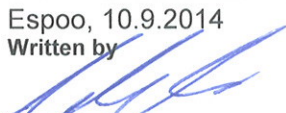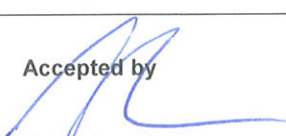# Pre-evaluation of a new process for capture of CO₂ using water

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Confidentiality: Public

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Pre-evaluation of a new process for capture of CO_2 using water	
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Summary

A new concept for CO_2 capture by absorption into water was briefly assessed. In this concept, CO_2 is captured from flue gas in a pressurized bubble-type absorption column. Desorption of CO_2 takes place by flashing the water at sub-atmospheric pressure (0.4 bar). This leaves a relatively high concentration of CO_2 in the water. The new concept introduces a post-desorber that enables lowering the CO_2 concentration of the water further by flashing the water stream into the flue gas. This enables a higher CO_2 capture efficiency at chosen pressure level than possible with other water CO_2 capture concepts. The preliminary energy requirements and equipment cost seems to be similar to those of amine-based CO_2 capture processes. However, more work is needed to verify these preliminary results. The water-based CO_2 capture concept requires no chemicals, which is a clear environmental advantage over amine-based concepts. The water requirements are still very high so for the process to be feasible (in terms of energy requirements) it requires an external source of cooling water, i.e. the process needs to be located next to a large river, a large lake or the sea. Also, while the preliminary results indicate that the new water-wash concept could possibly be competitive to amine-based processes for CO_2 capture at a small scale (~50 kt CO_2 per year), more work is needed to assess the performance and cost of the concept at a large-scale power plant (~1 Mt CO_2 per year). Since the water-based concept requires ten-fold more solvent circulation than amine-based processes it is possible that at larger scales amine-based processes may be favourable (e.g. due to space requirements and technical challenges related to circulation of very large amounts of water). Still, the new water-based CO_2 capture concept seems promising based on this initial assessment and warrants further work.

Confidentiality	Public

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Preface

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Contents

1   Introduction

The Fibre Laboratory at Mikkeli University of Applied Sciences (MAMK) recently announced that they have developed a new carbon dioxide (CO_2) capture process (MAMK, 2014). The process has been developed by Teijo Linnanen and Hannu Kuopanportti at MAMK in collaboration with Control Express Finland (CEF) Oy, Mekateam Oy and Wetend Technologies Oy. A patent application has been filed and a patent was granted this spring (Kuopanportti & Linnanen, 2014).

The process separates carbon dioxide from flue gases using water, making the process more environmental friendly than other capture processes that require chemicals. According to the press release, the method has been verified by experimental test runs in a pulp mill environment. Although the water absorption method requires large amounts of water the water is recycled in the process. Current plans are to do further testing of the process in collaboration with industry.

The goal of this short assessment was to give a "second opinion" on the validity of the new process concept and its suitability for carbon capture and storage (CCS) and identify possible obstacles, bottle-necks or "show-stoppers" for the new concept. The work was performed in the framework of Cleen Ltd.'s Carbon Capture and Storage R&D Program (CCSP).

2   Methods and limitations

Time and resources were the main limitations for this study. The new process was assessed by a short literature review, validation of main claims by process modelling, as well as a brief cost comparison to conventional CO_2 capture processes using literature data. The process cost assessment were very coarse, taking into consideration mainly energy requirements and solvent costs, as well as investment costs based on literature data and personal experience. The cooling requirements were not compared to those of the amine-based processes.

3   Background

Separation of CO_2 by water (water wash) is an old physical absorption technology that was previously important for the purification of synthesis gas for ammonia production (Kohl & Nielsen 1997). The advantages when using water as an absorbent are relatively simple plant design and an inexpensive solvent. The principal disadvantage of the water wash absorption process is very poor CO_2 removal efficiency leading to high pumping load (of water) and relatively impure CO_2 stream.

A simple water-wash process for carbon dioxide removal is presented in Figure 1. In its simplest form, the water-wash process consists of a an absorption tower operating at elevated pressure, a flash tank where CO_2 is desorbed from the water by pressure reduction, and a pump to return the water to the top of the absorber. In the process shown in Figure 1 a power-recovery turbine has been added to recover part of the power available from the pressure reduction and a degassing tower has been added to release more CO_2 from the water and thus enable a higher capture efficiency when the water is returned to the top of the absorber. Kohl & Nielsen mention that the low-quality fuel gas can either be combusted or recompressed and returned to the absorber inlet.
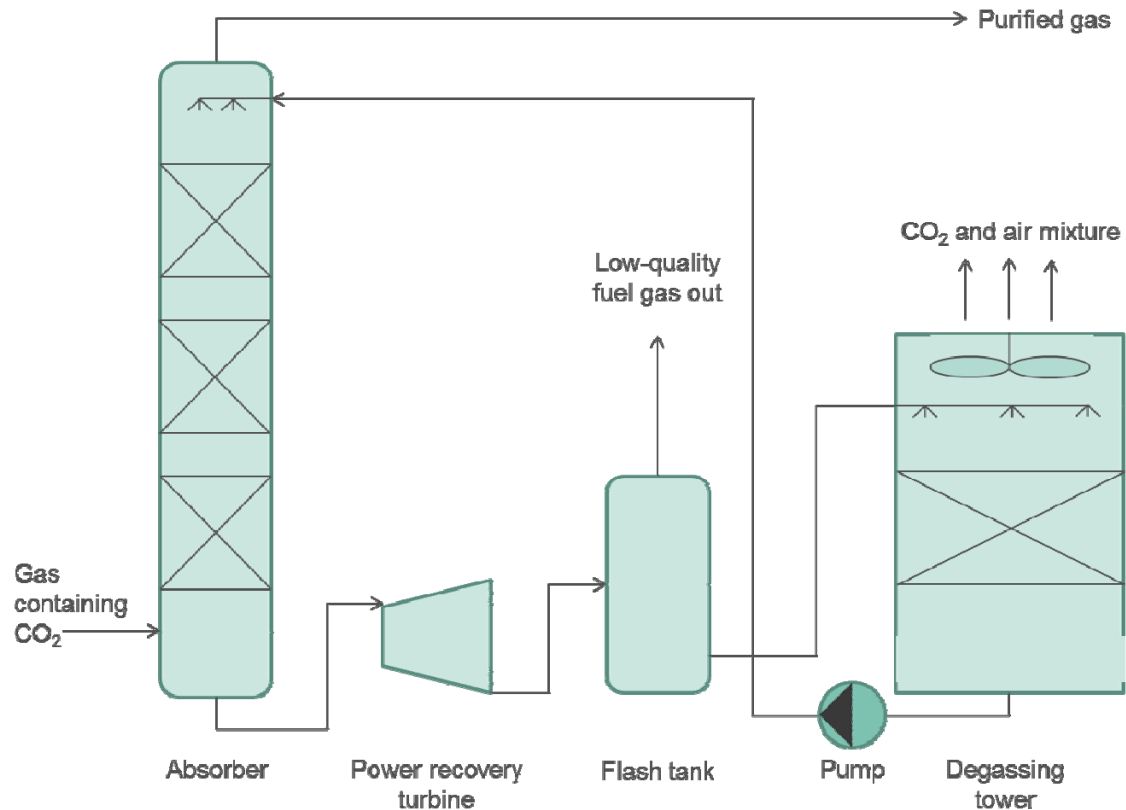
Figure 1. Simplified flow diagram of a process for absorption of carbon dioxide from gas streams using water (after Kohl & Nielsen 1997).

The solubility of CO_2 to water defines the theoretical maximum for the removal process. Lower temperature and higher pressure increase the solubility leading to a lower water circulation rate. For example, the solubility of CO_2 at 1 bar CO_2 and 20°C is 2 g / kg H_2O, whereas solubility at the pressure of 10 bar CO_2 and 10°C is around 20 g CO_2/ kg H_2O. Therefore, the process is considered economically useful only for gas streams having a partial pressure of CO_2 higher than 3.5 bar (Kohl & Nielsen, 1997). The water wash process has been mostly replaced by more efficient processes using either chemical solvents (like monoethanolamine, MEA) or physical solvents (like methanol of the Rectisol process or dimethyl ether of polyethylene glycol, DEPG, of the Selexol process) that have a higher capacity for carrying CO_2 than water (Table 1).

However, water wash is still used in industry in Europe today, mainly for biogas upgrading. For example, in Sweden there are 11 biogas upgrading plants that use water wash for CO_2 removal (Tynell et al. 2007). A simplified flow diagram of the process is presented in Figure 2. The raw biogas contains 25-55% of CO_2, which is removed in order to increase the methane content of the gas. The water wash plant consists of an absorption tower (operating at 6-10 bar and 10-20°C), a flash column (operating at 2.5-3.5 bar) for removing absorbed biogas and other gaseous components, and a desorber, where CO_2 is stripped from water using air at atmospheric pressure. Since part of the CO_2 absorbed in the water is released together with other gases in the flash tank, the gas from the flash tank is recompressed and returned to the absorption column. However, since much more carbon dioxide than methane is dissolved in the water, the composition of the released gas in the flash column will normally be 80-90% carbon dioxide and 10-20% methane, while the water transported from the flash column to the desorption column will contain most of the carbon dioxide absorbed but less than 1% of the methane in the raw biogas (Bauer et al., 2013). The water flow rate in biogas upgrading varies between 120-220 dm^3 H_2O/m^3 raw biogas, depending on process conditions (Bauer et al. 2013, Haagen et al. 2001).

Table 1. Comparison of the solubility of CO_2 in various physical solvents.

	Temperature (°C)	Solubility (dm^3/dm^3)
Methanol	-25	13.4[1]
DEPG	25	3.63[1]
Water	20	0.88[2]

[1] Burr (2008)
[2] Seppänen (1991)

Water wash has not previously been considered suitable for CO_2 capture for Carbon Capture and Storage (CCS) purposes and the possibility to use water as a CO_2 solvent is very seldom mentioned in CCS-related literature. As pointed out by Herzog et al. (2009), water is much more soluble to CO_2 than to N_2, but its capacity for CO_2 capture is so low that capturing industrial-scale amounts of CO_2 would require the circulation of very large water flows. In addition to this, the flue gas needs to be pressurized, which would demand much more compression power than current CCS concepts demand, where only the separated CO_2 fraction is compressed.

Using air for regeneration of the water dilutes the separated CO_2 and is therefore not an option when the aim is to capture pure CO_2 for transportation and storage. Thus, the options to remove absorbed CO_2 from the water are either a desorber with a reboiler or a staged vacuum flash of the CO_2-rich water.
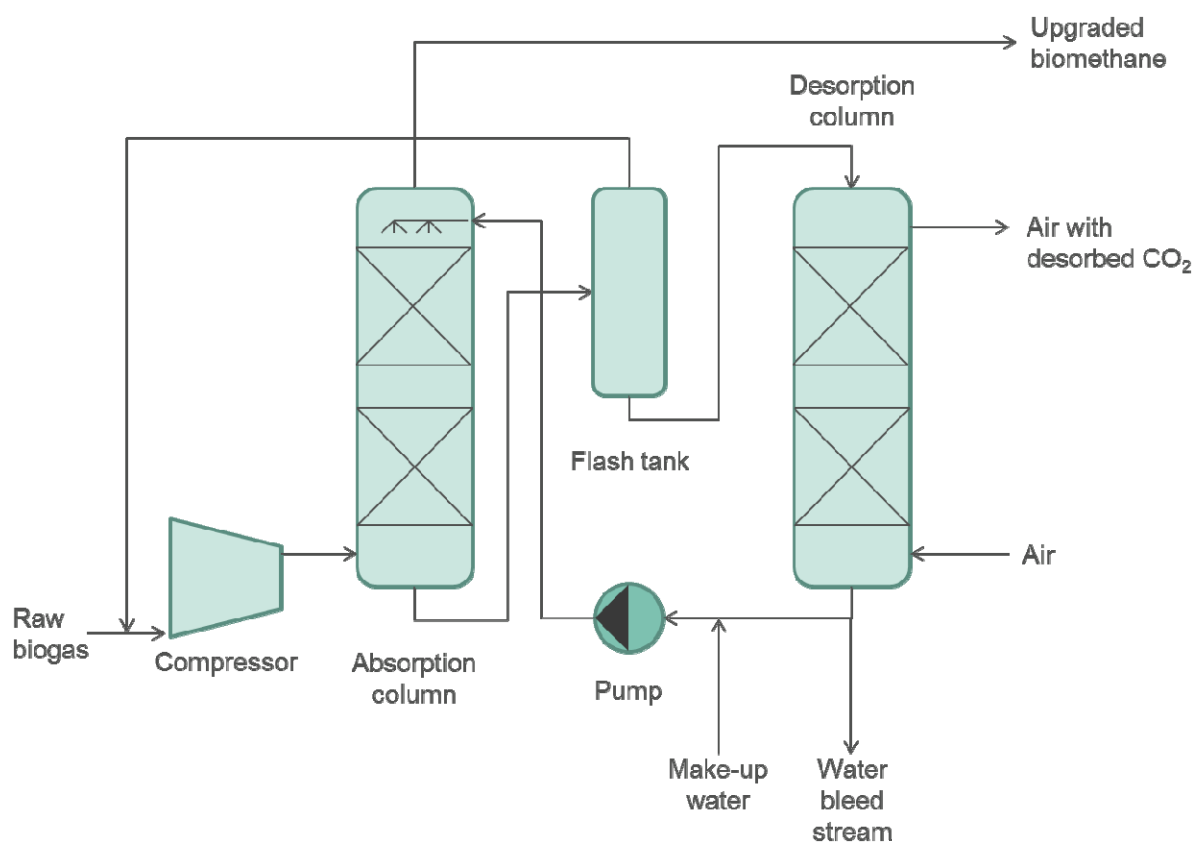
Figure 2. Simplified flow diagram of a water wash process schema for biogas upgrading (after Bauer et al. 2013).

Suomalainen & Arasto (2013) evaluated the suitability of a water wash concept for CO_2 capture from flue gases produced by partial oxy-combustion (Suomalainen & Arasto, 2013) using Aspen Plus. These flue gases contain a significantly higher concentration of CO_2 than those from combustion with air. Here, a two-staged flash was used to strip the absorbed CO_2

from water. The lower flash pressure was chosen to be 0.7 bar, optimising between the power required for pumping the water back to 10 bar and the CO_2 concentration left in lean water. A significant removal efficiency of 86 % was obtained. The power consumption was 31 MW, over 25 times higher than that of the amine absorption process, but on the other hand there was no steam consumption (amine absorption process required 120 MW steam). Over half of power requirements of water wash process came from the flue gas compression, and one third of the power requirements came from the water pump (Figure 4).
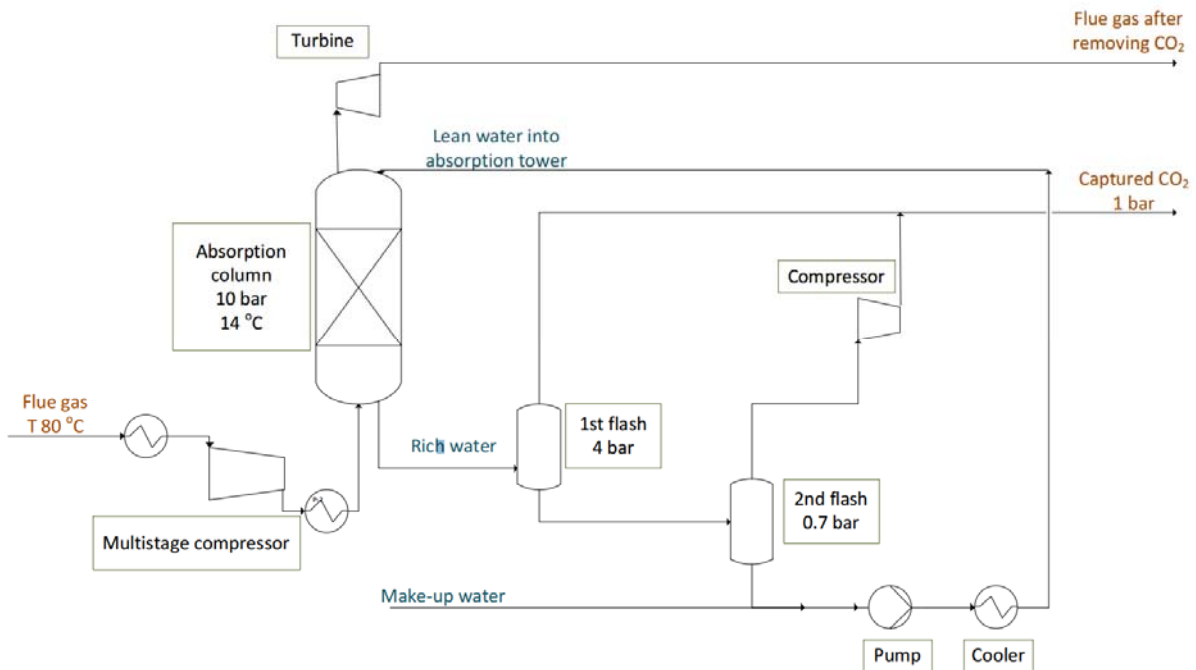
Figure 3. Water wash process for CO_2 removal from flue gas containing 37 vol-% CO_2 (Suomalainen & Arasto, 2013).

Table 2. Comparison of main process values from Aspen simulations of water wash and amine absorption processes (Suomalainen & Arasto, 2013).

	O_2 in enriched air	CO_2 in flue gas	Dried flue gas flow rate into absorption tower		Solvent circulation rate	CO_2 removal efficiency	Power consumption	Steam consumption
	% (vol)	% (vol dry)	kg/s	m³/s	kg/s	%	MW	MW
Water wash	44	37	89	6.0	11400	86	31[1]	-
Amine absorption	44	37	90	63	1032	90	1.2	120

[1] This value does not include power required for cooling flue gas and water.
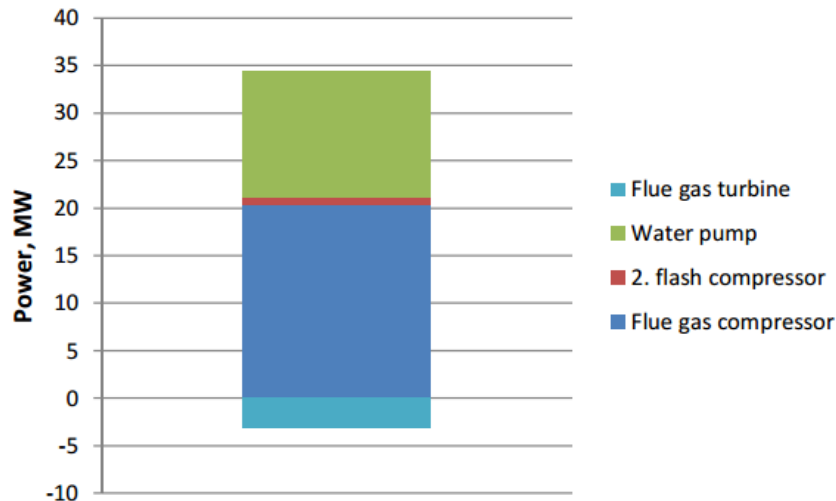
Figure 4. Power consumption and generation in a water wash absorption concept (Suomalainen & Arasto, 2013).

Although packed-bed water absorption columns are typically used for water scrubbers in biogas applications, the use of bubble-type water absorption columns was already assessed by Houghton et al. in 1957. It was found that bubble-type water absorption columns were superior to the packed-bed type for absorbing large quantities of carbon dioxide.

4 Description

The new process concept, patented by Kuopanportti & Linnanen, is described in Figure 5. CO_2-rich flue gas (typically containing <15 vol-% CO_2) is first washed in a pre-scrubber with a small amount of water to remove water-soluble (sulphurous) gas compounds. Flue gas is then led through a post-desorber into a compressor that raises its pressure and temperature. To lower the temperature of the flue gas, a heat exchanger is used. The gas is bubbled through a water-filled absorption column (counter-flow), which causes CO_2 (and some nitrogen) to dissolve into the water. The resulting CO_2-lean flue gas exits the absorber and is heated up in the heat exchanger. The CO_2-lean flue gas in then led through an expander, in order to recover some of the mechanical power needed by the compressor to pressurize the flue gas to 3-8 bar. CO_2-rich water exits the absorber into a flash tank that functions as a pre-desorber: by lowering the pressure to 1.6-2.5 bar most of the nitrogen absorbed by the water in the absorber is released, which raises the purity of the final CO_2 product gas. However, some CO_2 is released as well, so in order not to lower the CO_2 capture efficiency of the system the gas stream is returned to the post-desorber. From the pre-desorber the CO_2-rich water is led to the desorber, where CO_2 is desorbed from the water by further lowering the pressure to 0.3-0.8 bar. After the desorber the water still contains some CO_2. Therefore, the water is led into the post-desorber, where the CO_2 concentration of the water is further reduced. According to the authors, the post-desorber both improves the CO_2 capture efficiency of the system and increases the CO_2 concentration of the CO_2 product gas: a capture efficiency over 80% and a CO_2 product gas purity 90 mol-% CO_2 can be achieved, using the process parameters above. The minimum energy requirements of the capture system, 0.35 MWh/t CO_2 can be achieved at 4.5 bar absorption, 0.4 bar desorption and a process water temperature of 5°C (Kuopanportti & Linnanen, 2014). However, using a higher absorber pressure would reduce the mass flow requirements of water. Therefore, in recent development work performed on the process higher absorber pressures are favoured (Linnanen, 2014).
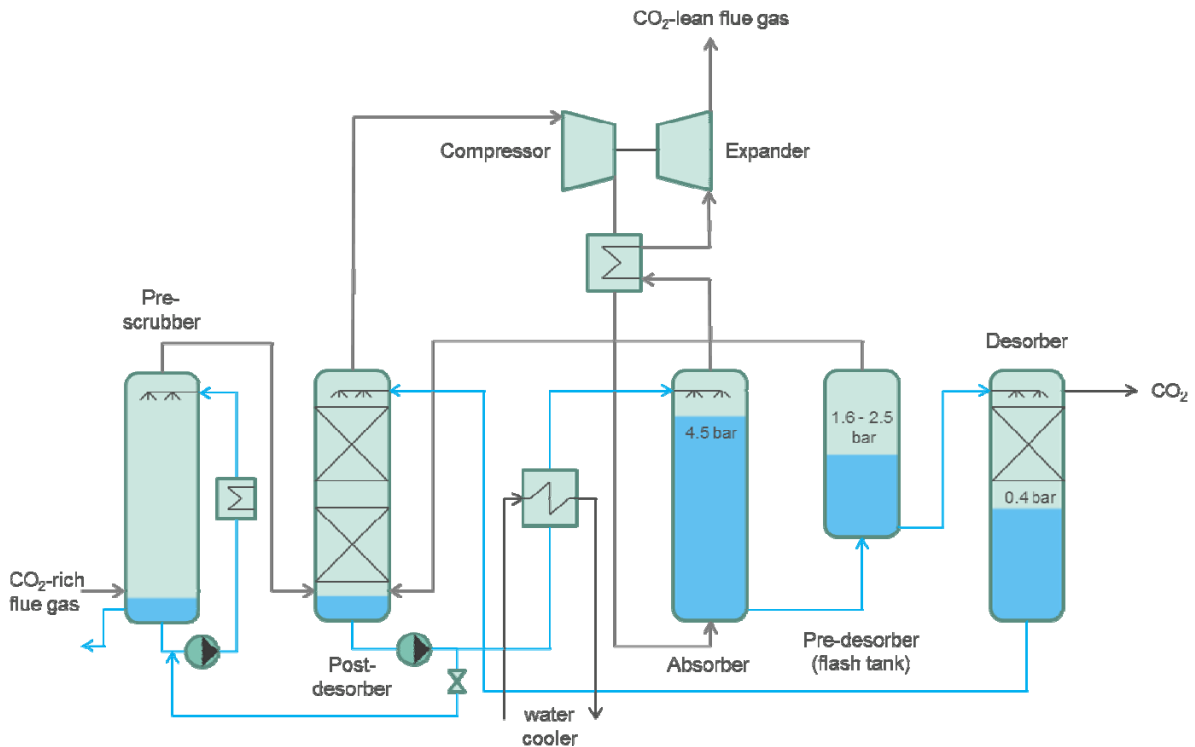
Figure 5. Simplified flow diagram of new process for CO$_2$ capture by water wash (after Kuopanportti & Linnanen, 2014).

5 Assessment of the new CO$_2$ capture process concept

5.1 Similarities and differences to similar concepts

The process concept suggested by Kuopanportti & Linnanen is in essence a water wash-based CO$_2$ separation process that has been further developed to maximize the capture efficiency and CO$_2$ product quality. The use of a staged desorption with recompression of the gas from the first flash tank is a practice which is also used by commercial water-wash processes (Figure 2), although the purpose of the staged desorption in commercial processes is to prevent emissions of biogas. Also, since commercial water-wash processes aim at biogas purification, not CO$_2$ capture, CO$_2$ is removed in the desorber by degassing the water with air, making it unsuitable as such for producing a CO$_2$ product gas. Suomalainen & Arasto (2013) also used a staged desorption with sub-atmospheric pressures in the second desorption stage, but in their concept the gas from the first flash tank is mixed with the CO$_2$ product gas, putting higher requirements on the subsequent purification of CO$_2$ (Figure 3).

The bubble-type absorption column seems better suited for capturing large amounts of CO$_2$, since absorption in a bubble-type column can be 3-10 times faster than in a packed bed column (Houghton et al., 1957). Therefore, the reactor volume required for absorbing the same amount of CO$_2$ using a bubble-type column is roughly one third to one tenth of that required by a packed bed column. According to the inventors, the design of the absorption column aims at having both the gas phase and water phase as close to theoretic equilibrium as possible. Therefore, the height of the column needs to be made long enough to ensure that close-to equilibrium conditions are met (a minimum of 2-4 m), while the width of the absorber is specified according to the CO$_2$ yield.

5.2 Assessment of the process concept

The new process concept has two clear differences in comparison to commercial water-wash processes: the use of a bubble-type absorption column and the concept of the post-desorber. Although the benefit of a bubble-type absorption column over packed-bed absorption in water wash of CO_2 is known (Houghton et al., 1957), the concept of the post-desorber seems to be new.

In order to assess the benefits and drawbacks from the post-desorber, and at the same time double-check the process modelling results by Linnanen (2012), the new process concept was modelled using Aspen Plus.

5.2.1 Considerations regarding modelling of CO_2 solubility in water

The process simulations by Linnanen (2012) was carried out with Balas process simulation software. In Balas equation of state calculations are based on the Soeva-Redlich-Kwong (SRK) method and liquid activity coefficients are based on the UNIFAC method. In case of missing parameters a predictive calculation is performed by Balas. In modelling of a water wash process Suomalainen & Arasto (2013) used an equation of state calculations called the Predictive Soave, Redlich and Kwong (PSRK) method. This property method was chosen due to its accuracy to reach the same CO_2 dissolution results as presented in Kohl & Nielsen (1997 p. 428). The solubility of CO_2 in water is derived from an Aspen flash reactor model using a mixture of 100 % gaseous CO_2 and 100 % pure liquid water.

Table 3. Comparison of the equilibrium solubility data of CO_2 in water at total pressures of 1 and 5 bar.

	Temperature (°C)	Partial pressure of CO_2 (bar)	CO_2 content (vol-%)	Solubility (kg CO_2/kg H_2O)
Solubility data at equilibrium[1]	5	1	100	**0.003 [1]**
Aspen (PSRK) at equilibrium	5	1	100	**0.002**
Solubility data at equilibrium [1]	5	5	100	**0.013 [1]**
Aspen (PSRK) at equilibrium	5	5	100	**0.012**

[1] Reference Kohl & Nielsen 1997 p. 428, solubilities estimated from a figure of solubility curves.

When comparing the results from the Balas model to those from the Aspen PSRK model, a slight difference in the CO_2 solubility equilibrium was noticed (Table 4). As the calculations for the theoretical maximum capture efficiency of the process is based on maximum solibility the difference in the solubility equilibria causes also a difference in the efficiency calculations. Since the CO_2 concentration level at the chosen pressures and temperatures is very low it is possible that the difference is due to low accuracy of the equation of state methods at low concentrations. It is not possible to evaluate which calculation method provides more realistic concentration in the conditions of this process without more experimental work.

Table 4. Comparison of CO_2 solubility results at equilibrium calculated by Balas (Linnanen 2012) and Aspen PSRK (the same input values).

		Balas (Linnanen 2012)	Aspen PSRK
CO_2 content in rich water after the absorber	w-%	0.24	0.19
CO_2 content in lean water after the last desorber	w-%	0.10	0.09

The experimental work by Linnanen has been carried out methodically and extensively both for individual process components and by running a lab-scale process pilot (with gaseous CO_2 concentrations measured simultaneously at four different points using multiple Geotech G110 CO_2 analysers). The results of the experimental work are based on measuring concentration of CO_2 in various gas streams of the process. The dissolved CO_2 concentration in lean/rich water in the experiments was calculated based on the gas measurements. The CO_2 capture efficiencies achieved with the pilot were lower than those attained by modelling. At the best experimental set point, using an absorber of 5 m height Linnanen attained a CO_2 capture of 60% efficiency, while the equilibrium model gave a maximum efficiency of 75%. However, the experiments confirmed that using a higher absorption column enhanced significantly the capture efficiency. Based on the experiments Linnanen calculated that a column height of 10 m is needed to achieve near-equilibrium conditions in the absorption column.

5.2.2 Assessment of the post-desorber

The post-desorber is a packed-bed column, which operates close to atmospheric pressures (the pressure of the flue gas). When the water exits the main desorber it still contains dissolved CO_2 corresponding to the partial pressure of CO_2 in the desorber (0.4 bar in the example in Figure 5). However, the partial pressure of CO_2 in flue gas before the post-desorber is low (for instance, the partial pressure of a flue gas stream at 1 bar containing 15 vol-% CO_2 is 0.15 bar), which causes additional CO_2 to be released from the water, both raising the CO_2 absorption capacity of the water stream and increasing the CO_2 concentration in the flue gas (Linnanen, 2012). In addition, as the minimum CO_2 concentration in the exiting gas stream from the absorber is limited by the amount of CO_2 dissolved in the incoming water to the absorber (due to the equilibrium between dissolved and gaseous CO_2), the post-desorber increases the maximum CO_2 capture efficiency that can be achieved at a given pressure and temperature (Linnanen 2012). However, the additional CO_2 released from the water into the flue gas stream increases the volume of flue gas that needs to be compressed (by approximately 5 %).

The results from the Aspen modelling calculations support the assumption that the post-desorber indeed improves the maximum attainable CO_2 capture efficiency at chosen absorber pressure (Figure 6). Without the post-desorber the CO_2 concentration in the lean water is higher, which leads to a lower maximum capture efficiency as described above. In order to reach the same capture efficiency without the post-desorber as with the post-desorber at the chosen set of process parameters (same pressure level in absorber) either the desorber pressure must be lowered, the desorber temperature raised, or a combination of these. Although a lower pressure than 0.4 bar could also be used in the desorber, it would require more expensive equipment vacuum pumps (Linnanen, 20149 and raise the power requirements significantly. Also, raising the temperature in the desorber would require more cooling water.
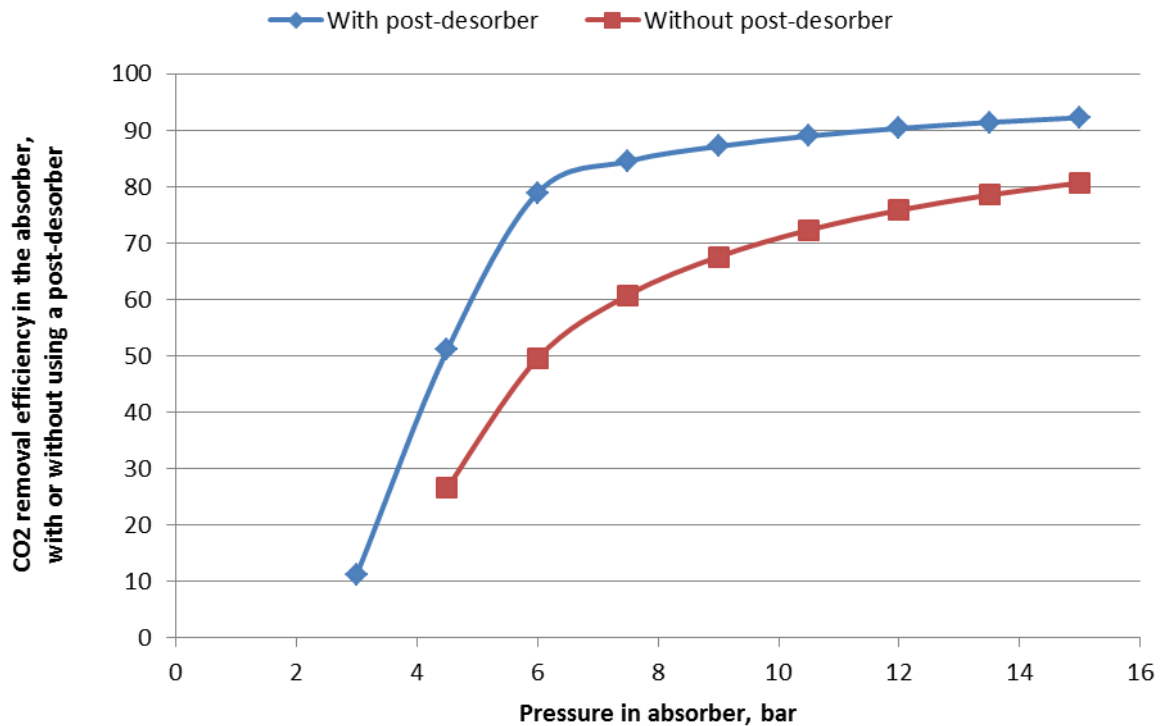
Figure 6. Comparison of CO_2 removal with or without post-desorber depending on the pressure in the absorber. Input values of the absorber are either the values of flue gas and lean water coming from the post-desorber (with post-desorber) or the values of flue gas and lean water before water wash (without post-desorber). CO_2 removal efficiency is calculated by dividing the mass flow rate of CO_2 in flue gas after absorber by the mass flow rate of CO_2 in flue gas entering the CO_2 removal process.

5.2.3 Requirements due to the poor solubility of CO_2 in water

One of the main drawbacks with using water as a solvent for CO_2 capture is the poor solubility of CO_2 in water (Table 3). For instance, at 4.5 bar absorber pressure 830 t of water needs to be pumped through the process for capturing 1 t of CO_2 (Linnanen, 2012). This raises the feedwater temperature with 0.2 °C that requires 0.2 MWh/t CO_2 of cooling. To cool the feed water an external source of cooling water is needed, i.e. the process needs to be located next to a large river, a large lake or the sea. The minimum energy requirements by Linnanen (2012) are presented assuming that the process water can be kept at 5°C, which is not realistic, since this could only be achieved during the colder half of the year and using an extremely large heat exchanger to allow a temperature difference of 0.2°C over the heat exchanger. A more realistic approach would be to aim for a 15°C temperature of the feed water during winter. During summer, it would naturally be higher. According to Linnanen (2014) raising the temperature of the feed water from 5°C to 15°C would increase the total power requirements of the capture process with 19%, or from 0.34 MWh/t CO_2 to 0.4 MWh/t CO_2. Additionally, the cooling requirements of 0.2 MWh/t CO_2 needs also to be taken into consideration.

5.3 Comparison with amine-based CO_2 capture processes

The new concept was preliminarily compared with a CO_2 capture system using amine-based solvents, which is the current state-of-the-art for CO_2 capture from flue gases (or post-combustion capture of CO_2) for both new-build and retrofit. CO_2 removal using amine-based solvents is a well-understood and widely used technology and currently hundreds of plants

use this technology for removing CO_2 from natural gas, hydrogen and other gases with low oxygen content (Rochelle, 2009).
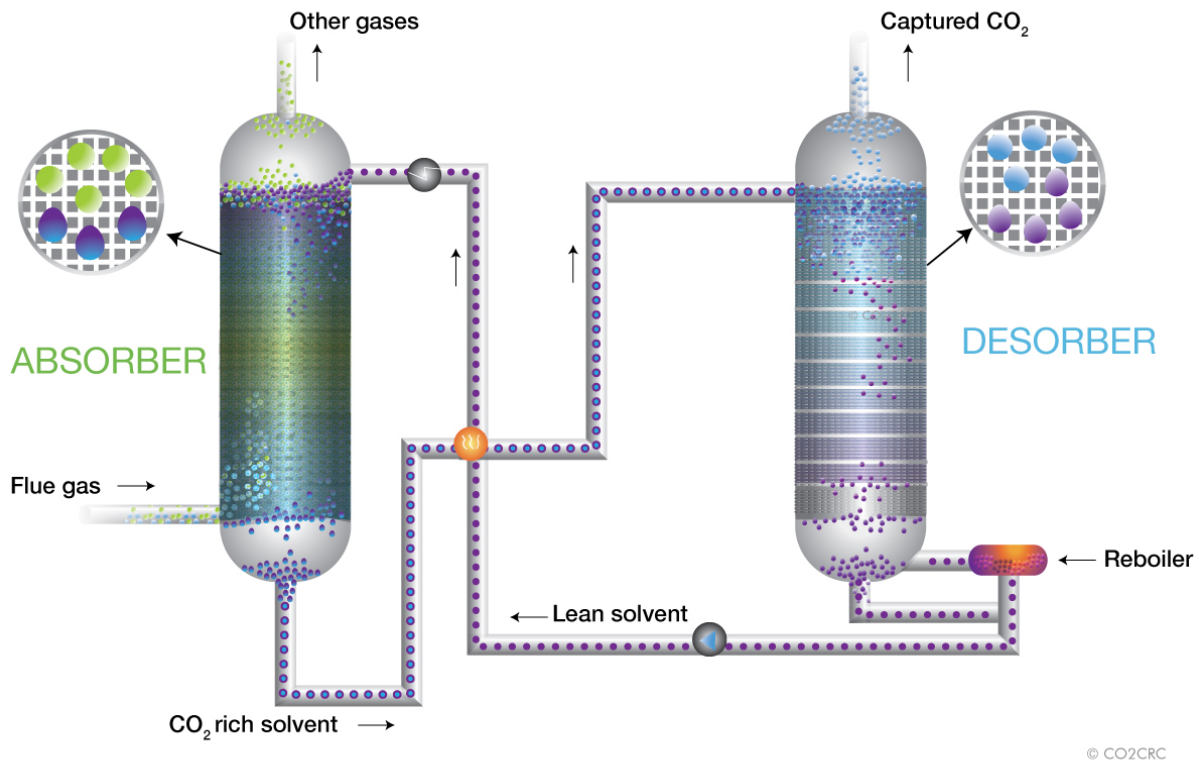

Figure 7. Simplified absorption process for post-combustion capture systems using amine-based solvents (image copyright by CO2CRC).

In systems based on absorption technology the solvent absorbs CO_2 at typically 40–60°C (Hetland et al., 2009). The solvent leaving at the bottom of the desorber is then heated to typically 120°C in a reboiler where the CO_2 is stripped off, and a hot CO_2/steam mixture is introduced to the lower section of the desorber unit (Figure 7). The CO_2 stream will then ascend through the column (counter-current of the trickling rich solvent) and leave the column at the top. It then diverts to compression and dehydration throughout multiple stages before a sufficiently pure and dense CO_2 stream is ready for transport to the storage site. The temperature levels in the absorber and desorber and the reboiler duties are different for various amine-based solvents and for different process designs.

5.3.1 Preliminary comparison of energy requirements

The main operational costs come from the energy requirements of the processes, but comparing the energy requirements of the processes is not straight forward. Amine-based processes demand both heat (steam) and power, while the water-wash process demands only power. As CO_2 capture processes are typically applied to a power plant or other industrial facility generating the CO_2, steam from the process can be used for meeting the heat requirements. In a power plant, the steam requirements from the amine-process can be diverted from the low-pressure part of the steam turbine, which lowers the electricity output of the power plant. The impact the processes have on the efficiency of a power plants is different depending on the type of power plant (combined heat and power plant or condensing) as well as on how the capture process is integrated into the power plant. The impact of amine-based processes on condensing power plants has been assessed in numerous studies, but most of them have been made for large power plants (>> 100 MWe).

Typically, a post-combustion CO_2 capture facility is designed for removing around 90% of the CO_2 in the flue gases. The amine-based process requires mainly heat for the regeneration of the solvent and electric power for compression, pumps and fans. A generic aqueous solution of monoethanolamine (20–30% MEA) is used in many studies and pilots, however, with some proprietary additives that prevent corrosion and foaming. Many proprietary additions and mixtures are also being developed in order to lower the energy demand of CO_2 capture. According to IPCC (2005), the values for the heat requirement for the leading absorption technologies ten years ago were between 2.7 and 3.7 GJ/tCO_2, depending on the solvent and power plant type. Recently, energy requirements as low as 2.2-2.4 GJ/tCO_2 has been reported using advanced solvents (Just, 2013). Typical values for the direct electricity requirement for the processes are 0.02-0.09 MWh/t CO_2 depending on the power plant type, and the compression of the CO_2 to 110 bar will require an additional 0.11 MWh/t CO_2 (IPCC, 2005). Due to the energy required by the capture process, the electric efficiency of a condensing power plant is typically reduced by approximately 9–15 %-units.

The water wash CO_2 capture process requires only power to drive the compressors and pumps as well as cooling water for cooling the feed water entering the absorber. Therefore, there does not seem to be much benefit to be had from integration with the existing power plant. As pointed out previously, the power penalty of the water wash process was in the case by Linnanen (2012) calculated for a feed water temperature of 5°C (0.34 MWh/tCO_2), although a more realistic temperature of the feed water would be 15°C during winter time. This would raise the energy requirements with 19% to 0.40 MWh/tCO_2. As can be seen, the energy requirements of the water wash process are dependent on how cool cooling water can be provided to cool down the feed water and therefore dependent on the local sea/lake/river water temperatures. In biogas application, a feed water temperature of 10-20°C is used, but typically additional cooling is required, which additionally increase the CO_2 capture energy requirements. The cooling energy requirements were not assessed in more detail in this preliminary study.

Table 5. Comparison of power loss to a power plant for the CO_2 capture processes studied (units: MWh/t CO_2 captured).

	Water capture (Linnanen, 2012)	MEA CO_2 capture retrofit to a coal fired power plant (Abu-Zahra et al. 2007a&b)	MEA CO_2 capture retrofit to a coal-fired power plant (Ramezan et al. 2007)
Auxiliary power requirements from CO_2 capture (incl. compression and conditioning)	0.40[3]	0.18-0.19	0.16
Power loss due to MEA regeneration steam requirements	0	0.19-0.24[1]	0.21[2]
Total power loss due to CO_2 capture	**0.40**	**0.37-0.43**	**0.37**

[1] Not directly given in the source, therefore calculated using total power requirements & auxiliary power requirements. The MEA regeneration energy requirements used in the reference were 3.9-3.0 MJ/kg CO_2
[2] Given by the source. The MEA regeneration energy requirements used in the reference were 3.6 MJ/kg CO_2
[3] Cooling requirement of 0.2 MWh/t CO_2 not included in the number.

When comparing the power penalty of the water wash process to that of an amine processes for a condensing coal-fired power plant the overall plant power loss (due to the energy requirements by the CO_2 capture process) seems to be of the same order of magnitude (Table 5). The auxiliary power requirements include the power need for compression and purification of CO_2. However, it must be noted that the results compared are taken from different studies. Perhaps most important to note are the parameters related to the incoming flue gas stream from where CO_2 is captured. In Linnanen's case the incoming flue gas has a

CO_2-concentration of 21.2 w-% and the mass flow of CO_2 is 35 t/h, while the corresponding values used in the study by Ramezan et al. (2007) is 19.7 w-% CO_2 with a mass flow of 392 t/h. In order to be comparable, the energy requirements are therefore compared per tonne CO_2 captured. It is also important to point out that both literature cases to which the water capture process is compared use slightly conservative (i.e. high) energy requirements for the solvent regeneration, since they assume that MEA is used. New solvents and solvent mixtures are being developed that have lower regeneration heat requirements (well below 3 MJ/t CO_2). Therefore, this comparison gives only a preliminary comparison of the energy requirements of the different processes and a more detailed techno-economic investigation is required.

Like other CO_2 capture processes based on physical absorption the water wash process benefits from a high partial pressure of CO_2 in the flue gas stream: the higher the partial pressure of CO_2, the more efficient the water wash process. Therefore, less compression power is required for flue gases containing a high partial pressure of CO_2.

5.3.2 Comments on investment costs

Linnanen (2012) presented investment costs estimates of the water wash process, designed to capture 75% of the CO_2 produced by a combined heat & power (CHP) plant (incoming CO_2 concentration in the flue gas 21.2 w-%) with a boiler duty of 16.5 MW, producing a stream of 1.6 kg/s CO_2. The investment costs for the process equipment for the water wash process were estimated by an engineering office to 3 M€. However, this covers only the process equipment for the water wash. The total investment cost has been estimated to 9 M€, including the cost for the CO_2 liquefaction facility, but excluding the cost for a pre-scrubber (Juutilainen, 2014).
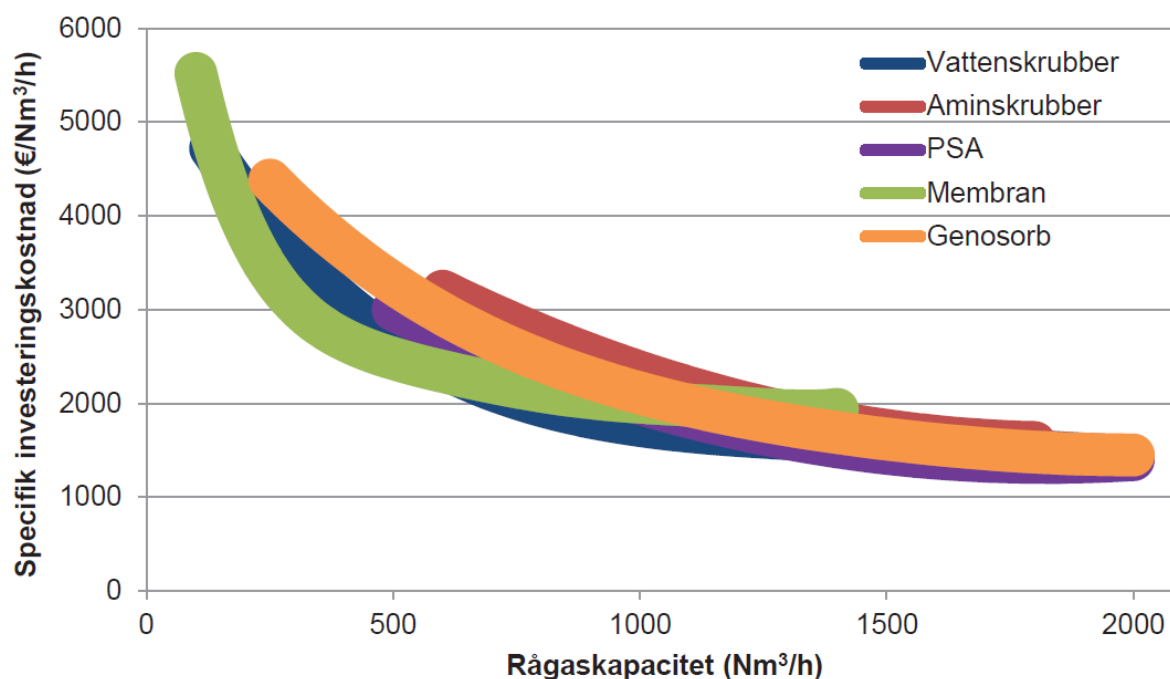
Figure 8. The specific investment cost of water scrubbers, amine scrubbers, pressure-swing absorption units and membrane units as a function of raw biogas throughput (Bauer et al. 2013).

According to our previous experience a reasonable CAPEX frame for an amine-based CO_2 capture plant would be in the area 10 – 30 M€ for a plant of this scale. In some specific cases, using modular delivery of standard size process equipment and commodity MEA solutions that are not tailor made for higher efficiency, the price could come down to 5 M€.

But the drawback with these standardized modular solutions is that they are not tailored to the site and may require a higher rate of MEA make-up and a significantly higher steam rate.

In small-scale, commercial biogas purification, water-based CO_2 separation processes have slightly lower investment costs than MEA-based processes (Figure 8), while the operational costs for an MEA-based process are slightly lower than those for a water-based process (Bauer et al. 2013; de Hullu et al. 2008). Unfortunately, the figure covers only relatively small plants with a raw gas capacity up to 2000 m^3n/h, while the flue gas feed in the case by Linnanen (2012) is over ten times higher (~26.000 m^3n/h, However, the water-based CO_2 separation processes used in biogas purification (Figure 2) do not capture the CO_2 and are therefore simpler than the new water-based process for CO_2 capture (Figure 5). Also, the CO_2 partial pressure in biogas is higher than in flue gas, which is beneficial for physical absorption of CO_2.

The investment cost for the water-based CO_2 capture process at a large scale (>1 Mt/a CO_2) have not been assessed. Since very large amounts of water is circulated in the process (830 t H_2O per t CO_2 captured) the equipment needed grows very large and it is possible that extra cost comes from land area use and technical requirements. A larger scale might also offer better integration opportunities for chemical solvent-based CO_2 capture processes that require steam and not electricity, However, more work is needed for determining this.

5.3.3 Environmental impact

One clear benefit of the water wash concept over the amine-based capture processes is the use of solvent: while the amine-based capture process requires make-up of monoethanolamine due to the formation of heat stable salts that cannot be regenerated, the water wash process uses only water. The need for make-up is roughly 1.5 kg / t CO_2, adding about 1.6 €/t CO_2 captured (Abu-Zahra et al. 2007b). In addition, a large-scale CO_2 capture process cause airborne emissions of nitrousamines and nitroamines that are considered carcinogenic and an environmental concern (see for instance Karl et al. 2011). Due to the low solubility of CO_2 830 t of water needs to be pumped through the process per tonne CO_2 captured, but the water can be circulated and reused in the process. Still, the large amounts of water that needs to be handled may pose an engineering challenge at a large scale.

5.3.4 Purity of captured CO_2

CO_2 purity for capture installations is currently not regulated, but pipeline operators have put to effect stringent purity requirements for transportation of CO_2 due to the risk of corrosion in pipelines and compressors. This concerns especially water and acid gas traces such as SO_x and NO_x, in addition compounds that can cause formation of hydrates due to fouling issues (Walspurger and van Dijk 2012).

Straight from the desorber of the water wash process the CO_2 purity can be over 90 vol-%. From test runs of the pilot facility Linnanen (2012) reported a 94-95 vol-% CO_2 purity from the desorber, which seems to be on a similar level to amine processes. For instance, in amine capture the CO_2 concentration is 94-96 vol-% before conditioning (Aspelund & Jordal, 2007; Walspurger & van Dijk, 2012). The remainder consist mostly of water vapour and O_2 (0.5-0.9 w-% O_2), which require removal. For comparison, the oxygen concentration in CO_2 from oxyfuel combustion is 1.7 vol-%, while that of amine CO_2 capture contains only traces of oxygen (Aspelund & Jordal, 2007; Walspurger & van Dijk, 2012). The concentration of other impurities in the CO_2 from the water wash process has not to our knowledged yet been tested. According to Linnanen a CO_2 product gas purity of 99.5 w-% CO_2 could be achieved by conditioning the gas through distillation.

A suggestion for CO_2 purity is shown in Table 6, based on the work done by the European project DYNAMIS that aimed to establish recommendations for CO_2 transport for European CCS projects. As shown in the table, a gas purity of at least 95.5% is recommended. The water content is one of the major impurity concerns. According to Paschke and Kather (2012) the recommended water content should be limited to 600 ppm(v). For comparison, the Weyburn pipeline is restricted to contain less than 20 ppm(v), but it is possible to operate the pipeline with higher water contents if the oxygen content is very low, such as the Kinder Morgan pipeline that is restricted to less than 10 ppm(v) oxygen (de Visser et al., 2008). Therefore, it is possible that additional gas conditioning measures are required for lowering the oxygen concentration of the CO_2 gas produced with water wash.

Table 6. DYNAMIS CO_2 quality recommendations for CO_2 transportation (de Visser et al. 2008).

Component	Recommended concentration	Criteria used for recommended level
H_2O	500 ppm	Design and operation considerations
H_2S	200 ppm	Health and safety considerations
CO	2000 ppm	Health and safety considerations
SO_2	100 ppm	Health and safety considerations
NO_2	100 ppm	Health and safety considerations
CH_4	Aquifer: < 4 vol%, EOR: <2 vol%	ENCAP proposed limit
N_2	< 4 vol%	ENCAP proposed limit
Ar	< 4 vol%	ENCAP proposed limit
H_2	< 4 vol%	to be minimized
CO_2	> 95.5 %	

5.4 Considerations for biogas purification

According to literature water-based CO_2 separation processes are competitive alternatives to amine-based processes for biogas purification (Bauer et al. 2013). The investment costs for water-based purification processes are relatively low for a small plant, its operation and maintenance is simple, and the solvent used (water) is cheap and environmental friendly.

If there is no use for the CO_2 that is separated then the water-washing processes currently used for biogas are likely to be cheaper than the new concept, since these have fewer process units and lower pressure loss (packed-bed tower instead of bubble column). The CO_2 removal efficiency of the new concept in comparison to current water-washing processes is difficult to compare without a more in-depth assessment. On the one hand, the biogas process desorb CO_2 using air, which lowers the CO_2 content of the water stream more efficiently than what can be achieved using the desorber and post-desorber of the new concept, making the CO_2 removal more efficient. On the other hand, the new concept uses a bubble column, which is more efficient at removing CO_2 from a gas stream than the packed-bed absorber. But the bubble column needs to be about 10 m high, which corresponds to a pressure drop of about 1 bar, which is an order of magnitude higher than that in a packed-bed absorber. The water requirements are similar in both concepts.

6 Conclusions and recommendations

A new water wash process concept for CO_2 capture was briefly assessed. The main findings are the following:

- The main novelty in the new water wash concept is the use of a post-desorber for raising the CO_2 capture efficiency of the process.

- Results from process calculations performed in this work is in line with the results presented by Linnanen (2012), which indicate that the post-desorber indeed improves the maximum attainable CO_2 capture efficiency at chosen absorber and desorber pressure. In our calculations, the maximum benefit was attained for an absorber pressure of 6 bar and desorber pressure of 0.4 bar, where the CO_2 capture efficiency was 79% with the post-desorber and 50% without the post-desorber (Figure 6).

- The concentration of the CO_2 exiting the desorber (94-95 vol-%) seems similar to that of amine CO_2 capture (94-96 vol-%) before further gas conditioning is employed. If the captured CO_2 is to be transported by pipeline, the oxygen concentration (<1%) in the produced CO_2 needs to be lowered.

- The power requirements of the water wash capture process seems to be similar to that of the total power loss due to amine CO_2 capture retrofitted to a coal fired power plant (~0.4 MWh/t CO_2 captured).

- The investment cost for a small-scale facility (~50 kt/a CO_2) seems to be on a similar level to that of a similarly sized amine-based CO_2 capture plant.

- Using water as a solvent instead of a chemical has two clear environmental benefits: no make-up chemicals are needed and no solvent-related process emissions are generated.

- The cooling requirements of the feed water are very high, making the process depending on an external source of cooling water, i.e. the process needs to be located next to a large river, a large lake or the sea for providing cooling energy needed.

The results from this brief study indicates that the main benefit from the new water-wash process concept is that it enables a higher CO_2 capture efficiency at chosen pressure level than previous water CO_2 capture concepts presented in literature thanks to its post-desorber. Thanks to the post-desorber a lower pressure level can be used for achieving the desired CO_2 capture efficiency than without a post-desorber, which lowers the energy requirements of CO_2 capture with water. Using water instead of a chemical as CO_2 solvent has a clear environmental benefit. Due to the low solubility of CO_2 830 t of water needs to be pumped through the process per tonne CO_2 captured, but the water can be circulated and reused in the process. Still, the large amounts of water that needs to be handled may pose an engineering challenge at a large scale.

However, it must be pointed out that due to limited resources the purpose of this study was mainly to give a preliminary assessment and not a complete techno-economic assessment. So although the energy requirements and equipment cost seems to be on a similar level to those of amine-based CO_2 capture processes, more work is needed to verify this and give more precise figures.

Like other CO_2 capture processes based on physical absorption, the water wash process is more efficient at higher partial pressures of CO_2, Therefore, a more comprehensive techno-economic evaluation and comparison of this process with other CO_2 capture processes based on physical absorption is justified.

While the preliminary results indicate that the new water-wash concept could be competitive to amine-based processes for CO_2 capture at a small scale (~50 kt CO_2 per year), more work is needed to assess the performance and cost of the concept at a large-scale power plant (~1 Mt CO_2 per year). As the water-based concept requires ten-fold more solvent circulation than amine-based processes it is possible that at larger scales amine-based processes may be favourable (e.g. due to uncertainty regarding investment costs for water wash capture at a large scale), but this remains to be investigated.

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