KN05 - Towards Carbon Neutral Primary Aluminium Smelting via Carbon Dioxide (CO_2) Capture

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Abstract

There is a growing awareness that primary aluminium smelters must reduce the Scope 1 direct-related GHG emissions of the smelting processes. In this study, the options of CO_2 capture technology for these Scope 1 reductions in lowering the GHG footprint will be discussed.

Since the use of carbon anodes as a leading technology is still in the forecast for many decades to come, technology is needed to reduce the direct CO_2 emissions from the electrolysis process. Presented will be the potential of the application of CO_2 capture from pot ventilation gases. This is challenging, and shown will be what hurdles need to be overcome and how to integrate this technology in a smelter operation to arrive at a good, viable technical solution and economically feasible capture of CO_2. A review of worldwide activities in this industry is provided and reveals that this is all new. Therefore, comments are provided about how the application of CO_2 capture technology can be moved closer to commercial implementation. A technology roadmap is suggested, along with comments on how not only suppliers, but the industry must work together to advance the development of CO_2 capture processes.

Keywords: Carbon capture and storage (CCS), Carbon neutral aluminium, Greenhouse gas emissions (GHG), GHG footprint, CO_2 capture, primary aluminium.

1. Introduction

All industries are affected by measures to combat climate change. The primary aluminium industry is not different and must introduce changes to reduce its GHG emission impact. If we focus on primary aluminium smelting, the use of carbon anodes is a critical part in the equation. There is no question that the Holy Grail is to be able to operate the electrolysis process with inert anodes but there is now a common belief that we are still some years away before ~~we see~~ large scale commercial application of the technology will be possible. An important question for an existing smelter is “Is it possible to convert the traditional process to the inert anode process?” and if so can, “When can the conversion be realized and at what cost?”. Today, there is no answer to those questions. What is known is that options are needed so alternative strategies can be evaluated. In this paper, the focus is on the option of applying (post) CO_2 capture technology for the direct process emissions from the electrolysis process.

2. GHG Emissions from the Aluminium Industry

First, it must be identified in what position, with respect to GHG emissions from the aluminium as a whole. A lot of good work is done by the International Aluminium Institute (IAI) to provide a large amount of information on this and other relevant topics. It is recommended to visit their website to retrieve a copy of their documentation. Using this, only a short summary is required as an introduction.

To put things in perspective, according to the International Aluminium Institute (IAI), the global aluminium industry emits an equivalent amount of CO_2 of 1.1 billion tonnes per year [1]. That contributes to 2 percent of the total GHG emissions from all industrial sources.

A breakdown is provided in the following table:

Table 1. 2018 Total Aluminium Sector Emissions (Mt CO_2eq) [1].

	Bauxite mining	Alumina refining	Anode production	Electrolysis	Casting	Recycling*	Semis production	Internal scrap remelting	Total
Electricity (indirect)	0.6	16.9	-	670.6	-	3.1	9.5	2.5	703
Non CO_2 GHGs (direct)	-	-	-	35.4	-	-	-	-	35
Process CO_2 (direct)	-	-	6.4	92.6	-	-	-	-	99
Ancillary materials (indirect)	-	14.8	19.3	6.4	-	-	-	-	41
Thermal energy (direct/indirect)	2.6	124.3	6.4	-	6.4	15.6	19.0	8.4	183
Transport (indirect)	-	15.4	-	18.7	-	-	-	-	34
Total (cradle to gate)	3	171	32	824	6	19	29	11	1,095

From this data it is directly clear that the largest contribution is made by the electrolysis process. In the next section, this is looked at in more detail, also because the objective is to capture the CO_2 from the process gases.

3. GHG from Aluminium Reduction

3.1. General Overview

For a smelter, the breakdown is well known and was reported many years ago by Lorentzen et al. [2]. The following table is retrieved from this publication:

Table 2. Life-cycle GHG emissions from a modern primary aluminium smelter [2].

Source	Hydro Electric Power	Gas-fired Power	Coal-fired Power
Unit	kg CO_2 eq/kg Al	kg CO_2 eq/kg Al	kg CO_2 eq/kg Al
Alumina production	1.80	1.80	1.80
Anode production	0.30	0.30	0.30
Electrolysis - Carbon	1.50	1.50	1.50
Electrolysis - AE	0.30	0.30	0.30
Casthouse	0.06	0.06	0.06
Electric power	0.00	5.80	13.60
Total	**3.96**	**9.76**	**17.56**

Looking at the data, it can be recognized that there are direct emissions (Scope 1) and indirect emissions (Scope 2). The management of a smelter needs to address them all, but that requires

very different strategies. The biggest challenge for most smelters is the source of power, as often the smelter is connected to a grid and it receives the power "as is," depending on the power generation types used by the operators. On top of that, the smelters can only try to influence the mix of power in a grid by working with the power companies, but it relies on the (long-term) progress the power companies make in making their portfolio of power generation greener with hydro, wind, solar, and/or other sustainable types of power.
The same is true for alumina. A smelter will continue to purchase this from refineries and will probably do so in the future, knowing that an added decision factor on the spec-sheet will be the CO2eq value of a particular alumina.

A smelter has most control over the Scope 1 emissions. For the casthouse, fuel switching is available, including electrification or using hydrogen as a fuel. In fact, in this area, some good progress is already being made today.

That leads us to the electrolysis process and the production of anodes. These are considered in one effort because Broek [3] already demonstrated that the off gases from the baking furnaces can be treated in one place by combining them with the potline ventilation gases. This is not a very common practice but can be found in Aluminium Dunkerque, France.

Anode effects occur when there is a lack of local alumina concentrations in the bath leading to a shift in local voltages that enable the formation of perfuorocarbon gases (PFCs). These are strong GHG gases with a GHG intensity for CF_4 of 6 630 and for C_2F_6 of 11 100, respectively.

A reduction of anode effect related GHG gases is achieved by modern process control. Great progress has been made over the past years and modern cell technologies have very low GHG related emissions from anode effects. Irrespective, PFCs will be present in the off gases from cells and are accounted for. However, PFCs do not get scrubbed in the alumina dry scrubber, nor in a wet SO_2 scrubber. The same is applicable for a CO_2 scrubber that is discussed later.

That leaves us with the process gas from anode baking and electrolysis. This is reviewed in greater detail in the next sections. However, first it is needed to establish a design basis for estimations calculations.

3.2. Design Basis

The following list is the design basis for a fictive aluminium smelter that is used in the examples that follow. It represents a mass balance for a smelter with 360 cells at 400 kA producing just short of 400 000 tonnes of aluminium per year from the electrolysis cells (not the casthouse).

1. Number of electrolysis cells 360
2. Line amperage ..... 400 kA
3. Cell efficiency ..... 94 %
4. Annual availability (2000 days life) ..... 99.65 %
5. Annual metal production ..... 396 800 t/year
6. Alumina requirement ..... 761 900 t/year
7. Anode dimensions ..... 1650 × 660 × 675 mm
8. Anode weight before/after slotting ..... 1 125 / 1 109 kg
9. Anode current density ..... 0.95 A/cm^2
10. Net carbon consumption ..... 425 kg/t Al
11. Anode changes ..... 554 units/day
12. Gross carbon consumption ..... 566 kg/t Al
13. Sulfur content of bakes anodes ..... 2.23 %
14. Anode production ..... 4 fires, 189 anodes per section

15. Fire cycle ..... 33 hours (for net zero anodes)
16. Anode production net/gross ..... 550 / 552 units/day
17. Green anode demand ..... 552 units/day
18. Green anode weight ..... 1 178 kg
19. Pitch content ..... 13.5 wt%
20. Coke deliveries (2.75 wt% S) ..... 147 900 t/year
21. Pitch deliveries ..... 33 360 t/year
22. Pot exhaust flow ..... 9 500 Nm^3/h per cell
23. Overall gas collection efficiency in cells ..... 99 %

3.3. Production of Anodes

In this paper, also is included the production of anodes within the smelter. A large number of smelters import anodes from third parties which makes the concept simpler, and the CO_2 capture plant will only see the potline ventilation gases.

There are four firing ramps in the anode baking furnace (ABF), and each has a control system for the firing. The flow of flue gases is a function of the natural gas fired by the manifolds, the burn of volatiles, and the amount of air ingress through leaks and crevices. The latter is a function of age of the ABF as over time more leaks start to occur for obvious reasons. The fumes from the ABF are acidic by nature, and any water will lead to corrosion in the main ring and ducts, resulting in gaps where air can leak in.

During the baking of anodes, there is a point when anodes reach the temperature range where volatiles (pitch) start to release into the flues and burn. If enough oxygen is present, then the combustion will be complete. The injection of natural gas remains stable, so that this amount of heat and flue gases comes on top of the main flue gas flow. If there is not enough oxygen, then the firing controls detect this, and can increase the draft on the furnace, and/or reduce the injection of natural gas. This dynamic is built in the control system, so for this exercise the starting point is a stable gas volume per fire.

The following is the calculated flue gas flow from the baking furnace under four fires:

Table 3. Anode baking furnace flue gas characteristics.

Item	Unit	Value
Total flow to the fume treatment center (FTC)	Nm^3/h	150 000
Gas composition:		
N_2	Vol%	90.26
O_2	Vol%	5.2
CO_2	Vol%	2.4
H_2O	Vol%	2.1
SO_2	mg/Nm^3	800
CO_2 output:	kg/h	7 136
	t/yr	62 513
	kg/t Al	158

This flow equates to ~5 500 Nm^3 of gas per tonne of anode produced, which is in good agreement with guidelines. In this is considered an amount of air ingress (10 %) to include any leaks and aging of the furnace. Considered here as well is that there is packing coke that is lost (10 kg/tonne) and that some anodes experience a loss of material (1.25 % of the scrapped baked anodes) due to exposure to flue gases because of cracks in the flue walls.

To cross-check, Edwards [4] presented a value of 204 kg CO_2 per tonne Al for an oil-fired ABF. A clarification was that if the conversion to natural gas is made, that this value is reduced by 30 % to 143 kg/tonne Al. The calculated value of 158 kg CO_2/t Al is in good agreement with this.

3.4. The Electrolysis Process

It is widely reported that the ventilation gases from aluminium cells hold around 1 volume percent of CO_2. In this section, this is substantiated by some process calculations to gain insights into how this concentration arrived at this level and if there are any factors that have an impact on it.

3.4.1 The Speciation of Carbon in the Electrolysis Process

During the electrolysis process the anode is constantly consumed. The control system seeks to establish a constant anode-to-cathode distance requiring the anodes to be lowered at very low speeds like in millimeters per hour. The anode is not 100 % made of carbon and holds some other elements too, but in general, its main constituents are sulfur, 'inerts' and carbon. From the model, calculations is obtained 2.23 wt% S, 0.50 wt% other, and 97.27 wt% C in a baked anode.

The production of metal from one electrolysis cell is as follows:

Production = 0.33555 x 400 kA x 94 % = 126.17 kg/h Al

This amount requires a certain amount of carbon, but the carbon does not only get consumed in the reactions to form aluminium. There is a list of other destinations for carbon as shown in the next diagram:

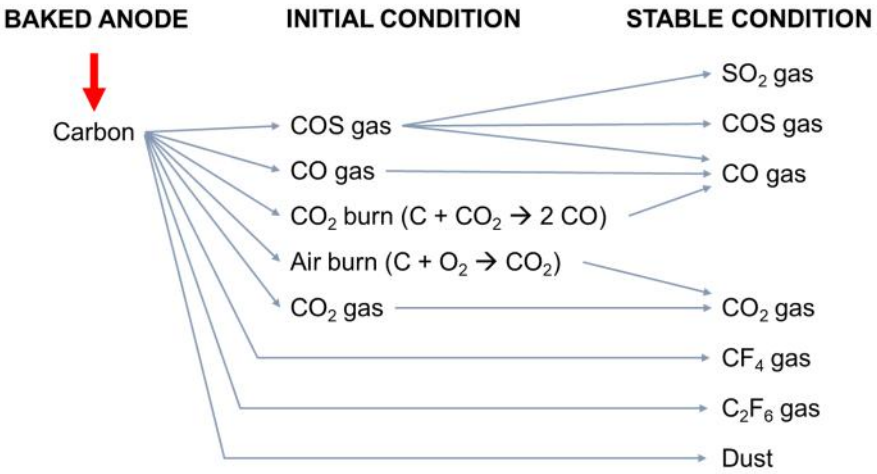

Figure 1. Speciation of carbon in the electrolysis process.

The model provides for the following breakdown following the speciation that is described in the above figure. Only the results are shown here.

The ranges in the sixth column are referenced against data published by B. J. Welch and they are in good agreement or close enough to accept them. For example, the amount of CO gas results in a stack concentration of 1 150 mg/Nm^3. This is consistent with stack measurements performed in a GTC in a smelter with AP-30 type cells and with DX type cells.

Table 4. Speciation of carbon from the process model.

INPUT		CONSUMER				PRODUCT
	kg/h		kg/h of C	kg C/t Al	Range	kg/h
Carbon	51.744	COS (g)	0.022	0.176	n/a	0.11
		CO (g)	0.843	6.677	2 – 5	11.62
		CF_4 (g)	0.00013	0.001	n/a	0.0009
		C_2F_6 (g)	0.000009	0.00007	n/a	0.0001
		Carbon dust	0.379	3.00	2 – 14	1.26
		Air burn	6.727	53.31	28 – 75	-
		CO_2 burn	2.070	16.40	14 – 28	-
		CO_2 (g)	41.705	330.52	350 – 353	171.42
			====== +			
		Check balance	51.744			

The PFCs are based on the models introduced by G. Marks, so they are simple, but an accepted tool to make predictions for the two main PFC gases.

All sulfur is initially COS gas but quickly coverts to CO and SO_2 when air is present. In the model the universal conversion of 95 % is applied based on work done by M. Hyland [5].

3.4.2 Cell Ventilation Gases

The resulting process gases from the electrolysis cell is 100.0 Nm^3/h and contains 87.2 volume percent CO_2. With an overall gas collection efficiency of 99 % of this 99 Nm^3/h finds its way in the ventilation gases that go to the gas treatment center (GTC). The other fraction is released into the potroom and leaves through the roof ventilator.

In the process gases are also present HF and SO_2 gas. Both have extensive models behind them for the calculation of the release of these components. The results here are derived from the HF evolution model from Haupin and Kvande (18.2 kg HF/t Al) and a mass balance for the sulfur release (20.1 kg/t Al).

The pot exhaust flow that is induced by the GTC is 9 500 Nm^3/h per cell. This leaves the cell, which means that the amount of air that is drawn into the cell is 9 500 – 99.0 equals 9 401 Nm^3/h.

The air used in the calculations is at 35 °C and has a relative humidity of 50 %.

The conclusion of this is that the cell exhaust indeed holds around 1 volume percent of CO_2, and that the CO_2 is mainly originating from the carbon consumption in the electrolysis process. However, there are further steps in the process affecting the final gas composition for use in the CO_2 capture plant.

Table 5. Results of the model calculations for the cell exhaust composition.

	ELECTROLYSIS GAS		VENTILATION AIR		CELL EXHAUST GAS		
	kg/h	Nm^3/h	kg/h	Nm^3/r	kg/h	Nm^3/h	volume%
CO	11.5	9.2			11.5	7.95	0.097
CO_2	169.7	86.4					
COS	0.1	0.04			0.11	0.04	<0.001
HF	2.27	2.54			2.27	2.54	0.027
SO_2	2.51	0.88			2.51	0.83	0.009
CF_4	0.0009	<0.01			0.0009	<0.01	<0.001
C_2F_6	0.0001	<0.01			0.0001	<0.01	<0.001
		===== +					
		99.0					
O_2			2,735.4	1,914.8	2,735.4	1,914.8	20.16
N_2			9,031.4	7,221.7	9,031.4	7,221.7	76.02
H_2O			209.9	260.9	209.9	260.9	2.75
CO_2			6.9	3.6	176.6	90.0	**0.95**
				===== +		===== +	===== +
				9,401.0		9,500.0	100.00

3.4.3 Air Additions During Transport and Gas Cleaning

In aluminium smelters the following diagram represents the path of gas cleaning before the gases are discharged into the atmosphere. Because the CO_2 capture plant needs some form of quenching, an SO_2 scrubber is included since this is becoming more and more the standard in smelter design.

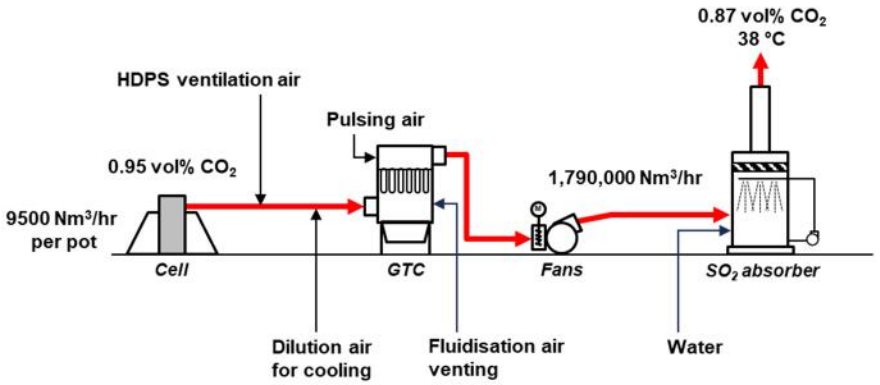

Figure 2. Process schematic for the gas cleaning steps prior to discharge from the stack.

The current design of the ventilation system has several air additions to it:

1. Ventilation air from the HDPS system or other pot alumina feed system. This is typically between 50 000 and 70 000 Nm^3/h per GTC.
2. Air is often used to cool the total ventilation flow, and this is a substantial volume. During the summer smelters often need to use an additional 15-20 % (!) of air to stay below the maximum temperature of 130 °C for the GTC process.
3. Pulsing air from cleaning filter bags automatically enters the process. These volumes are relatively small and normally in the range of 1 200 to 2 500 Nm^3/h per GTC.
4. Venting the fluidization air into the GTC is a common practice so that any alumina dust is captured in the filters. In most cases, this is between 15 000 and 20 000 Nm^3/h per GTC.

While this is part of the current design of the ventilation and gas treatment systems, it does have an impact that it dilutes to CO_2, and the figure shows that the gases leave the cells at 0.95 vol%

but arrive at the CO_2 capture plant with a concentration of just 0.86 vol%. This includes a dilution effect from the water that evaporates in the SO_2 scrubbing system.

This means that the designers may need to find different approaches to manage the venting of air and the cooling of gases in order to minimize a dilution effect on the CO_2 concentration.

3.4.4 Combining Cell Ventilation Gases with Fumes from the Anode Baking Furnace (ABF)

Typically, the fumes from the ABF and the ventilation gases from the cells are treated separately. There can be circumstances that it makes sense to combine them to target a more effective removal of SO_2, for example. In this case, this can also apply to CO_2, because if the gas volumes are combined, more CO_2 becomes available for absorption in the CO_2 capture plant.

When the gases from the cells are combined with the clean fumes from the FTC, the following flowsheet is established:

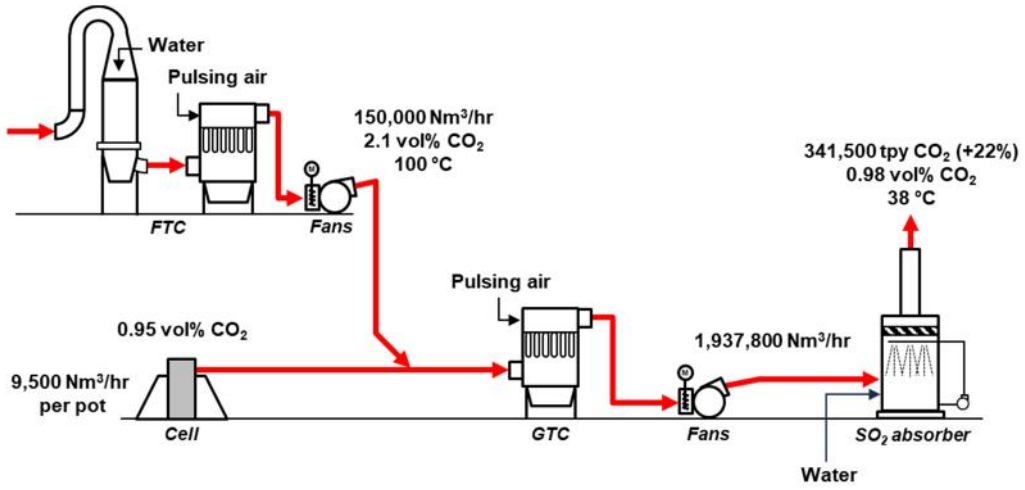

Figure 3. Process diagram with combined cell ventilation gases and FTC fumes.

The main result of this combination is that the CO_2 concentration is maintained when leaving the SO_2 scrubber. The total amount of CO_2 that is available has increased by 22 %. Under normal circumstances, this is diluted down to 0.87 vol%. To accommodate the flow, the GTC will have to be operated with two more filter compartments (28), or the capacity must be present by using extended surface filter bags (star-type bags).

REEL Norway provides FTC technology that employs heat exchanger technology to replace the evaporative cooling tower. The result is a cooled dry gas and heat that is available through the hot water generated in the heat exchanger. Because there is no injection of water and compressed air, there is less dilution of the CO_2 concentration. A process model shows that the CO_2 concentration in the clean off gases is now 2.3 vol% instead of 2.1 vol% with evaporative cooling.

3.4.5 The Use of Heat Exchanger Technology

Over the past years, the use of heat exchanger technology has progressively increased in smelter applications. It has been proven to be effective and reliable. It also has several different designs so that it can be applied in retrofit situations too.

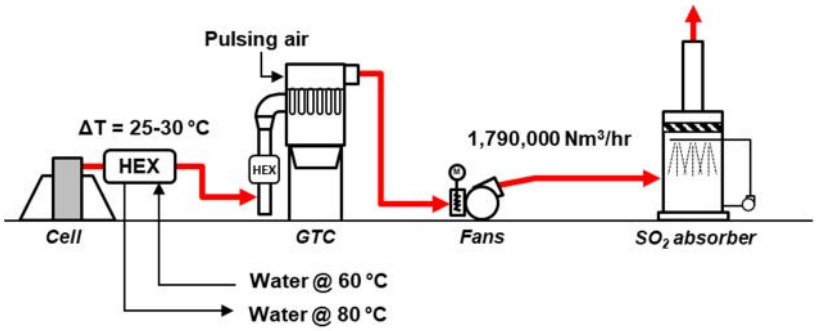

Figure 4. Process schematic presenting the use of heat exchanger technology.

The first model of the technology is a heat exchanger design that connects to a single cell. These are smaller units, but the piping network is more complicated, especially so close to electrolysis cells.

A second model is the heat exchanger that is placed in the collector ducts near the cells. In this case, the volume of gases is combined from several pots, and this gives it the opportunity to be effected in a collector duct. It is also easy to install it in an existing duct system.

Figure 5. An EHEX type heat exchanger installed in line 4 at Aluminium Bahrain (Source: REEL Norway).

A third model is really for new GTC systems and is a model that is integrated in the inlet duct of each filter compartment. It is effective and provides a level of redundancy whereby it follows the maintenance schedule of filters. If a filter is out of service (N-1 operation), then the heat exchanger can also be inspected. The design is even made such that a heat exchanger can be replaced with a spare unit, something that is not possible in the large units in collector ducts. These units need a bypass duct.

The technology is well proven, but operating in a range that is only partially useful for integration with CO_2 capture plants. The CO_2 regeneration plant needs a lot of energy, and the use of the heat exchanger is extremely useful for this. But the amounts of energy are larger than is extracted in current operating modes, so the technology needs further development to be more effective for that.

3.4.6 Gas Composition Entering the CO_2 Capture Plant

In the GTC the HF is removed from the gases by 99.5 %, and in the following SO_2 scrubber the SO_2 is reduced by about 93 %.

In the example, calculations of a scrubbing process are used based on the addition of lime. In this process, the slurry circulates over the absorber leading to adiabatic cooling of gases to 38 °C. Here, the seawater process may have an advantage because this is a once-through process where the gases are cooled by the incoming seawater. If the seawater temperature is 10 °C, then the gas temperature is more like 12-15 °C. In the Middle East, this is closer to 30 °C since the water in the Gulf is much warmer. But in essence, it leads to a cooler gas going into the CO_2 capture unit, which helps the energy balance and absorption of CO_2.

Table 6. Composition of the gases leading to the CO_2 capture plant.

COMPONENT	GAS COMPOSION		
	kg/h	Nm³/h	Volume%
CO	2070.4	1 655.7	0.09
CO_2	31 850.0	16 211.0	**0.87**
COS	19.8	7.4	<0.01
HF	0.01	0.01	<0.01
SO_2	28.2	9.9	<0.01
CF_4	0.16	0.04	<0.01
C_2F_6	0.01	0.00	<0.01
H_2O (g)	109 884.0	136 628.6	7.28
O_2	515 644.8	360 964.9	19.23
N_2	1 702 507.6	1 361 354.6	72.53
Particulate	1.3	-	-
H_2O (liq)	140.7	-	-
	========= +	========== +	
	2 362 147	1 876 832	

In this table is also shown a component labeled 'H_2O (liq)'. This is the amount of water that carries over from the scrubber as fine droplets. Inside the absorber are mist eliminators, but they always let a very small amount of very fine droplets through. This value represents this.

4. CO_2 Capture Based on Scrubbing Using Solvents

In this section, it is explained what CO_2 capture technology is and how it integrates into the cell ventilation system in a potline. There are various methods to capture CO_2 and many of them are under development. Here, too, a key consideration is that the method must be applicable to a large volume flow of gases. Because the Technology Readiness Level (TRL) of solvent scrubbing with monoethanolamine (MEA) is very high and the most likely candidate for a capture plant to be built in the next 5 years, this is our focus in the paper. However, the principles can be applied to other methods and solvents as well.

4.1. Basic Flowsheet in Aluminium Smelting

The base case is to take an existing ventilation system and add a CO_2 capture system to it. This results in the Figure 6 basic flowsheet.

The assumption is that the CO_2 capture plant is a new addition. That means it ties in with the existing ventilation system, which in this case is at the stack of the SO_2 absorber. With a tie-in, a bypass function is created so that in case the CO_2 capture plant is offline, the clean gases can be emitted from the existing stack.

As shown, the existing fans are not upgraded. Booster fans are installed to overcome the additional pressure drop across the CO_2 absorber. Because the absorber uses a packing, the increase is large, and the existing fans may not be able to be upgraded because of this.

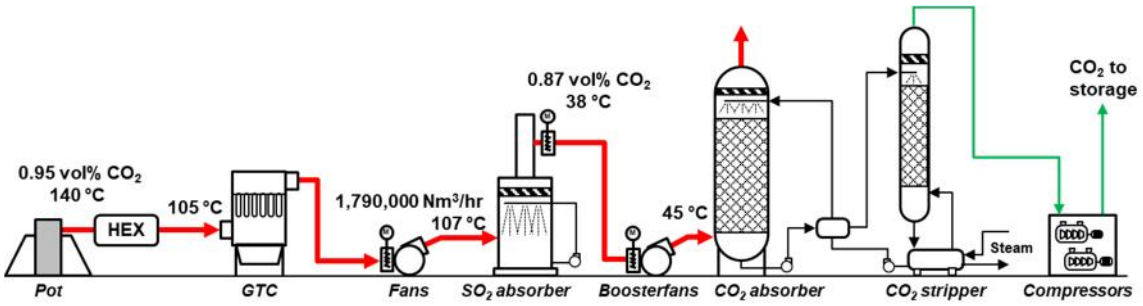

Figure 6. Basic flowsheet of an integrated CO_2 capture plant connected to a single GTC.

Later, this flowsheet will play an important role in explaining the impact if changes to the system design are made to seek cost savings in the (post) CO_2 capture plant.

4.2. Amine Solvents

Amines are organic compounds linked to ammonia. In the case of CO_2 absorption, the compound also contains a hydroxyl (OH) group. For the removal of CO_2, there are several amines available that each have their pros and cons:

1. MEA.....Monoethanolamine
2. MDEA.....Methyl-diethanolamine
3. AMP.....2-Amino-2-methylpropanol
4. PIPA.....Piperazine
5. DGA.....Diglycolamine
6. DEA .....Diethanolamine
7. DIPA .....Di-isoproposaolamine

Monoethanolamine (MEA), with the chemical structure $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$, provides for fast reactions during absorption and requires a higher level of energy to release the CO_2 in the stripper (because here the amount of CO_2 is relatively small, this higher steam requirement is not considered a major drawback). It is overall a reliable solvent and probably the most used one in post-combustion applications. The strength used in the application is a 30 wt% MEA solution, the wt% is restricted by corrosion aspects.

Amines were introduced to acid gas scrubbing many years ago. When natural gas is produced it contains considerable amounts of H_2S and CO_2 gas. These are acid gases and need to be removed before the natural gas goes to the consumers. Scrubbing the gas with amine solvents is extremely effective. However, in this application there is no oxygen (O_2) in the gases that are treated.

Amines react with oxygen and lose their ability to absorb CO_2. When CO_2 capture became a thing 10 to 15 years ago, the CO_2 that is to be captured is now from boiler gases. These gases are the products of combustion; hence, the application is called ‘post-combustion’. Amines can do the job, but a loss is incurred due to the side reaction with oxygen.

Amines not only absorb CO_2 but also can react with other acid gases like HF and SO_2. The reaction products are no longer providing absorption of CO_2, so this results in a loss of solvent as well. It is therefore a common practice to clean the incoming gases from SO_2, etc. to minimize this. However, an economic calculation can be made where the cost of SO_2 scrubbing is weighed against the cost of replenishing the amine solvent.

Being an organic compound, amines also have some volatility. It is typical that the CO_2 absorber loses a small fraction of MEA with the top gases. Often a top gas scrubber is installed to recover the MEA before it is discharged.

Lastly, amines can also break down when exposed to high heat. It is important that the reboiler in the stripper column is controlled properly to avoid these side reactions.

The amine products that form from reactions with O_2, SO_2, etc., are called heat stable salts. A special filter is applied to separate these from the process after which they are disposed of or in dedicated process reclaimed and (partly) returned to the solvent.

4.3. Absorption of CO_2

The first step in CO_2 capture is the actual absorption of CO_2. This takes place in an absorber that if filled with packing material. The solvent is sprayed on top of the packing, and by gravity, the solvent flows though until it is collected at the bottom. The following diagram is a representation of the absorption part of the capture plant.

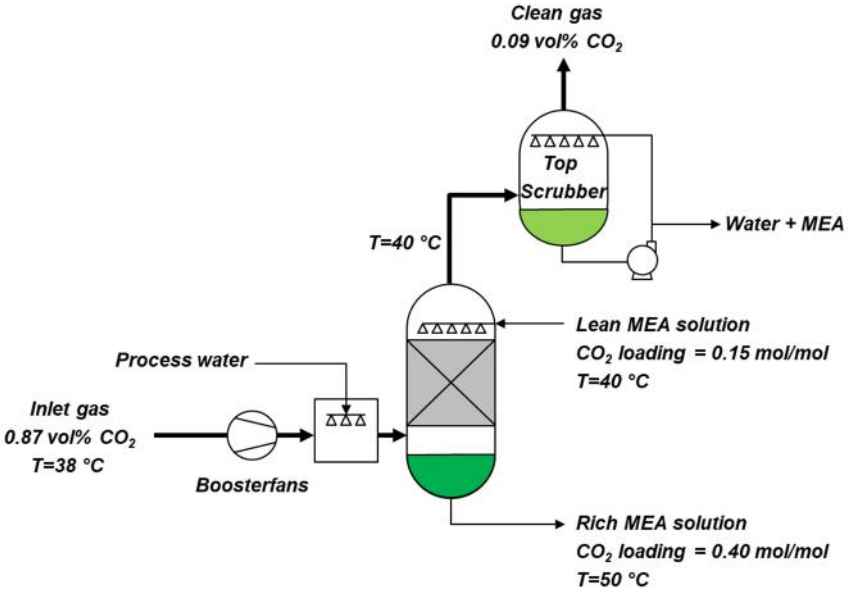

Figure 7. Process diagram of the absorption part of the CO_2 capture plant.

Because the boosterfans increase the temperature of the gases by about 7-8 degrees, the gases dry a bit, and with a simple quench system, 100 % saturation is restored, and the temperature is also reduced a bit. The surplus of water can be returned to the SO_2 scrubber since at this point there is no MEA in the solution yet.

During absorption the following reactions take place:

1. Absorption of CO_2 : $CO_2(g) + H_2O \rightarrow H_2CO_3$
2. Reaction with MEA: $MEA + H_2CO_3 \rightarrow MEACOO^- + H_3O^+$ (exothermic)

The actual reactions are quite complex, but this simplification is a good representation of what happens with CO_2. Additional information is that the absorption should take place at temperatures ideally below 50 °C. The absorption reaction is, however, exothermic, so the temperature inside the column increases as the solvent comes down. If large amounts of CO_2 are absorbed, then it may require interstage cooling to control the temperatures. However, in our case the amount of

CO_2 is low, so with a smart design this can be avoided. A good option is to provide extra cooling of the solvent stream that enters the top of the absorber. This is called the lean-solvent because the loading of CO_2 is at the lowest at this point of the process. If this stream is cooled to 40 °C, for example, then this provides for a good cooling effect inside the column.

In order to make this work, the absorber must operate at internal gas velocities around 3.0 to 3.3 m/s. because the gas volume is so large, this range of gas velocities makes the tower dimensions comparable to that of a large SO_2 scrubber. In the example, the absorber diameter at 3 m/s is 15.8 meter. This sounds very large, but in power plants some absorbers have a diameter of 20 meter so this 15.8 meter diameter is not excessive, relatively speaking. On a side note, in China many aluminium smelters now have installed single SO_2 scrubbers based on the power plant design. They use the limestone/gypsum process and in this application the diameters are in the same range as for the projected CO_2 absorber.

To allow the gas velocities to be in this range, it is likely that a compromise must be made regarding the height of the packing. If the free passage inside a packing is high, then more vertical height is needed to provide for the right amount of mass transfer surface to complete the absorption to a desired level.

The flow of solvent is in the range of 500 to 1000 m^3/h. The solvent is regenerated in the stripper (next section) but not all the CO_2 is driven off the solvent. It is more practical to allow a small loading in the regenerated solvent. The loading is expressed in mol CO_2 per mol of solvent and in the regenerated, or lean, solvent the value is in range of 0.10 to 0.15 mol/mol. After the solvent passes through the absorber the loading is in range of 0.40 to 0.45 mol/mol. From this point and on the solvent is referred to as 'rich' solvent.

As can be seen in the chemical reactions, the solvent is acidic in nature. That means that the absorber and piping are made from stainless steel to prevent corrosion. Again, this is not of concern as power plant scrubbers are also made from stainless steel. A popular choice is Duplex 2205 (UNS S32205) for the absorber tower.

Using simulation software, a process designer can put together a design for the CO_2 absorber playing with the CO_2 loading of solvent, the heat balance, and a few other parameters like packing type. During the preparation of this paper the PPS software was used, which is a rate-based process simulator that accurately predicts the MEA process. One of the key findings is that the absorber can be designed for a CO_2 removal efficiency of 85 to 90 %. It is not recommended to go beyond 90 % at this stage in the deployment of the technology in smelters. There is still a lot to learn of the application and designing absorbers with more than 90% removal efficiencies exponentially drives up the cost.

4.4. Stripping of CO_2

Now that the CO_2 is absorbed by the solvent, a process is needed to release the CO_2 in a pure form so that it can be taken elsewhere. One of the key characteristics of amines is that if heat is applied, the absorption of CO_2 is reversed, and pure CO_2 gas is released. This takes place according to the following reaction:

$$\text{Desorption of } CO_2: \quad MEACOO^- + H_3O^+ + \text{Heat} \rightarrow MEA + CO_2(g) + H_2O$$

The rich solvent is pumped up to the top of the column that recovers the CO_2. Because the CO_2 is basically stripped from the rich solvent, this column is referred to as the stripping column or stripper.

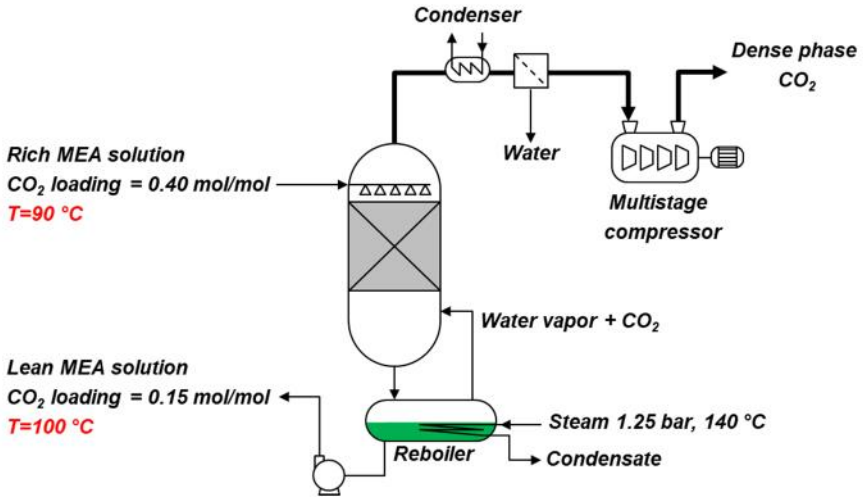

Figure 8. Process diagram of the stripping section of the CO_2 capture plant.

The solvent is distributed over a packing inside the column and flows down to the bottom. Below or on the side of the column is placed a so-called reboiler. This is a vessel that holds steam coils though which steam (1.25 bar, 140 °C) runs and condenses. The heat is transferred into the liquid solvent that starts to boil. By keeping the column under pressure, the reboiler can be operated with an overhead temperature of about 110 °C. That means heat is being put into the solvent and CO_2 is starting to release. Also, water evaporates, and a combination of water vapor and CO_2 gas rises through the column.

The top gas goes through a condenser to cool down the gases and let the water vapor turn into liquid so that it can be separated from the CO_2 gas. The CO_2 gas goes to a multistage compressor system where it is pressurized to approximately 75 bar to bring it in dense phase conditions. In that state the CO_2 is a vapor but with a density of a liquid. In this state, it is best to transport it to the end-user. CO_2 can be transported in ships and typically this is done with CO_2 at -54 °C and 7 bar pressure [6].

A side stream is taken from the reboiler to extract lean solvent from the stripper. This is cooled against the incoming rich solvent and returns to the top of the CO_2 absorber. This closes the loop where the solvent goes around and around and acts as a conveyor belt to transport CO_2 from the absorber to the stripper.

4.5. Complete Process for CO_2 Capture

Until now, we have discussed the individual steps of absorption and stripping. In the following process diagram, the whole CO_2 capture process is presented as it is intended for use in aluminium smelting.

There are some items not discussed in previous sections. One is the use of heat exchangers to heat or cool the solvent where needed. The rich solvent is heated to 90 °C using the hot lean solvent. However, this does not cool down enough to directly to the absorber. For that reason, a dedicated heat exchanger is installed to cool the solvent to, for example, 40 °C.

Also is shown how fresh MEA solvent is added to the process. There is a purge that is represented by the filter for heat stable salts. These accumulate over time and with intervals the filter is used to extract the salts for disposal.

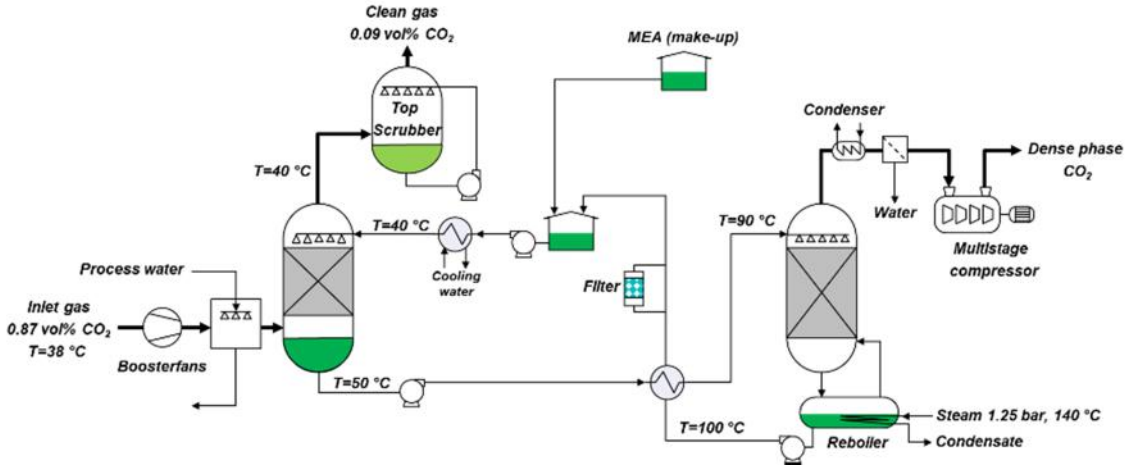

Figure 9. The full process flow diagram for a CO_2 capture plant in a smelter (one GTC).

4.6. End-Uses for the CO_2

This topic would deserve a full paper on its own so without going into many details, it is of interest to understand what use there is for the captured CO_2.

4.6.1 Underground Storage

The majority of CO_2 today is stored underground. The following options are used:

1. Mineralization in saline aquifers
2. Depleted oil and gas reservoirs
3. Coal seams
4. Mineralization in underground volcanic structures (Iceland)

4.6.2 Enhanced Oil Recovery (EOR):

Enhance oil recovery is a scheme where water and CO_2 are co-injected in a mature oil reservoir to pressurize the well and squeeze more oil out. Hence, its name 'enhanced oil recovery'. A large fraction of the CO_2 stays in the oil reservoir and is sequestrated.

4.6.3 New applications

There are many applications being developed because the more, the better. We need many solutions if CO_2 is captured on global scales. Examples are enhanced plant growth in greenhouses and conversion to (bio)fuels and chemicals.

5. CO_2 Capture Integration Aspects in Aluminium Smelters

There are several aspects to review that concern the integration of CO_2 capture in an aluminium smelter.

5.1. Heat Integration

A critical part of designing the CO_2 capture process is managing heating and cooling requirements. The process in the reboiler alone requires 1.25 to 1.50 tonnes of steam per tonne of CO_2 removed. This is equivalent to 3.6 to 4.0 GJ/t of CO_2.

By default, there is an electric power type steam generation unit that comes with the CO_2 capture plant. At least the boiler feed water should be heated using hot water that arrives from the HEX heat exchangers that are recovering heat from the pot ventilation gases (see also Figure 3).

If heat needs to be dumped, then this can be done by heating up the process water of the SO_2 scrubber. This way the scrubber is used as a heat sink.

In some cases, there are onsite power generation units like steam turbines. An option can be to, like in Al Taweelah, add a steam generator to make steam for the stripper units. Or, to use some steam that is already produced for an alumina refinery, in the stripper reboilers.
These options are site driven and must be studied carefully in each case. The better heat integration takes place, the lower the operating costs will be.

5.2. Reduced Pot Ventilation Flow

In the basic flowsheet all ventilation gases from the GTC and SO_2 scrubber are directed to the CO_2 absorber. It results in a tower with a diameter of almost 16 meters and a height that will exceed 20 meters. Furthermore, if the concentration of CO_2 were higher, then the driving force in the absorption process is higher too. It can result in a lower requirement for packing material and reduce the height of a column. Because it is theoretically possible to lower the pot ventilation flow to increase the CO_2 concentrations, there is an added benefit that now the total flow is reduced by a large amount. In several papers [7] reference is made to this principle but none of them go into detail. In this paper, it is included, and an attempt is made to analyze it to provide useful insights.

5.2.1 Standard Flowsheet

First, there is the standard flowsheet with design characteristics. The pot exhaust flow has two main functions, which are a) removing heat released from the crust and maintaining the heat balance of the cell, and b) providing means to capture the emissions from the cell. Because the flow requirement is higher to control gas temperatures, this is the governing case. It is therefore a leading factor in the analysis.

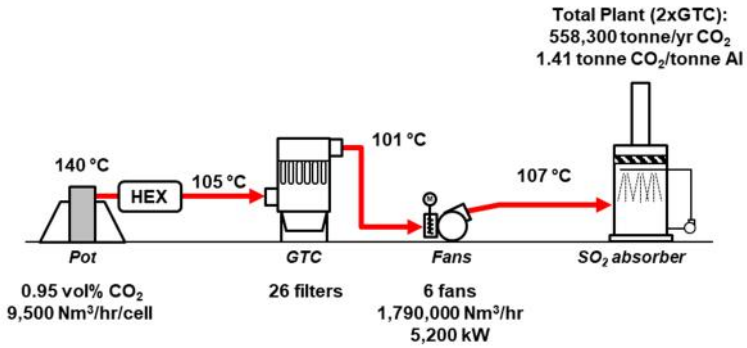

Figure 10. Standard flowsheet with 9 500 Nm^3/h per cell without CO_2 capture plant.

The next flowsheet shows the process after a CO_2 capture plant is added as a retrofit. Note that if this is integrated into a new smelter, the boosterfans can be omitted.

Findings and observations:

- The use of dilution air for gas cooling should be avoided not to dilute the CO_2 concentration. It is one of the reasons that heat exchanger technology (HEX) should be used.

- To push the flow through the CO_2 capture system, the boosterfans draw an additional 6.4 MWh/h of power to make the total 11.55 MWh/h.
- The CO_2 removal is set to 90 % resulting in the capture of 502 500 t/yr of CO_2
- Leaving the economics aside, this flowsheet can be established with current technical means. In other words, this can be installed within the next 3-5 years.

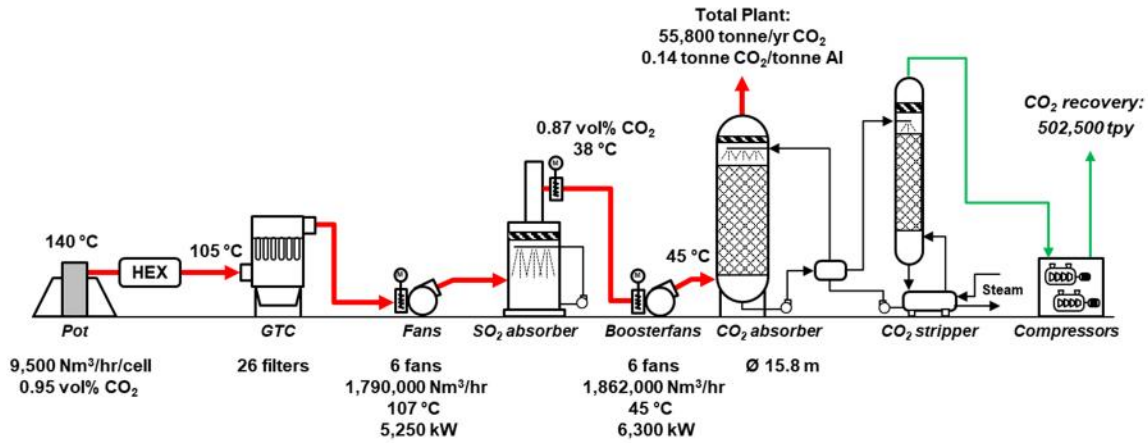

Figure 11. Standard flowsheet with 9 500 Nm^3/h flow per cell and CO_2 capture.

5.2.2 Reduced Pot Exhaust Flow to 50 %

In this scenario the pot exhaust flow is reduced by 50 %. This provides for the following flowsheet:

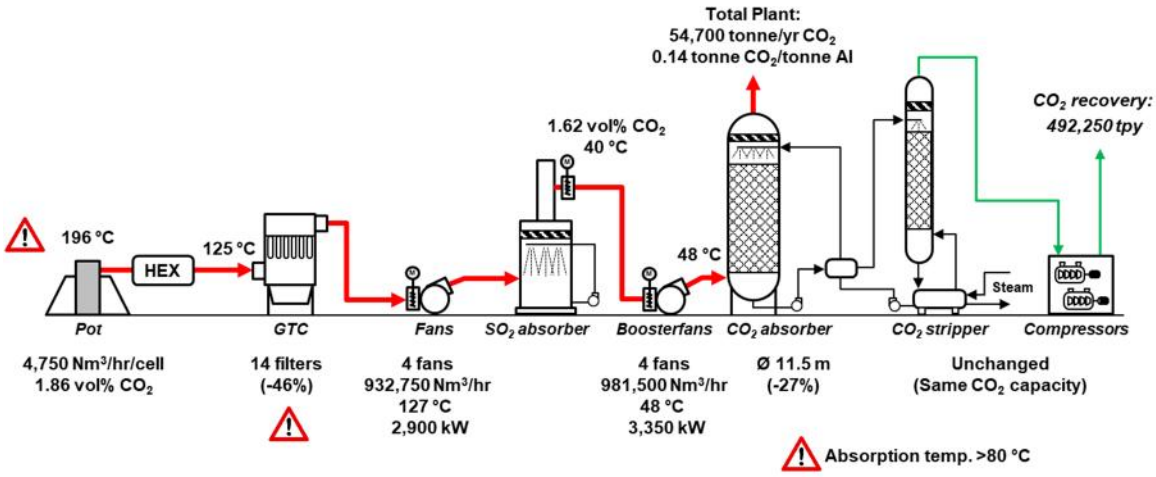

Figure 12. Flowsheet with results from a reduction in pot exhaust flow of 50 %.

Findings and observations:

- The cell exhaust temperatures are approaching the limits for which the superstructures are designed.
- The gas collection efficiency remains high but working in cells that are close to 200 °C will see increased emissions in the potrooms. Cells also will get lesser attention from operating staff now that working conditions have deteriorated.
- The heat exchangers have a very large duty and need to reduce temperatures >50 °C.
- The GTC is reduced in size (24 → 14 filters) but the alumina throughput is still the same. There is a limit to which the number of filters can be reduced to ensure good scrubbing and

handling of alumina all in one. Halving the gas flows takes the GTC outside its normal operating window.

- The number of exhaust fans and booster fans is reduced to 4 and 4, respectively. The combined power consumption is down to 6.3 MWh/h, a reduction of almost 50 %.
- The diameter of the CO_2 absorber is reduced by 27 % to 11.5 meters.
- There is a potential for higher solvent temperatures in the absorber. This is likely to require interstage cooling.
- The stripper etc. remains unchanged since the CO_2 recovery capacity is the same.

5.2.3 Reduced Pot Exhaust Flow to 25 %

In this scenario the pot exhaust flow is reduced to 25 % to get in range of 4 vol% CO_2 in the gases.

This provides for flowsheet in Figure 13.

Findings and observations:

- The cell exhaust temperatures are well beyond the temperature limits for which the superstructures are designed.
- Operating the cells at 295 °C in the superstructure will have several challenges. Emissions will be much higher in general, but also into the potrooms. It is unknown if these temperatures do anything to the integrity of the crust. It is an important insulating part of the process, and it may be that more holes in the crust will form. Lastly, the hooding is made from aluminium covers. At these temperatures, they may have to be made sturdier or must be replaced, which is far from ideal.
- The venting of fluidization air from alumina handling systems makes a large impact on the CO_2 concentration. In this scenario, the alumina handling system in the potrooms are disconnected.

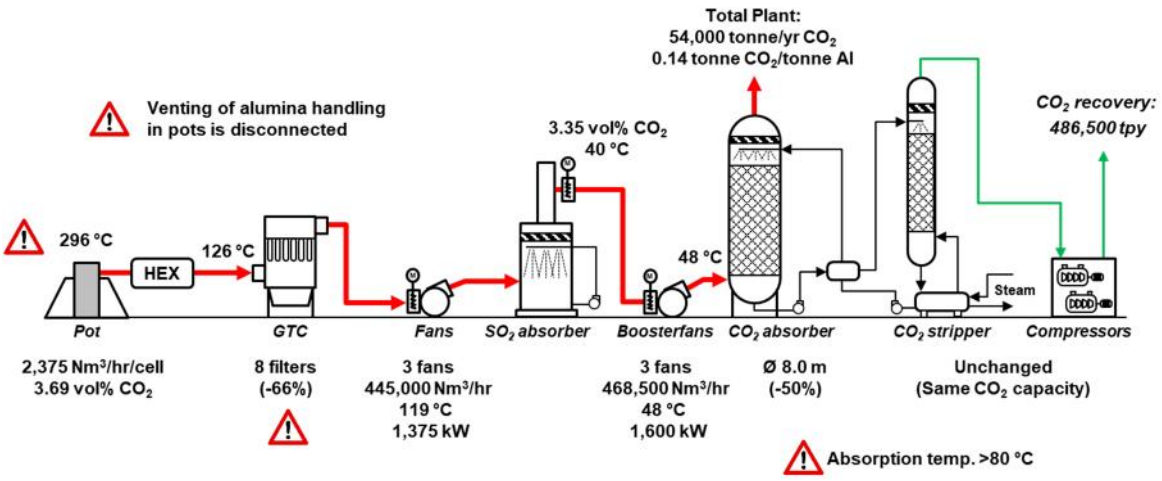

Figure 13. Flowsheet with results from a reduction in pot exhaust flow to 25 %.

- The heat exchangers need to remove a very large amount of energy (~7 MWh) from the ventilation gases to bring it under 130 °C in the inlet. The energy intensity should be considered for production of steam that can be used in the reboiler. However, the current technology is not ready for this yet.
- The size of the GTC is reduced to one third of the original size. In the existing GTC only 8 out of the 24 filters are operating. However, this requires serious changes to the alumina handling systems. On top of that, the concern is that the alumina load per filter is too high to handle.

- One option is to use filter bags in the GTC that withstand higher temperatures. However, the drawback of operating a GTC beyond 130 °C is that HF formation in filter cake exponentially goes up. HF outlet concentration will be a multiple of normal values. That said, this will be captured in the SO_2 scrubber, but the cost to replenish the fluoride with AlF_3 goes up too.
- Only three main fans are required for the main fans and for booster fans. The total power on all fans is reduced to 3.0 MWh/h.
- As expected, the size of the CO_2 absorber is reduced by 50 % to 8 meters in diameter. However, interstage cooling is required because the liquid volume is reduced so that more heat per liquid volume is accumulated.

5.2.4 Alternative Method(s) to Reduce Pot Exhaust Flows

REEL Norway is investigating a new idea to place a small GTC on a single cell combined with a heat exchanger to treat the ventilation gas on each cell [8]. The novelty is that a fraction of the cooled, treated gas can be returned to the cell to displace an equal amount of air that otherwise enters the process. If the discharge of the GTCs is collected, then a small volume of ventilation gases can be passed on to the next steps for treatment like SO_2 scrubbing and CO_2 capture. Also, the resulting CO_2 concentration should be higher making it easier to remove in the absorber.

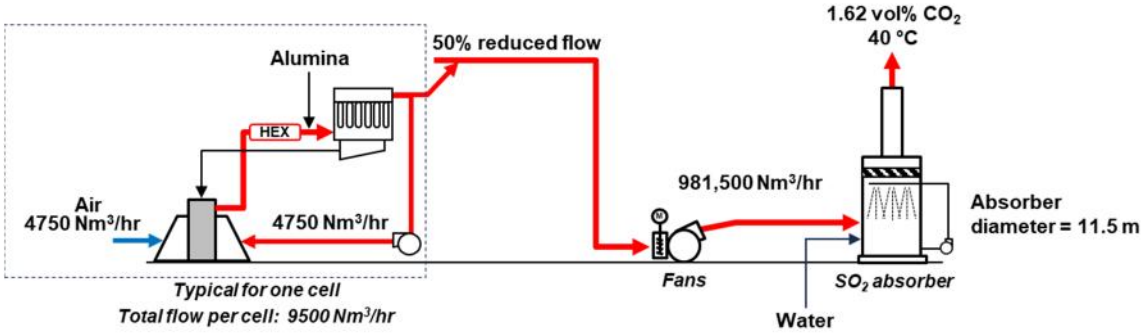

Figure 14. Process schematic of pot gas recirculation [9].

Shown is an example of a 50 % gas flow reduction. Technically, it may be possible to even go to reduction levels closer to 90 %. In that case the CO_2 concentration dramatically increases while gas flows are only a fraction of the original amount. This may be too extreme, and an optimum is to be found somewhere in between, but this has a high potential as an enabling technology.

Considering many of the findings and observations above, this idea overcomes many of the challenges from reducing the pot gas exhaust flows. If it can be made to work, again, then it can be an important tool for integration of CO_2 capture.

5.2.5 Conclusions from the Evaluation of Reduced Pot Exhaust Flows

The analysis of the different scenarios leads to some general conclusions:

- It reveals that the temperature is a critical parameter in the evaluation of reducing the total ventilation flow. A key bottleneck is operating superstructures with elevated temperatures. It puts a risk on mechanical strength of the structure, and it has a negative impact of keeping emissions in check.
- The heat exchanger technology is a critical tool to make this successful no matter what percentage of reduction is targeted.
- With current technologies, it is possible to add a CO_2 capture plant to an existing ventilation/gas treatment system; however, this will be at full flow or maybe at a slightly

reduced flow rate. The maturity level of some needed technology is not there yet to make more drastic reductions in flow.

- Looking closely at each scenario of pot exhaust flow reduction (100 % →50 %→25 %) gives the impression that there is an optimum somewhere. Further analysis should include more parameters to seek this optimum. This analysis, for example, omits any cost reduction in steel structures, reduced column heights in the CO_2 absorber, and any changes in steam requirements.
- The idea of pot gas recirculation is promising and can make a difference to achieve the principle of reducing the flow from the pots.
- Concerning the question 1 vol% CO_2 or 4 vol% CO_2, it is perhaps best to start by including CO_2 capture in a normal or slightly modified ventilation system with 1.0 vol% CO_2. That way all technical means are known, and the risks are low. Over time, steps can be taken to further optimize the gas flows, and thus the costs.

6. Current Activities in CO_2 Capture in Aluminium Smelting

When in 2010 the first paper was written regarding using CO_2 capture in aluminium smelting, not much has happened. But in recent years there is an urge to start developing this option to reduce CO_2 emissions directly from the smelter. Here are some current activities that are reported on in the public domain.

- Hydro Aluminium (Norway) started looking into using solvent type processes for CO_2 capture. Then, in 2021 Hydro invested in Verdox, a US based company that is spun off from MIT. The Verdox technology is very innovative and based on the used of impregnated membranes where a potential placed on a membrane makes it either an acid or a base. When in 'base' mode it can absorb gases like HF, SO_2 and CO_2. It loads up and when it reaches its maximum capacity it is changed into a regeneration mode. The potential is changed and one by one the acid gases can be released. This means a future industrial system can remove HF, SO_2 and CO_2 in one go. At least these were the initial principles. The technology readiness level is still very low, but it has a unique impact if it can be made to work.
- Aluminium Dunkerque (France) is getting ready to link up with a CO_2 hub that is created in the port of Dunkerque. It conducted studies together with EDF to investigate the potential of use solvents for CO_2 capture from the process gases. A pilot plant has been designed and currently a request is made with the French government to fund the project. It could lead to a first pilot in 2024/2025 timeframe.
- Rio Tinto (Iceland) and Carbfix plan use Rio Tinto's land surrounding the ISAL smelter for onshore CO_2 injection in the world's first carbon mineral storage hub, the Coda Terminal. Liquified CO_2 will be imported by ship from industrial sites across North Europe for storage.
- Before the smelter permanently closed, Aluminium Delfzijl conducted a study into the application of solvents for CO_2 capture. It is worth mentioning that the project was driven by favorable subsidies by the Dutch government to store CO_2 in depleted gas fields. An innovative element that was considered is the transportation of dense phase CO_2 by Carbon Collectors in barges to the North Sea gas fields operated by Neptune Energy. This flexible way of transportation is an enabling technology for CO_2 capture.
- Both EGA and Alba have activities that involve the potential use of CO_2 capture in their operations. In the case of EGA, this focuses on their gas turbines and their collaboration with GE. Similarly, in 2022, Alba signed a collaboration agreement with Mitsubishi Heavy Industries to do something similar.
- Lastly, in Australia CSIRO's post-combustion capture (PCC) research program is taking an interest in aluminium smelting. Using a proprietary solvent that is less prone to degradation by oxygen in the gases, efforts are underway to find opportunities to trial a solvent based CO_2 capture process.

7. Notes Concerning a Technology Road Map

In general terms, the road map is to scale up the application of carbon capture technology in aluminium smelters. Most reachable is the use of solvents. This is not perfect but with focused pilot trials a lot can be learned for a first commercial size implementation in five to seven years from now. This includes alternative solvents that have lower energy requirements and/or are less prone to degradation by the presence of oxygen in the gases, and/or are non volatile and biodegradable.

Other methods for CO_2 capture continue to be developed in other industries. Some of them like Svante (Canada) already allude to their application in aluminium smelting. At some point, we may see a pilot system of this technology in a smelter, but in essence, it has a similar roadmap for scaling up the technology.

Verdox is very promising but still is long way from industrial application despite being powered by the resources from Hydro Aluminium. Its roadmap will entail several pilot trials from small to large to eventually arrive at a system that can be connected to a series of aluminium cells.

The analysis in section 5 shows that there is a real need for enabling technologies that can make a big difference in the implementation of CO_2 capture in aluminium smelting. There will be a great need for the full potential of heat exchangers. This technology needs a much larger operating window so that it can deal with higher temperatures and be integrated with the CO_2 capture plant.

A difficult area to change is the cell super structure. If we want to make this operatable for temperatures close to 300 °C, then some serious development work is needed. Plus, if a concept is created, we would want to have this tested over a long period of time (like several years) since this a critical item in the production process. The pot gas recirculation technology can overcome this challenge and has great potential. It is being piloted so, if successful, the implementation of this is not that far out.

8. Conclusions

The global aluminium industry is responsible for annually 1.2 billion tonnes of equivalent CO_2 emissions. This equates to 2 percent of the total industrial GHG emissions. It means the industry needs to take action to come up with solutions to reduce GHG emissions.

One option is to capture CO_2 from the process gases from aluminium smelting, and this is the single focus of this paper. Because this is a new application (in other industries CO_2 capture is already available on commercial scale), we are still on a path of discovery. The industry is close to installing one or maybe two pilot plants, but that is it. In this paper, an attempt is made to cover not only a standard CO_2 capture process, but also how this is integrated, and how the attributes of the electrolysis process match up with this.

Some fundamentals are shown why the electrolysis process results in ventilation gases with approximately 1 volume percent of CO_2. This is considered a value that fits in the lower range of the solvent processes for CO_2 capture, which are the most mature capture process available to date. From the calculations, it is clear that there are limited options to bring this concentration more in line with what is considered more economical (4 volume percent).

An analysis is performed to investigate the options to increase the concentration of CO_2 by reducing the amount of air that is drawn into cells for cooling purposes. Several steps are taken to reduce the flow from cells, and bottlenecks are identified. It is concluded that some bottlenecks

can be overcome by further development of technologies. However, a large bottleneck exists in the design of electrolysis cells, and this will require significant changes in the design to make it work at high temperatures.

A new technology concept is pot gas recirculation with localized scrubbing on cells and integrated cooling. If this works as intended, then this is a potential solution to allow reduced gas flows from cells while maintaining temperatures where they are today. The concept is being tested on a small scale and a pilot is expected very soon.

A key conclusion is that CO_2 capture can be installed with the technical means we have available today. It will be applied at levels of 1 volume percent CO_2, but this can be done with standard solvents like MEA. It may not be the most economic approach yet, but there is still a lot to learn, and it is unknown where the development will take us.

The road map for CO_2 capture is basically starting with piloting solvent-based processes like with MEA. From this some scale up steps are required before we arrive at a commercial scale; however, in other industries the technology is already applied at commercial scale so many learnings of that are available to developers.

The road map also holds the development of enabling technologies. These are key technologies that can remove key bottlenecks. For example, the heat exchangers need to move into a new operating range to extract a lot more heat from the gases than is currently the case.

On the short term, there is likely to be a first pilot plant in France at Aluminium Dunkerque. This will be based on a solvent process and integrated with a GTC. Aluminium Dunkerque does have a baking furnace connected to one GTC so we may see the combination at work. Other than that, there are only a few developments in this field.

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