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HANDLING CO_2EQ FROM AN ALUMINUM ELECTROLYSIS CELL

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Abstract

The increased focus on reduction of energy consumption and preserving our environment will affect a lot of industries in the coming years, and this will indeed be the case also for the aluminum industry. Hydro believes that aluminum is a part of a sustainable future and wants to take an active part in developing a more environmentally friendly production process. Most of Hydro's electricity used for aluminum production is based on water power, but the plants in Kurri Kurri, Australia and Neuss, Germany are based on coal power and our new smelter in Qatar will be based on gas power. This paper gives an insight in Hydro's plans for reduction of the carbon footprint from their primary production plants around the world by keeping their focus aiming at elimination of AE and production of CF gases. Hydro also has developed a gas suction technology enabling partial CO_2 capture from their electrolysis cells, as well as reduction of the net gas suction volume, with promising results.

Introduction

Globally the aluminium industry emits over 300 million tons of CO_2-equivalents annually [1]. This is about 1% of the world's total emissions. These large numbers are increasing, not only because the consumption of aluminum is growing, but also because an increasing share of the production is derived from electricity made from fossil fuels [1].

Theoretically only 1.22 tons of CO_2 (which equals to 333 kg C) is being produced per ton of aluminium according to the standard equation:

$$\frac{1}{2}Al_2O_3+\frac{3}{4}C\rightarrow Al_{(l)}+\frac{3}{4}CO_{2(g)}$$

but because of reduced current efficiency, anode burn-off, and anode effects the amount of CO_2 equivalents is considerably higher.

The back reaction giving loss in current efficiency (CE) increases the amount of CO_2 to 351 kg C/ton Al (CE = 95%) and 370 kg C/ton Al (CE = 90%). In addition anode air burn gives a loss of 30-70 kg C/ton Al and carboxy attack causes a loss of 20-30 kg C/ton Al.

The biggest controllable contributor to CO_2eq emissions is the anode effects where PFC gases are being produced. The lowest anode effect frequencies are 0.02 – 0.10 AE/day for Prebake cells and 0.25 – 0.50 AE/day for Søderberg cells. It seems obvious that the industry has to work hard to reduce the anode effect frequency, but more importantly reducing the anode effect duration. As long as AE occurs, the focus on early anode effect detection and effective quenching procedures must be of first priority.

Another important contributor is the so-called start-up anode effects. Hydro, among others, has developed procedures for AE-free start-ups with both gas and graphite preheating [2], and is now developing a procedure to obtain the same good results with coke-bed preheating.

In the short term PFC elimination represents the “lowest hanging fruit”. It is inconceivable that if the Hall Héroult process had been developed during the last ten years, the occurrence of anode effects would not be tolerated at all. They are simply a historical artifact and are almost completely avoidable. The real difference between smelters is focus and determination, as well as an appreciation of the true cost of anode effects [1].

In the period 1990 to 2010 the aluminium industry as a whole will have reduced the greenhouse gas emissions (PFC) per ton of aluminium by 80% [4]. The last 20% will be more challenging to reduce, and it seems logical to start thinking of capturing the CO_2 too. We cannot reduce the production of CO_2 per ton aluminum below the theoretical possible number, because this is a part of the Hall-Héroult process with carbon anodes. A literature survey performed summer 2008 did not identify any publications on CO_2 capture from aluminum electrolysis cells.

A sustainable aluminum industry

This is what Hydro has said in public about Carbon Capture and Sequestration [4]: There is presently no proven, alternative technology available, although substantial research is being done. In the longer term new aluminum smelters may be designed to operate without carbon anodes or to capture and potentially store the CO_2, given a CCS infrastructure. Hydro's technology organizations in Årdal and Porsgrunn, Norway, and Neuss, Germany, with 170 employees, are highly dedicated to the effort of developing new technologies, including environmental solutions. Hydro scored highest among aluminium companies in Dow Jones Sustainability Index ranking in 2008 [5], for the third year in a row. The report cites Norsk Hydro's "excellent risk management and compliance systems" as reasons for its success in the survey, and cites the company's smelter in Sunndal, Norway, as an example of how innovation can improve energy use and lower emissions [6]. Hydro believes that a sustainable business is also a profitable solution [7], supported by others [8].

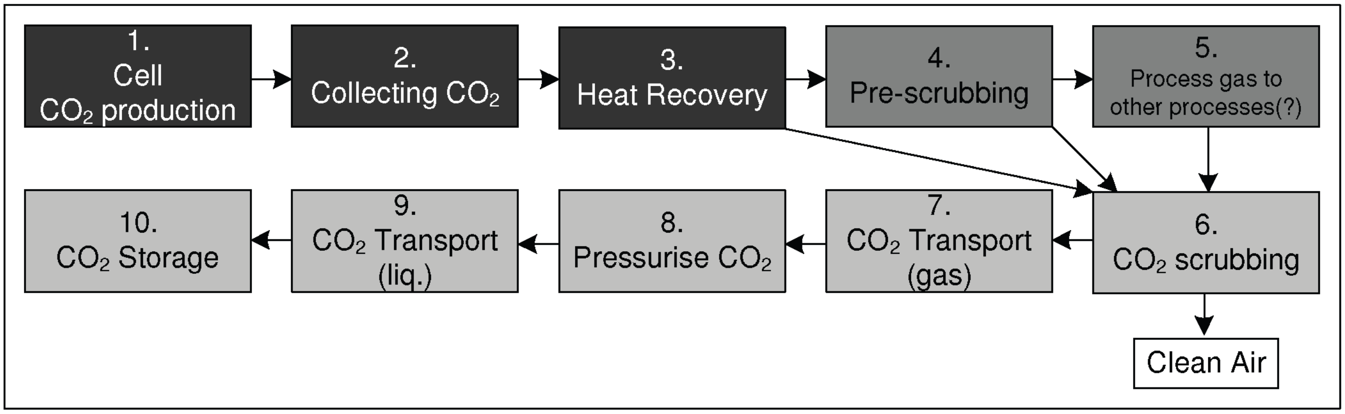

Figure 1: CO_2 value chain showing CO_2 capture, handling and storage.

The CO_2 value chain from an aluminum producer's perspective

The CO_2 value chain that Hydro have to consider can be illustrated in Figure 1, showing 10 process steps that need to be controlled. The boxes 1-3 (cell related) illustrate what we need to keep as in-house core competence, the boxes 4-5 (gas pre-scrubbing and gas to other processes) are something we need to understand and handle properly, while the five last boxes indicate what we might consider asking someone with necessary know-how and expertise to take care of. However, some knowledge about the downstream processing of CO_2 is necessary within an aluminum company too.

The amount of CO_2eq being produced depends on the source of electricity used. Natural gas-fired power plants emit 0.4 kg CO_2 per kWh of electric power, while coal-fired power plants emit 0.9 kg CO_2 per kWh of electric power.

Table 1: Typical values for kg CO_2/kg of primary aluminium produced for three scenarios, produced by water-, gas- and coal-fired power plants, respectively.

	Water power kg CO2 eq/kg Al	Gas-fired power kg CO2 eq/kg Al	Coal-fired power kg CO2 eq/kg Al
Alumina production	1.80	1.80	1.80
Anode production	0.30	0.30	0.30
Electrolysis	1.50	1.50	1.50
Anode effects	0.30	0.30	0.30
Casthouse	0.06	0.06	0.06
El-power	0.00	5.80	13.60
Sum	**3.96**	**9.76**	**17.56**

The numbers in Table 1 clearly show that the source of electrical power is the main contributor to emissions of CO_2, and the focus should then be on the gas- and coal-fired power plants.

However, both amine and chilled ammonia used for CO_2 capture need a lot of heat to release the CO_2 from the adsorption media (use steam). Since aluminum pots release about 50% of the input energy as heat there should be some synergies between heat recovery from the electrolysis cells from process gas, side walls and anode yokes [9] and a CO_2 scrubbing plant.

Combining an electrolysis plant with other CO_2 emitting processes such as power plants and its like should also be considered. Since the process gas released from the aluminum scrubbers used by the aluminum industry contains so much oxygen, this gas may be purified further and used as burning fuel in a gas- or coal-fired power plant. The benefits are obvious: sequential use of process gas increases the CO_2 concentration to be captured, which is advantageous. In addition one can then split the cost of CO_2 capturing between several CO_2 producers (see Figure 2).

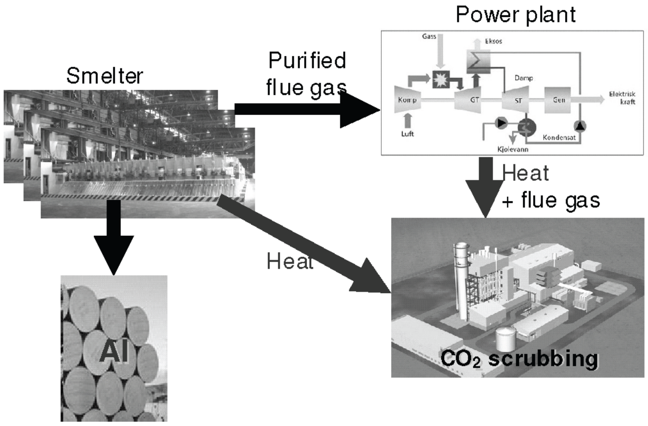

Figure 2: A sketch of the synergies between heat recovery and CO_2 handling from an integrated aluminium smelter.

Pot suction

The production of aluminium creates at lot of different off gasses, mainly CO_2 with traces of Carbon Monoxide (CO), but also significant amounts of Oxygen (O_2), Hydrogen Fluoride (HF) and Sulphur dioxide (SO_2). Modern smelters remove most of the HF and SO_2 before the residual off gases are released to the atmosphere, but not CO_2. In order to remove all the process gases being released from the pot and to cool the cell properly, the standard suction design involves numerous integrated suction points in the superstructure. The suction system drag in a lot of false air from gaps and joints in the pot's superstructure keeping a negative pressure inside the top hoods to ensure proper capture of all the process gases produced in the pot. The gas collected is comfortably cold for the superstructure (100-150°C), and the off-gases are strongly diluted by the false air. In addition the design is keeping the temperature below the upper temperature limit for the filter bags inside the Fume Treatment Plant.

As illustrated in Figure 3, in all modern Prebake cells the superstructure (2) has several individual integrated point feeders. The gas collection system (3) has numerous suction points to balance the pressure difference internally in the superstructure, and to the pot room atmosphere. Since at least one anode normally has to be replaced by a new anode every day, modern Prebake pot have a superstructure with many covers (4), hooding the area between the cathode shell and the anode superstructure (2) to prevent the process gases from entering the pot room. The process gases extracted is then entering the conventional fume treatment plants, with off gases ready for further treatment (purification). Hydro Aluminium has a gas collection efficiency of 99.5% for new greenfield technology installations, by means of a system increasing the suction volume significantly when doing pot tending, called Pot Tending Suction (PTS). This is in practice done by flipping a valve, changing the suction mode from the cell from Normal to PTS increasing the suction volume significantly. The PTS ventilation system makes the anode change routine etc. with several covers removed from the pot, possible with virtually no losses of process gases to the pot room atmosphere as a result.

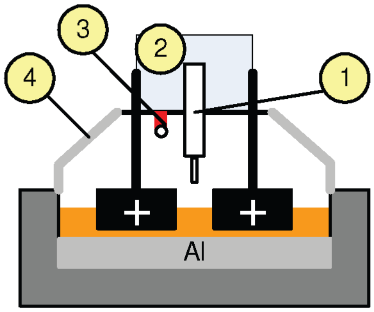

Figure 3: A sketch of a cell with controlled ventilation.

There has not been much focus on CO_2 scrubbing since it is a part of a natural circle, but the recent focus on how CO_2 impacts the climate change has changed the focus. The cost and the design limitation of modern electrolysis cells for CO_2 capturing and sequestration are the low concentration of CO_2 in the flue gas, which typically is about 1%. To remove low-concentration CO_2 is both challenging and expensive and information about this has not been found published anywhere in the open literature. The cost of CO_2 sequestration generally decreases with increasing CO_2 concentration in the process gas.

Functional description of the Distributed Pot Suction (DPS) device

Hydro has designed a device where one can combine feeding of the raw material alumina to the cell and at the same time extract a more CO_2-concentrated process gas from a hole in the top crust in the cell. This is not standard procedure in the aluminium industry today. The three main net effects one obtains regarding the process gas are:

1. Less total volume of gas extracted from the pot with the potential to reduce the overall fume treatment handling,
2. As a consequence of 1, the gas collected are warmer than before and hence more suitable for heat recovery
3. Suction of less “false air” into the gas collection devices increases the concentration of CO_2 in the process gas significantly, enabling CO_2 capture and sequestration with standard technologies used for CO_2 capture from electrical power plants.

To obtain maximum gas collection from the DPS, one can design the collection cap on the alumina feeder in many ways. One of the prototypes we designed had a single wall collection cap (see the CFD modeling results of the collection efficiency in Figure 7). Another version of the suction cap had double walls where the suction velocity between the double walls is significantly higher than in the centre (See Figure 8). This extra suction creates an artificial “air wall”, which gives a more efficient process gas collection from the hole in the crust. One can also blow air through this joint, with the penalty of using more of the compressed air in the pot room for this application.

Figure 4 shows Hydro’s patented device where the crust breaker is marked with (1); the breaker is attached to the DPS main parts, i.e., (2) through (4). During operation the normal gas flow in the pot superstructure is relayed through the DPS, and a DPS point is placed in each of the feeding points of the pot. The suction for the DPS is introduced through a dedicated duct connected in point (2). The alumina is then feed from a fluidized feeder in point (3). Inside the collection device (4) there is a double wall, splitting the suction introduced into two, where the peripheries of the device are only a thin slot, i.e., increasing the velocity of the gas sucked through this slot, while the gas suction rate through the centre of the device will be much lower. The alumina which is feed through the connection tube (3), will not be picked up by the gas, since the alumina tube (3) penetrates both the walls of the double walled device (4). Hence, the alumina will be introduced into a low velocity gas flow and not picked up.

When the gas is drawn through point (2) it will be collected into a main duct/manifold on the pot superstructure conveying gas from all fed points. The idea is that this gas can be transported from this transition point to a heat exchanger and thereafter to the fume treatment systems (i.e., fluoride recovery and SO_2 removal) and introduced from there to any commercial CO_2 scrubbing system able to handle the actual concentrations of CO_2.

When the pot is to be serviced, the main collection duct for DPS on the superstructure is closed, and the main ducts in the pot superstructure are activated to support Pot Tending Suction (PTS) from the pot (i.e., 15 000 - 25 000 Nm^3/h, depending on the cell size and shape).

Because the suction device is mounted on the point feeder, a damaged or old feeder can be replaced by a new one during operation by releasing the old one and easily replace it with the new one.

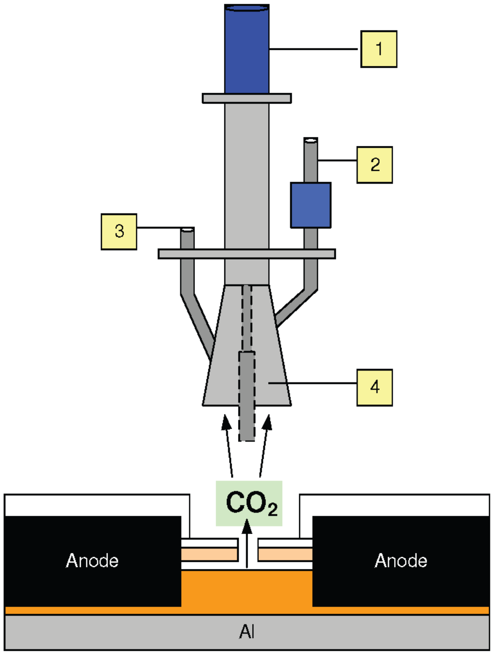

Figure 4: Alumina point feeder with distributed pot suction

The up-concentrated flue gas is warmer than normal, which makes it suitable for heat recovery. On the other hand, the warm gas may damage the superstructure and electronics placed there. One way to solve this new challenge is to thermally insulate the gas-collection tubes within the superstructure and to the place where the heat recovery can occur outside the cell. Off gases from several cells can be connected to the same heat recovery unit. The flue gas is then sent for classical fume treatment removing dust, HF, and SO_2. Depending on whether one connects the off gases to another process as combustion air or directly to a CO_2 scrubber unit, the gas might have to be purified sufficiently for not damaging these process steps.

Operational Results

The measurements were using a TESTO 350/454 flue gas analyzer. The instrument is well proven and documented for these types of analyses, and an internal calibration was done against a known CO_2 gas composition.

Figure 5 shows the CO_2 concentration in a cell with a traditional gas collection system.

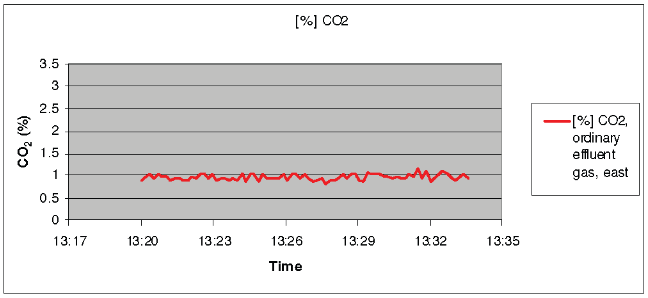

Figure 5: CO_2 concentration from a standard Hydro electrolysis cell with a normal suction system.

The first measurement campaign showed successfully that there was a significantly higher CO_2 concentration in the DPS system compared to the normal suction outlet. For all the measurements the concentration was more than 50% higher. The values were somewhat dependent on the flow rate through the DPS system, but it was not as linear as expected.

A second measurement campaign confirmed the properties of the DPS prototype, however, with somewhat lower concentration differences than found previously. The discrepancies between the measurement campaigns were most probably caused by poor duct integrity and leakages outside the pot superstructure. The last measurement campaign also showed that CO_2 concentrations up to almost 4% could be achieved by reducing the suction rate while still maintaining a good hooding efficiency on the superstructure.
All the measurements confirmed that the DPS concept has potential for collecting concentrated process gas from the pots.

To investigate the maximum achievable CO_2 concentration through the DPS, the normal suction rate was decreased to one quarter of the standard rate. Close to the end of the measurement period the normal suction rate was decreased further, utilizing the DPS as the only process gas collection system, still at some 1750 Nm^3/h. The results that were obtained are shown in Figure 8. The first decrease yielded a fairly constant CO_2 concentration around 2.5%. Closing the normal suction system completely showed that the potential with the governing suction rate lies around 4%.

Figure 6 shows the CO_2 concentration under varying conditions from “normal” to the left, to “pure DPS collection“ to the right.

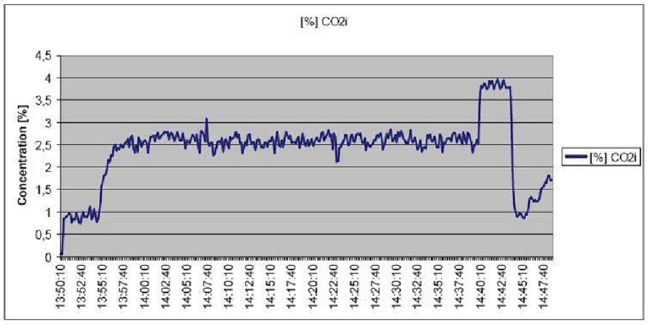

Figure 6: CO_2 concentration from a standard Hydro electrolysis pot with varying suction rates.

Figures 7 and 8 show results from CFD (Computational Fluid Dynamics) modeling of the process gas collection system. Configuration of the cap is shown with both a single and a double wall design, respectively. One can see from Figure 8 that the double wall design gives a more efficient process gas collection.

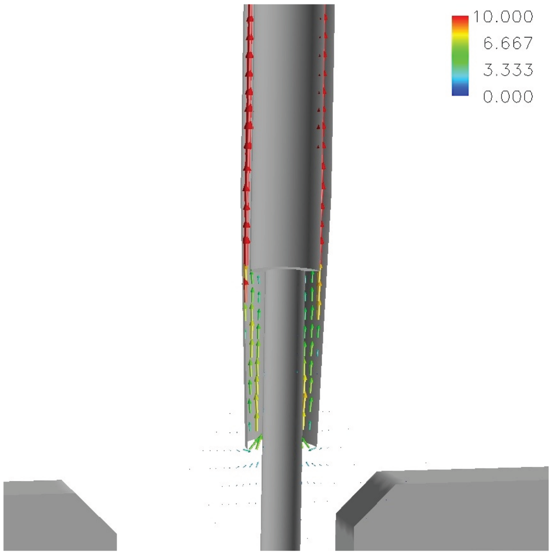

Figure 7: CFD modeling showing gas collection around the feeder, with single wall DPS.

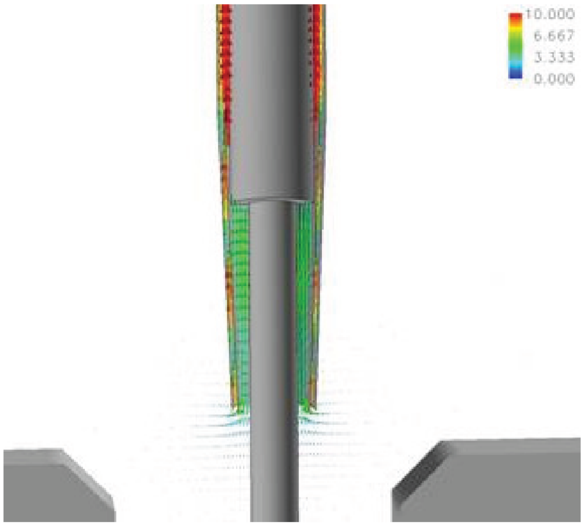

Figure 8: CFD modeling showing gas collection around the feeder, with double wall DPS.

CO_2 Capture Challenges

The following challenges have to be dealt with regarding CO_2 capture:

- How much CO_2 is it possible to collect? A typical CO_2 collection efficiency may be 90%, while an amine scrubber collects about 85% of the CO_2 in the off-gas. Then Hydro Aluminium would still emit 25% of their CO_2 production to the atmosphere.
- Cost of CO_2 capture and storage (CCS). A CO_2 quota typically presently costs 200 NOK/ton, while the CCS costs about 700 NOK/ton. With an annual aluminum production of 2.5 million ton per annum, these numbers give an annual cost of 1.4 billion NOK for amine scrubbing, and "only" 500 million NOK if we emit CO_2 directly to the atmosphere, i.e., we do nothing. However, these costs are expected to change inversely to each other (CCS down, CO_2 quota up).
- Heat recovery must be exploited to make this project economically viable. How to combine heat recovery from the shell side with the off gases and anode yokes must be considered carefully with respect to design and cost
- The heat balance of the cell may change significantly with reduction in suction rate. The increased heat stress put on the cell superstructure must be analyzed carefully.
- A warmer superstructure will generate more HF gases, and HSE is therefore an issue.
- Long term test needed to evaluate the suitability with the DPS system regarding clogging/deposits, mechanical stability, effect of long-time heat exposure etc
- A gas power plant producing 350 MW/year will consume about 2000 tons of amines per year. In addition the amine scrubber produces about 4000 tons of special category waste, which probably has to be deposited of as special waste. The knowledge of these wastes and the impact on the surrounding environment are not fully understood.
- A full size CO_2 scrubbing plant is planned to be built at Kårstø in Norway, but this may be considered as a giant pilot plant, because such a large plant has never been built before. Some new challenges are expected to arise, and an absolute date is not yet set for the completion and start-up of this plant. The initial cost for the Kårstø CO_2 capture plant is estimated to be 1.5 billion NOK.
- National and international cooperation are needed.
- An infrastructure for CO_2 handling and transport does not yet exist in areas where the Hydro Aluminium plants are situated.
- The key challenge for CO_2 storage is: One needs to build trust and gain public acceptance. Many risks have been identified and these lead to skepticism, although technology and science are known.

Internal use of steam may reduce the cost of CCS from 700 to 500 NOK/ton, illustrating the importance to evaluate concepts where heat recovery from an aluminium smelter with other processes and CO_2 scrubber will be very valuable.

Conclusions

Aluminum may become an even greener metal than today. Technically, the aluminum production process can be a close to zero climate gas producer The first step (actually ongoing) is to focus more on lower specific energy consumption, and eliminate the anode effect frequency. A natural second step is related to recovery of energy from the main heat loss sources, like cathode linings and gas exhaust systems. A third step may be CO_2 gas cleaning related to the electric power generation, and finally, collecting and cleaning CO_2 from the reduction process itself may be a technically possible future scenario.

The collected gas has a higher temperature and concentration of CO_2 than traditionally, which makes it more suitable for CO_2

scrubbing and heat recovery. Our initial measurements at one of our test cells in Årdal indicate that CO_2 concentration similar to what a gas power plant produces is possible to obtain. The technology groups in Porsgrunn, Årdal, and Neuss plan to develop our new concept even further, and we think it will be possible to achieve a cell and potroom design ready for CO_2 capture within the next 5 years. The goal is to send this process gas to a suitable CO_2 scrubber plant, whenever this technology is developed and industrialized. Hydro is in the process of teaming up with suitable partners/suppliers that can handle the CO_2 emissions from our cells.

Hydro Aluminium's goals:

Based on the current focus on the environmental impact that CO_2 has, Hydro as an aluminium company will work to achieve the following targets:

1. To prepare cells for collection of the CO_2 produced during electrolysis as concentrated and as hot as possible
2. Make ready for collection of the off-gases for energy recovery
3. Purify the off-gas to be delivered to a CO_2 scrubber plant
4. Evaluate other combustion processes, which can use the process gas from an aluminum smelter
5. Identify partners/collaborators who can strip off the CO_2 in our off-gases
6. Make sure the CO_2 gas is sent to someone who can utilize this gas for Geological Injection and/or Enhanced Oil Recovery (EOR)
7. Reduce the cost of CO_2 capturing to a minimum.

Our new electrolysis technology, HAL4e [10] is prepared for CO_2 capture and will be developed further in the years to come.

Acknowledgements

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