Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

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Chapter 10

CREATIVE CHEMICAL APPROACHES FOR CARBON DIOXIDE REMOVAL FROM FLUE GAS

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INTRODUCTION

Carbon dioxide capture costs need to be reduced more than marginally. This work was initiated because of the realisation that new and radically different ways of dealing with carbon dioxide capture from exhaust gas must be searched for in parallel with research on already established paths. Perceived limitations for improvements in these established paths is a driver for such research. Another is the sheer amount of exhaust gas that is thought to need treatment in the future. The target set for the present project was to produce ideas with potential for reducing carbon dioxide capture costs by at least 50% relative to a defined reference case.

In the past, carbon dioxide has been recovered from flue gases in cases where carbon dioxide has had a value in itself, either as an industrial gas or for enhanced oil recovery (EOR) purposes. This has been done under circumstances where such a concept was economically competitive, which was seldom. When added onto a power plant as part of a sequestration scheme, the focus on cost is even higher. Huge volumes of gas are involved in such schemes, and the equipment will necessarily become large.

The standard process for carbon dioxide recovery from flue gases is the familiar absorption–desorption cycle based on aqueous Monoethanolamine (MEA), an alkanolamine. The degradation by-products from this absorbent are identified as a significant waste disposal problem. This can be handled, but it has cost implications. The MEA-based absorption process typically lowers the efficiency of a modern combined cycle power plant by 10% points, which amounts to a little less than a 20% reduction in power output from the plant. Based on this energy loss, the net present value of the operating cost is of the same order as the investment cost. Improved absorbents are available, which reduce this energy loss from roughly 30 to about 7% points [1,2]. There is, however, limited scope for development of alkanolamines for this purpose.

Permeation membrane technology has little chance of making an impact since such processes are based on the partial pressure difference as a driving force. Cryogenics is quickly discarded as impractical due to the presence of water and the extensive heat exchange needed. It may be noted that the carbon dioxide itself is also known to cause problems in cryogenic plants as its triple point is −78 °C, although cryogenic processes for carbon dioxide separation exist [3].

A lot of research has been published on new adsorbents, but as yet no adsorption process has been described which is anywhere near being economically competitive with the standard process for the present purpose.

Very large sums of money have been spent over the past few years on research attempting to find ways of decarbonising the fossil fuel chain in order to meet the demands set by the recent focus on global warming.

In spite of all the money spent, the cost of capturing carbon dioxide is still much higher than the target perceived as acceptable.

On this background, the present work was launched with the mission of finding new paths to explore for recovering carbon dioxide from flue gas. Chemistry was flagged as the field to focus on, with the implication that the chemistry of carbon dioxide capture must be in place before any successful process can be designed.

The present problem is challenging and new solutions are required. A conscious effort in creativity was needed. This work has been carried out using formal tools for enhancing creativity. It was started by Norsk Hydro in 2001, and carried on under the sponsorship of the CO_2 Capture Project (CCP) in 2003. The initial work generating the ideas was performed by 16 chemists from the Norwegian universities plus the SINTEF group. The work in 2003 was done by the authors. The history of this work is summarised in Figure 1.

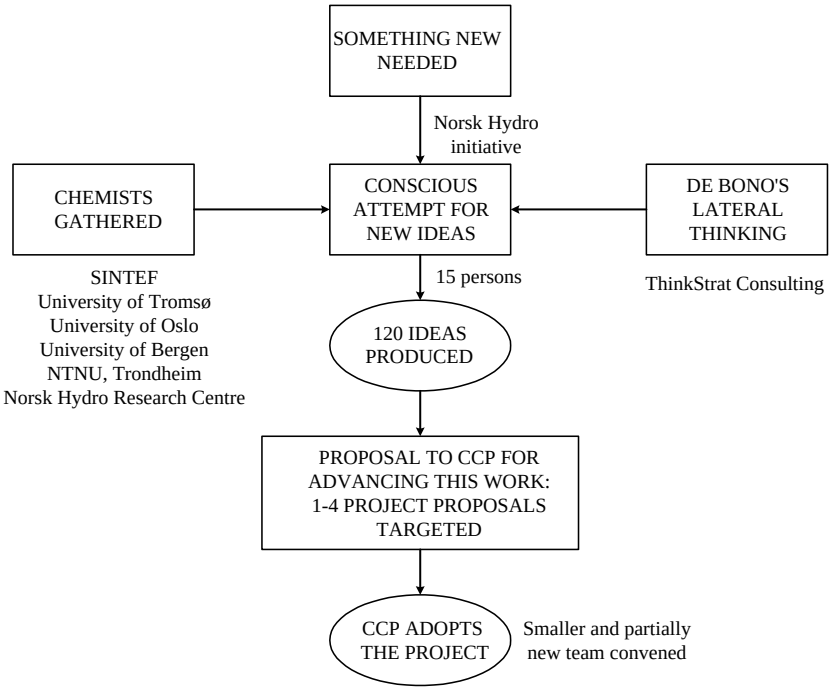

Figure 1: Background for and history of this work.

CHALLENGES IN CO_2 REMOVAL

Given a power plant run on natural gas using a combined cycle gas turbine, the partial pressure of carbon dioxide in the exhaust gas will be as low as 0.03–0.04 bar (corresponding to 3–4%). After heat recovery, the temperature of the flue gas will be in the region of 80 °C and the gas will be saturated with water. The oxygen level in the gas will be 12–14%, which is significant with respect to the degradation of the absorbent. There is fortunately no need to worry about the sulfur content as it will be next to nil; usually less than 5 ppm NO_x, however, is another contaminant of concern. Since carbon dioxide is a weak Lewis acid, the absorbent must necessarily be a base relative to carbon dioxide. This means that also other acidic compounds, like NO_x, in the gas are likely to interact with the carbon dioxide capturing material.

The sheer volume of exhaust gas from a large power plant represents a great challenge. (The actual volume is around 1 million m^3/h for a nominal 400 MW CCGT. Given a "wind speed" of 10 m/s (a fresh breeze), this would require a duct of 5.3×5.3 m^2). Since this is combined with atmospheric pressure and a need to keep the pressure drop low, this challenge becomes even greater. Removal of carbon dioxide from the exhaust gas can be done in many ways, but the volumes of carbon dioxide are such that regeneration of the medium used is a must. Clearly, the partial pressure of carbon dioxide must be lower than the value given above during desorption unless the equilibrium is shifted by altering some other viable parameter, e.g. the temperature. The need for a relatively pure carbon dioxide for disposal rules out the use of a dilution gas, of course, since it defeats the purpose.

While chemistry is the acknowledged focus, great challenges then still remain in the design of equipment for handling the huge amounts of gas involved. Gas turbines, in particular, need a low exit pressure for efficiency reasons. There is then a need to keep the pressure drop low, and this has implications for the size of the equipment. In the later stages of this project, some attention was given to equipment improvements although this was not a key focal point in this work.

THE FORMAL TOOLS FOR CREATIVITY

The use of formal tools to help the creativity can be considered the experimental technique for this project.

The work of de Bono on *lateral thinking* [4] was heavily exploited in this project. The use of his formal methods and techniques were essential for the successes achieved in this project. Importantly, the team included a consultant trainer qualified by Dr De Bono to teach and apply his creativity tools to facilitate the process in order to get the best out of it.

The illustration in Figure 2 gives an overview of the overall creative process. Once the problem to be addressed is identified, the process must start by defining the *focus* of the problem. It is very important to get this right because the defined focus will heavily influence the work to follow. Irreparable damage to the creativity could occur if the focus is too narrowly defined, and the work might get watered down if it was described too broadly. Our focus was initially set as:

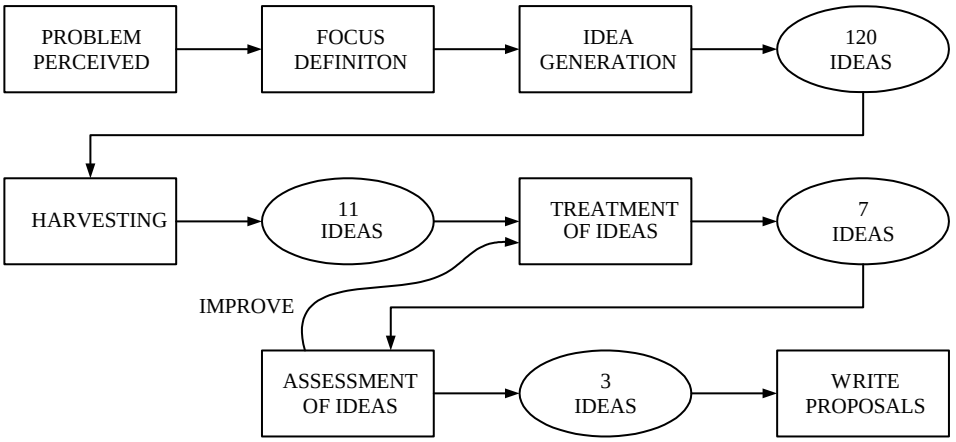

Figure 2: The work flow of creating, capturing, developing, refining and judging ideas.

How can we use carbon dioxide chemistry for the purpose of making a dilute carbon dioxide stream pure?

It was discovered during the ideas refinement stage that this needed refinement, and the focus was later in the process reformulated to:

In what new ways can chemistry be used to produce a pure carbon dioxide stream at a per unit cost which is lower than that of existing methods?

The cost issues were deliberately set aside initially so as not to unduly restrict our creative thinking in the early idea creation stage.

After the focus was properly understood, the first step for the assembled group was to list all ideas that came into the participants' heads. Lateral thinking techniques were employed when the flow of ideas stopped, and many more ideas were produced.

The term lateral thinking refers to a way of thinking that deliberately seeks changes in perceptions, concepts, and ideas through use of formal thinking tools (see Figure 2). Figure 3 highlights a key point in the philosophy. The benefit of the approach may be illustrated by imagining that a novel idea lies at point C whereas our normal way of looking for a solution would take us down the broad path to point B, a path that is easily travelled using our habitual approach. We require guided redirection with the help of thinking tools to get from point B to point C. There are several ways of doing this. A good example is the random entry technique, in which a random word is chosen and used by seeing how this word may be related to the problem in the broadest sense. With hindsight, it will be easy to see how the new and better solution could have been developed from A in the first place once the new solution C is found. This is illustrated by the dashed line in Figure 3.

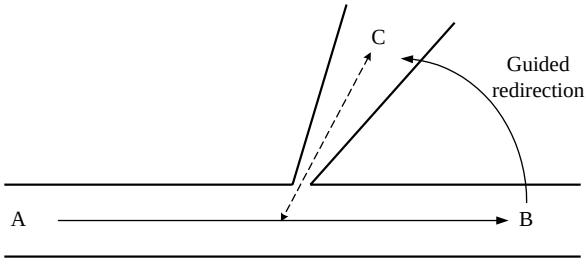

Figure 3: Illustration of the *lateral thinking* process.

At the end of the idea generation stage, 120 entries were listed as ideas. All these ideas were properly recorded and roughly sorted. This action proved to be essential because it took 2 years before we could assemble a part of the group to complete the job, but it would have been essential even with a 2-month break. Listing and sorting the ideas is time consuming, and a break in work at this stage is realistic.

Many creative processes end at this stage. Often the list of ideas is left with the problem owner who has little time on his hands, and the list is only half-heartedly worked at until the enthusiasm dies away. The idea generation effort was the spectacular part of the creative process with very visible results appearing in a short time. There was a need to shape the initial, very immature, ideas into something practical and usable, and this had to be done within a strict time limit and with financial constraints (5 months and 120,000 euro). This would be impossible to achieve without using some type of formal thinking process. The generated ideas were sorted in groups to ease the ensuing work.

The next step of the creative process was *harvesting* ideas, which is visualised in Figure 4. With as many as 120 ideas, there was no way a group could work at all simultaneously and arrive at a successful conclusion. There was a need to extract a manageable number of ideas from the list. This was done by tasking the work group to vote, with 10 votes each, on which ideas, based on their insight into the field, promised or revealed the most benefits, the greatest likelihood of answering the question posed in the focus statement, and whether they were feasible. Another group may have picked different ideas to work with, but that does not matter. The list was thus arbitrarily reduced to 11 ideas, the square root of the original number. The other ideas were not thrown away, but put on the side for later examination.

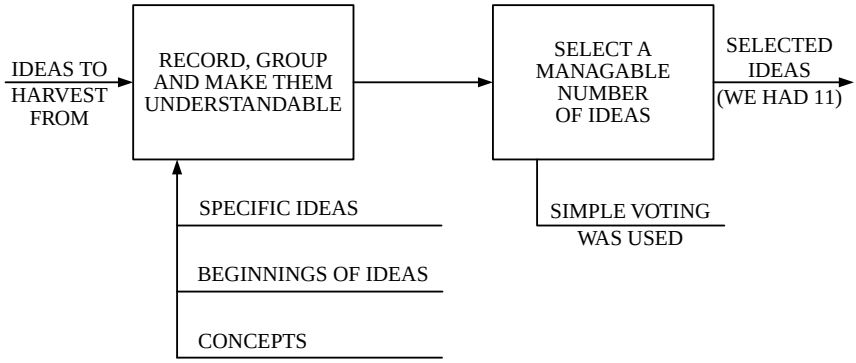

Figure 4: The process of capturing the ideas, *harvesting*.

The harvested ideas were checked for match with the defined focus and finally adopted by the whole group. The ideas were also sorted in the categories specific ideas, beginnings of ideas, and concepts [4]. The experience from our work is that the group dynamics created kept the process on the road. When one individual experienced a drop in enthusiasm and morale, the rest of the group kept going and provided morale boosting. If the group strayed or slackened the pace, the facilitator was always there the keep the effort going. A work process like this is possible only with motivated participants who believe and trust the system.

Once the harvesting was done, and this was and can be done relatively quickly, the next step is *treatment* of the ideas, and this is a laborious and time consuming, but essential, process needing the support of the group dynamics. Long days were worked to achieve progress on group assembly days. Individuals were assigned the role of being *idea champion*, and all ideas had its champion. Assignments were undertaken by group members, usually the idea champion, in between meetings to obtain more information on defined aspects of the ideas. Even an idea that looks unpromising at first sight may be turned around if its faults are corrected, and good ideas can be made even better by strengthening strong points. Ideas may also be used to extract a broader concept, which may then be developed into a better idea. There are more points to treatment, but these were the key points in this case. See also Figure 5.

As it happened, a couple of the ideas were discarded during the treatment process because it became evident that no one in the group could see them working out, but this was only done after attempting to turn the ideas around. There was also a case for merging three of the ideas, see below. This was then done because each idea on its own could not meet our defined focus, but once merged they became very interesting. Once the short-listed ideas are treated to the extent possible within available resources, the ideas must all be assessed for focus and to see how practical they would be. This *assessment* is the final stage of the idea development. However, any idea may even after assessment be recycled for further treatment. This process only stops when the ideas have been made good enough or discarded. There is, however, the constraint of time and resources to such a process, and the foregoing is the ideal situation. Assessment is certainly good for highlighting the shortcoming of any idea, often its cost. At least one of the ideas was given further treatment at this stage, with significant improvement in potential cost as a result. The assessment work process is illustrated in Figure 6. This is further commented in the section on cost assessments.

Testing an idea for competitiveness is the ultimate test of how good it is. We endeavoured to make flowsheets for all ideas followed by a simple cost analysis since the present group is industrially oriented. In the research community, a cost analysis is traditionally shunned at this stage. It is argued by researchers that there is insufficient information. They would be right, but there is still a need to make a selection, or give a priority at least, since funding is limited. In our case, we assumed or estimated target properties for our ideas. The equipment in the flowsheet was roughly sized on this basis, and rough cost estimates were made.

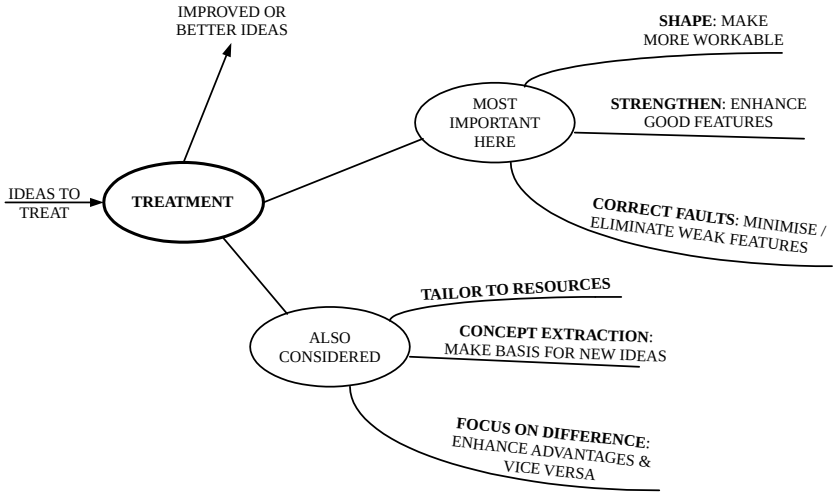

Figure 5: The process of improving the ideas, *treatment*.

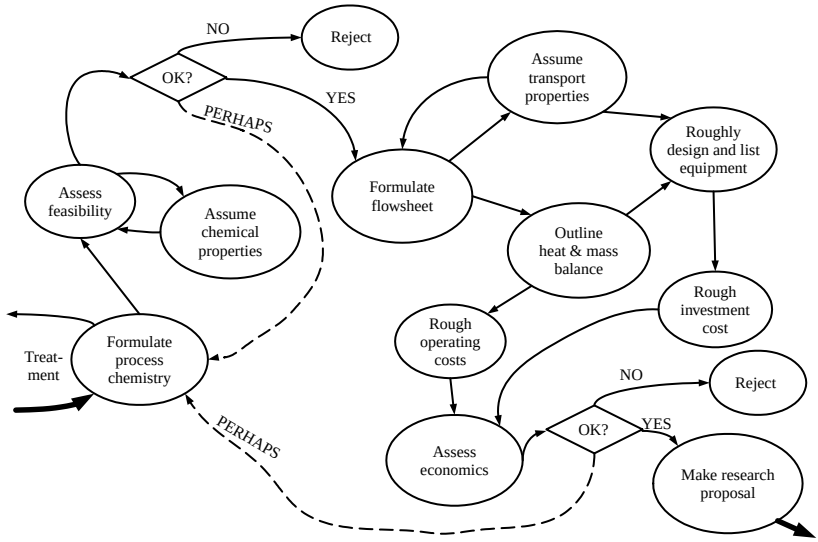

Figure 6: The judgement and improvement of ideas, *assessment* work flow.

There is an upside to this. The target properties assumed or estimated automatically become the research targets for each idea. These targets must be met in order to live up to the cost-saving potential perceived after the initial assessment. This is a good basis for starting a research project since it is then entered into with a termination trigger. Experience shows that research projects are often difficult to stop because the targets are often poorly defined, which easily works in the favour of those interests wanting to prolong a project. The technique described above ensures that the stop signal is well defined.

THE PROPOSED RESEARCH IDEAS DEVELOPED

The following broad topics have been identified as interesting research projects for capturing carbon dioxide from flue gas (or any other gas):

- Transition metal complexes.
- Biomimetic chemicals.
- Sonochemistry.
- Salt hydrates.
- pH controlling chemicals.

Fast Shaking Truck

The first three of the above ideas may be combined into an absorption–desorption cycle. It is foreseen that the transition metal complex would carry the carbon dioxide from the absorption section to the desorption section. Metal complexes with carbon dioxide have been discussed in the literature [5]. If needed, a biomimetic chemical could be added to enhance the rate of carbon dioxide binding, and the sonochemistry is foreseen as aiding the desorption. Together they form the basis for a process, but it is feasible to use any one of them on its own, possibly in conjunction with some other chemical, or chemicals. A process flowsheet for this concept is shown in Figure 7. This process was named the "Fast Shaking Truck" on the basis that the transition metal complex would "truck" the carbon dioxide from the absorber to the desorber while the sonochemistry would "shake" the carbon dioxide out, and the absorption could be speeded up by the biomimetic chemical by catalysing the absorption process ("fast") if needed.

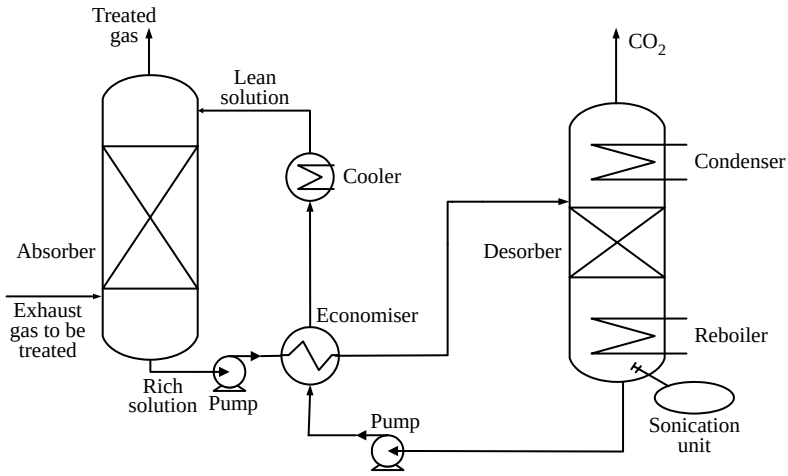

Figure 7: Process flowsheet for use of transition metal complexes, biomimetic chemicals and sonochemistry. The process referred to as "FST".

The basic assumptions made for this process are that:

- The cyclic capacity of the transition metal complex could be 0.7 mol CO_2/mole complex (or higher).
- Negligible degradation of the chemicals would occur.
- Regeneration can be aided by cheaper energy than the 5 bar steam used in the standard absorption process, in part aided by the sonification.
- Data for heat and mass transfer used for rough process sizing are reasonable.

The cyclic capacity is regarded as being a reasonable assumption. The regeneration assumptions are less well founded, but within the imaginable realm. The equipment implied is conventional, but some

assumptions have been made with respect to the sizing. The focus of early research must be the identification of which transition metal complex or complexes that holds promise based on some form of absorption equilibrium measurements. The target is to find a complex with promising cyclic capacity to build the process on.

Melting Point Swing (MPS) Process Using Salt Hydrates

There is already evidence in the literature [6] of salt hydrates that bind carbon dioxide. The interesting property is that carbon dioxide is bound in the melt and desorbed on solidification. Melting points can be found at temperatures enabling the use of low-grade heat. The literature has described hydrates with melting points in the range 40–60 °C. Since the absorption–desorption cycle operates across the hydrate's melting point as explained above, it is referred to as the MPS process.

Figure 8 shows a process flowsheet for the MPS cycle. Since it essentially consists of a single apparatus with an external pump, it may be more appropriate to refer to it as an equipment sketch. Here the exhaust gas from the heat recovery & steam generating (HRSG) plant is fed without further cooling. In the absorber section, the salt hydrate melt will absorb the carbon dioxide. This process is exothermic and will heat the gas and the melt. The next section up is the hydrate-melting process. Here the still warm exhaust gas is routed through the solid hydrate particles that will trickle towards the bottom as they melt while taking energy from the gas. The gas that has had its carbon dioxide level reduced, is then vented. The carbon dioxide rich melt is pumped from the bottom of the tower to the top where it passes through a chamber where the water content is controlled by contact with an atmosphere that has its water content in turn controlled by contact with an adsorbent. From this section, the melt is allowed to flow onto, e.g. spinning discs with internal cooling. These discs can be designed with very high heat transfer coefficients, and the spinning combined with the surface design will fling the solidified melt off to the perimeter where the particles are collected and allowed to flow to the melting section. The carbon dioxide will desorb when the melt solidifies on cooling.

The basic assumptions made for this process are that:

- 5% (wt) CO_2 are absorbed out of absorber stage.
- Waste heat may be used to drive the cycle.
- The melt will solidify in solids that will flow and not agglomerate.
- The melting process by direct gas contact will be feasible.
- There will be negligible degradation of the chemical used.
- Data for heat and mass transfer used for rough process sizing are reasonable.

The capacity for carbon dioxide absorption is optimistic judged by the referenced literature. The use of waste heat to drive the cycle on the other hand seems reasonable in view of the described process solution. The spinning disc section is certainly a challenge, but within the realm of what has been done with such equipment in the past. Many parallel discs will be required though. The melting section will also require chemical engineering ingenuity, but should not be beyond reality.

A vision has been created, and it can be checked in the lab with modest resources. That is the essence. The focus of early research is identification of salt hydrates that have an acceptably high affinity for carbon dioxide and a small enough temperature swing, followed by experimenting with the key process parts like direct contact melting and solidification on spinning discs.

pH Controlled Cycling

The use of pH controlling chemicals has been successfully introduced for absorbing SO_2 from flue gas [7]. On this basis it seems worth while to look for analogous systems to separate carbon dioxide. A process flowsheet for this concept is shown in Figure 9. As the flow sheet indicates, the process resembles a normal absorption–desorption process. However, it uses a pH-controlling additive to the carbon dioxide rich solution to lower the pH enough to force carbon dioxide out of said solution. This auxiliary pH-controlling chemical is precipitated in the crystalliser before the carbon dioxide lean solution is returned to the absorber with a pH that allows absorption of carbon dioxide. This concept is referred to as the pH swing process.

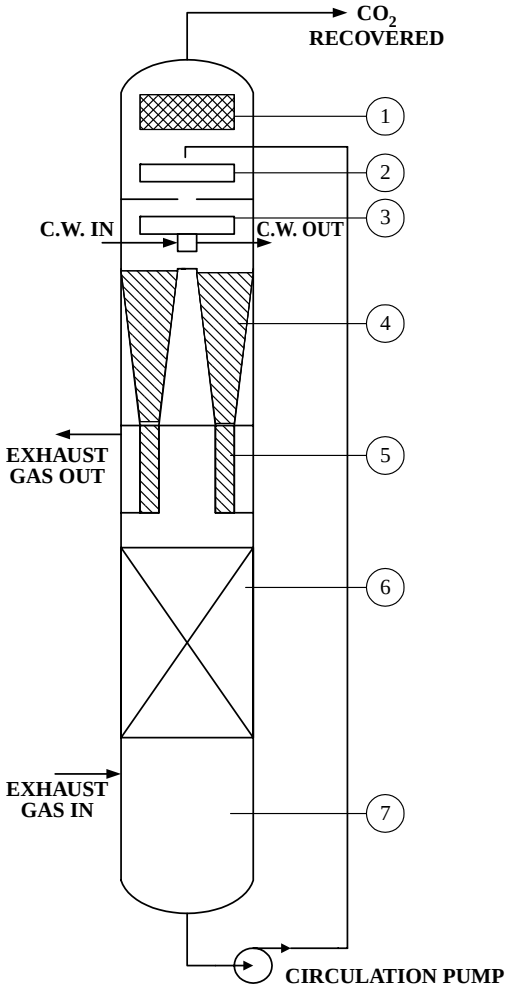

Figure 8: The apparatus for the melting point swing process, referred to as "MPS". (1) Dessicant to pick up water from the CO_2 removing chemical to control the water balance. It could be, e.g. silica gel. Water removal does not necessarily have to be done continuously. (2) A spinning disc, or discs, where heat is supplied internally to aid water evaporation. (3) A spinning disc, or discs, where cooling is supplied internally to solidify the CO_2 removing chemical. It is foreseen that the disc is flexible enough to flex with the temperature difference such that the solid does not grow on its surface. Alternatively, the solid will need to be scraped off. (4) Hopper feeders where the solid, hopefully in the form of grains that will flow is collected and routed to the next process step. It is also there to provide pressure drop to prevent significant amounts of gas to move through this bed. (5) Here the solid particles form a radial "reactor/bed", or "melter", where the warmer gas moves through radially in order to remelt the solid. The melted solid would drip down on and be distributed onto. (6) The packed bed absorber where the melt is flowing downward counter-currently with the gas that flows upward while CO_2 is absorbed. (7) Below the packed bed there is a sump that may hold the column's inventory of solid/melt.

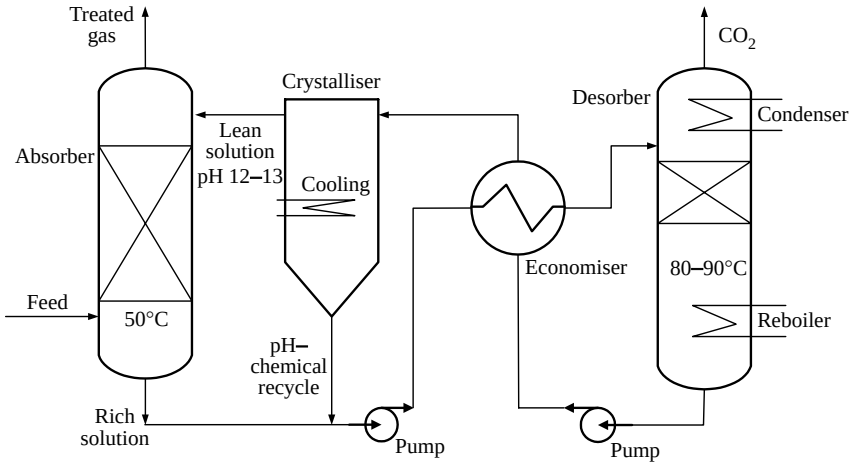

Figure 9: Process flow diagram for application of the pH swing principle, referred to as the pHS process.

The basic assumptions made for this process are that:

- A suitable pH-controlling agent can be found also for the CO_2 system.
- An absorbent compatible with the pH-controlling agent can be found.
- Data for heat and mass transfer used for rough process sizing are reasonable.

There is no way of assessing the probability of finding the required pH controlling chemical except to say that such a system has been found for SO_2 absorption, and that makes the assumption of its existence less optimistic. The rest of the assumptions seem reasonable if a success is scored regarding the key chemical.

What is needed is clearly defined. Any early research would need to focus on finding a workable pH-controlling system and would involve literature search and simple experimentation in the laboratory, possibly combined with molecular modelling.

COST ASSESSMENTS

The ideas created are clearly rough and in need of grinding at this stage. Many such ideas must be formulated and evaluated to find the really good one to solve the carbon dioxide separation from exhaust gas problem. Since many ideas must be worked on, it is clearly important to screen ideas at an early stage while spending on development is still low. A method was worked out here that allowed a first analysis of economic potential based on rough sizing of the processes.

The participants in this project were for this reason forced to make flowsheets for the processes before knowledge about chemicals and physical data were gathered. The unknown properties and data had to be assumed. Using this as basis there was little point in elaborating the chemical engineering of the processes. All possible shortcuts and rules of thumb were applied, and sometimes equipment was sized based on judged comparisons with known processes. In the end we arrived at what can be called “order-of-magnitude-costs”. It should be obvious that this is a coarse way of assessing the costs of a process, but it seems the only way open at such an early stage. This approach requires experience in judging what features of the process are the cost drivers and the stumbling blocks. The work process for this part of the assessment is illustrated in Figure 6.

The assumptions made can always be questioned, and it is the responsibility of the idea champion that the assumptions are on the optimistic side, and the idea is given all possible benefit of doubt. The aim is not to reject the ideas, but to uncover the potential they may possibly have. Ideas with overestimated costs will be rejected, but underestimation will give the idea a new chance. One idea was rejected at this point. Given that exploratory research is initiated, the assumptions automatically become targets to achieve. This means that progress of research can be checked early on in the development. With such early checking enabled, spending can be stopped early if it becomes clear that targets cannot be met. Research on these speculative ideas can thus be recommended with little risk of wasting large research funds.

TABLE 1
RESULTS FROM THE ANALYSIS OF THE PROPOSED IDEAS WITH RESPECT TO POTENTIAL FOR A 400 MW POWER PLANT

	"FST"	**pH swing (pHS)**	**Melting point swing (MPS)**	**Base case (BC)[c]**
Investment[a] (Meuro)	43	81	33	73
First fill (Meuro)	5	6	4	5
Sum investment	48	87	37	78
Investment relative to BC	0.62	1.12	0.47	1.00
Steam (meuro/år)	3.6	0.8	0	7.3
MEA or eq (meuro/år)	0.3	0.4	0.4	2.9
Other chem. (meuro/år)	0	0	0	
Maintenance (meuro/år)	1.72	3.24	2.64	2.92
Sum operating costs (meuro/år)	5.62	4.44	3.04	13.12
Opearting costs relative to BC	0.43	0.34	0.23	1.00
NPV (net present value) of "sum operating costs"[b]	43	34	23	100
Relative NPV of operating costs	0.43	0.34	0.23	1.00
Net present cost of CO_2 removal, meuro	91	121	60	178
Relative net present cost of CO_2 removed	0.51	0.68	0.34	1.00

[a] Only separation plant included.
[b] 10% rate of interest, 15 years considered.
[c] Ref(erence) Case, the MEA-based absorption process.

The assessment carried out as described shows that a 40–70% cost reduction potential in all cost aspects of the carbon dioxide separation process is possible if the chemicals with the right properties are found. The estimates show formal differences of potential between the processes. In view of the fundamental assumptions made, it may be questioned if the differences are significant although these assumptions are made with professional judgement. The pH-controlling chemical is, however, unlikely to give any saving on the investment side since extra equipment is foreseen, but there is a good possibility that the operating costs may be reduced substantially. For the other two process options, savings may be achieved in both investment and operating costs. The cost figures appearing in Table 1 are only given to highlight the merits of our findings. The absolute cost figures given here are not comparable with the official CCP cost figures given elsewhere in the book. They differ with respect to items included and cost estimation method used plus costs of operating items.

It must be pointed out that the processes described have synergies with other developments in the post-combustion decarbonisation field. Two of the processes would benefit from all improvements made to the equipment used in the standard absorption cycle. All three proposals would of course, benefit from any recycling of exhaust gas that reduces the amount of gas to be treated, a proposal that was fielded after this project was finished and assessment made. The predicted "unit cost relative to reference case" must be adjusted accordingly.

CONCLUSIONS

This project has demonstrated that working with formal thinking tools can succeed in producing promising ideas for further research; the cost of this project was around 0.12 million euro. Any research following such an exercise must, however, be classified as high-risk projects. It is thus important that criteria for when to stop or heavily support such research are defined early. This work explains how this can be done.

It is demonstrated how even roughly described ideas can be assessed for economic potential even before data are produced to allow proper process estimates. This may be done by making assumptions based on reasonable, or maybe better still, optimistic views of what could be achieved. The argument for being optimistic is that if the idea still does not show economic potential, then further research may safely be dropped. If potential is shown, then the assumptions made will be well defined research targets for the ensuing research project.

Three ideas were produced. It is expected that these ideas can be checked by early stage research for 0.1–0.4 million euro each.

It should be clear that this is research work at a very early stage, and the ideas have only just been formulated. Publication would normally come later, after positive results had been obtained. Carbon dioxide separation from flue gas is such an enormous challenge, however, that it is important to attract more people to do basic research. It is in this context that the present information is shared this early. Investigating these ideas is high-risk research. The more people engaging in such research, the higher the probability of at least one group succeeding.

Accepting the premise that the goal of cost-effective carbon dioxide removal will be reached through radical new thinking, more groups like the present one should engage in similar efforts. If it is further assumed that 100 such ideas are needed before one succeeds, the cost of getting and checking these ideas would be 33 times the cost indicated here, in the order of 20 million euro in all. New groups need to be encouraged to produce these extra ideas, and members with different specialities than the present group should be sought.

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