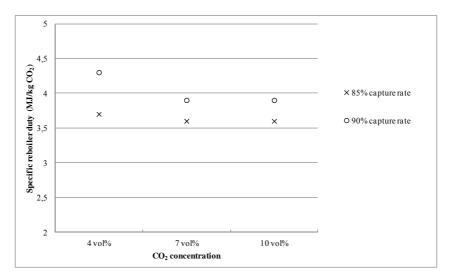


Fig. 4. Specific reboiler duty by CO2 concentration and capture rate as simulated in Aspen Hysys.

#### 3.3. Capture rate analysis

Traditionally, when discussing  $CO_2$  capture, capture rates of at least 85% and even up towards 95% are sought. This is reasonable when it comes to capture from power production, but might not be so for industrial production plants. The reason for this is that very few plants can provide the energy needed for  $CO_2$  capture in the existing facility. As a consequence when implementing a  $CO_2$  capture plant with the industrial plant, an energy plant is almost always needed. This will increase the investment cost, not only due to the extra plant, but also because more  $CO_2$  is produced in the energy plant which must be handled in the  $CO_2$  capture plant, hence the size increases. It is therefore important to analyse excess energy from the industrial production process that can be made available for this purpose.

Traditional aluminum production plants have (process gas content of 1 vol%  $CO_2$ ) excess energy. The aim of the current investigation is to analyse the effect of increasing the  $CO_2$  concentration to 4, 7 and 10 vol% on the  $CO_2$  capture efficiency. The consequence of increasing the  $CO_2$  concentration is an increased process gas temperature, but reduced flow rate. An energy analysis has been performed on the three cases and identified available energy is given in Table 1.

The Aspen Plus MEA based  $CO_2$  capture model is used to simulate the new  $CO_2$  capture rates based on the limited available energy. No changes have been made to the model from the investigation presented in Figure 3. Hence, the equipment sizes and flow rate of circulating solvent are the same. The results from the capture rate analysis are presented in Figure 5.

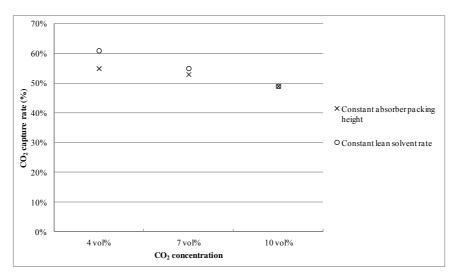


Fig. 5. CO<sub>2</sub> capture rate analysis.

The figure shows that just above 60 and 55% of the  $CO_2$  can be captured for the 4 vol% case depending on the two assumptions made. For the 7 and 10 vol% cases the  $CO_2$  capture rates are close to 55 and 50%, respectively.

The idea behind having a reduced capture rate, where the energy from the industrial process covers the needed energy could lowers the threshold for industry to adopt  $CO_2$  capture. The advantage of building a full-scale capture plant, 85 % or even higher, gives flexibility to the facility and keeping the option of higher capture rates open. On the other hand, building a smaller capture plant scaled according to available energy from the process gas (i.e. only part of the process gas is sent to the capture plant) will reduce the investment cost. In addition, new solvents with higher efficiencies are being developed resulting in higher capture rates in the smaller plant.

#### 4. Conclusion and recommendation

Based on the above investigation and the current assumptions, an increase in  $CO_2$  concentration from 1 to 4 vol% is recommended if a capture rate of 85 % is adopted. Further optimisation is needed for the 90% capture rate investigation. The actual cost of modifying the aluminium production cells is not considered beyond the fact that it is assumed that increasing the concentration further from 4 vol% would be more costly. In addition, the amount of energy that can be extracted from the process gas is greatest for the 4 vol% case. Using excess energy from the aluminium production will reduce both the investment and operational cost.

However, based on the results an increase to 7 vol%  $CO_2$  concentration warrants further investigation. The final recommendation will be based on overall technical and economical considerations.

#### 5. Further work

The work of this project is ongoing. Detailed cost estimation will be performed and recommendations for optimal  $CO_2$  concentration will be provided.

#### Acknowledgements

The authors wish to thank the Norwegian Research Council (the Climit program) and the industrial partners; Aker Clean Carbon AS, Elkem Thamshavn AS, E.ON Sverige AB Hydro Aluminium AS, NOAH AS, Norcem AS, and Noretyl AS for the financial contribution to this work.

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