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13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Operating considerations of ultrafiltration in enzyme enhanced carbon capture

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Abstract

Today, enzyme enhanced carbon capture and storage (CCS) is gaining interest, since it can enable the use of energy efficient solvents, and thus potentially reduce the carbon footprint of CCS. However, a limitation of this technology is the high temperatures encountered in the stripper column, which can deactivate the enzymes. One solution to this challenge is the use of ultrafiltration to retain the enzyme in the absorber unit. In this report, a base case of a CCS facility is used to model the impact of such membranes for use in a full scale CCS commercial plant. The base case has an approximate capture capacity of 1 MTonn CO_2/year, and is here operated for one year continuously. This publication compares soluble enzymes dissolved in a capture solvent with and without the use of ultrafiltration membranes. The membranes used here have an enzyme retention of 90%, 99% and 99.9%. Enzyme retention is the amount of enzyme that is retained in the absorption column in each cycle. These membranes were modeled with five stripper temperatures 60 °C, 70 °C, 80 °C, 90 °C and above 100 °C. Enzyme deactivation follows a 1st order rate and increases with increasing temperatures. It was found that for all stripper temperatures used in this model, deactivation rates were too high for continuous operation over 1 year, without adding additional enzyme, if an activity of at least 50% should be maintained. With increasing stripper temperatures the membrane retention requirement increased. To retain over 50% activity over a whole year at 70 °C stripper temperature required a membrane of 90% or higher enzyme retention, at stripper temperatures of 90 °C a membrane of 99.9% retention was required for the same result. Finally, it was investigated if stripper temperatures over 100 °C, where instant deactivation was modeled could be used. It was found that with enzyme retention of 99.9%, with instant deactivation, after 1 month 50% of the activity is lost. Thus the use of membranes in enzyme enhanced CCS might be restricted to temperatures below 100 °C, or temperatures the enzyme can withstand for shorter time periods.

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1. introduction

To limit further climate change, atmospheric CO_2 among other greenhouse gases must be reduced. One option for doing so is carbon capture and storage (CCS). This paper will focus on enzyme enhanced CCS, using carbonic anhydrase (CA) EC 4.2.1.1. Enzymes are beneficial for such processes since they enhance reaction rates, especially for bicarbonate forming solvents[1]. However, enzymes are not designed to operate under process conditions encountered in a CCS capture facility. Therefore one of the challenges encountered when using enzymes in such processes is the stability under these conditions, where enzymes may lose activity over time. Previous work has explored this by investigating the stability of one CA, especially suitable for CCS in terms of pH, temperature and solvent type at CCS relevant conditions. Although, the enzyme in question was significantly more stable than most enzymes under such conditions, long term studies (over several months) found that the enzyme was sensitive to higher temperatures[2,3]. Here the impact of these results, if these enzymes were to be used on an industrial scale, are investigated by modeling the stability of such enzymes in a theoretical commercial plant. Enzyme stability within a model framework for stripper temperatures ranging from 60 °C to over 100 °C compared for soluble enzymes with and without the implementation of ultra-filtration membranes. The membranes are explored with enzyme retentions up to 99.9%. The results are modeled for 1 year continuous operation of the facility.

The enzyme CA catalyzes hydration of CO_2 into bicarbonate (Reaction 1). It is therefore particularly useful in solvents which form bicarbonate, such as tertiary and hindered amines, and carbonate salts. These types of solvents have the advantage in that they have relatively low energy for desorption requirements, compared to solvents like primary amines, because they do not form covalent bonds with the absorbed CO_2. However, they are often impeded by slow absorption kinetics, which can either result in poor capture capacity or increased operating and capital costs due to a bigger absorber column. The addition of CA or another catalyst can alleviate this effect by enhancing reaction kinetics. Just like a conventional chemical catalyst, the enzyme does not change the thermodynamics of the reaction, it simply speeds up the reaction rate. This publication does not investigate reaction kinetics, since excellent examples of this can be found in literature[4–6].

Reaction 1:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$
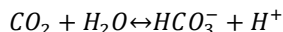
Nomenclature

CCS   Carbon capture and storage
CA   Carbonic Anhydrase

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2. Model framework

The base case is defined in Table 1 and illustrated in Figure 1, this is based on some publically available data from the Boundary Dam CCS facility, and is supplemented with information from experts in the field.
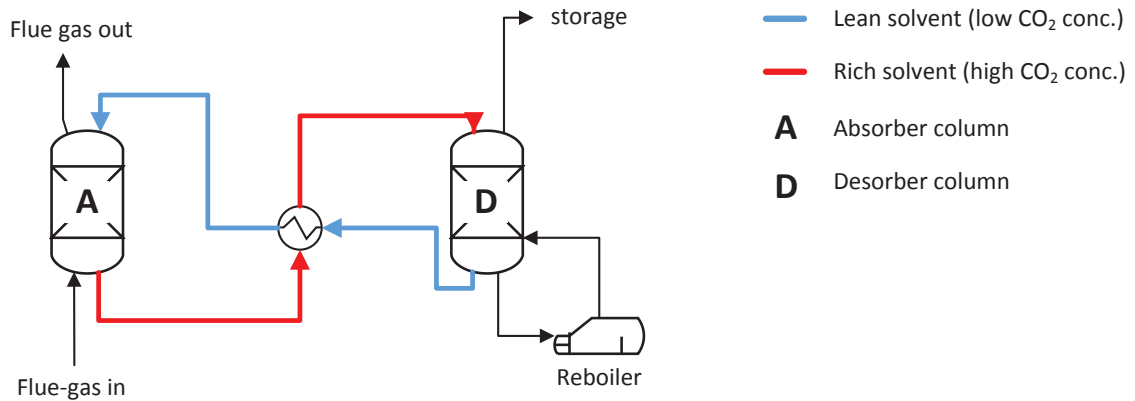
Figure 1: A typical solvent based carbon capture process. The flue gas enters the bottom of the absorber, a lean solvent (blue) counter currently reacts with the gas. At the base the rich solvent (red) is passed through a heat exchanger before it enters the desorber column. The CO_2 is the stripped from the gas and the lean solvent is regenerated. It will again pass through the heat exchanger before it re-enters the absorber column.

Table 1: Base case data, with a solvent volume of 2060 tonne, and a flow rate of 2000 tonne/hr.

	Residence time (min)
Absorber	11,4
Stripper	5,3
Hold-up	45,1
Total	61,8

Deactivation rates

The enzyme deactivation rates were obtained from previously published data[2], and follow first order reaction rates according to the following formula

$$A_t = A_i e^{-kt},$$

Where A_t is the activity remaining at a certain time point, A_i is initial activity (100%) ,k is the deactivation rate constant and t is the time at that time point.

Table 2: Deactivation with temperature

Temperature (°C)	50	60	70	80	90
Deactivation rate (h^{-1})	0	0.003	0.0054	0.0536	0.3860

In addition a stripping temperature above 100 °C was used in the calculations, instant enzyme deactivation is assumed.

Ultra-filtration membranes

Ultra-filtration membranes used in this study were calculated to have an enzyme retention of 90%, 99% and 99.9%. Furthermore the membrane flux was calculated for two specific membranes from the commercial membrane producer Alfa Laval, Table 3.

Table 3: Properties of commercial membranes used in this model.

Type	Selectivity (%)	Water permeability (L/m2*h*bar)	Source
Commercial	90	50	Alfa Laval
Commercial	99,9	400	Alfa Laval

3. Results

Enzymes can be used in a CCS facility by simply adding soluble enzyme to the solvent, and run the facility as before, as described in figure 1. This method of adding enzymes provides the maximal effect of the enzyme in terms of catalytic rates due to the lowest mass transfer limitations. For example, when enzymes are immobilized mass transfer limitations increase because the enzymes are not dispersed in the liquid. In fact it has been found that enzymes immobilized on packing is not a viable option for enzyme enhances CCS, due to mass transfer limitations[4]. In addition, this set-up enables the enzymes to catalyse both absorption and desorption. Finally, it has the lowest capital and operational costs since no additional cost for membranes and compression are added. However, as investigated in previous work, the enzyme deactivates at a significant rate at higher temperatures[2]. Therefore, the stability of such enzymes are investigated at different operating temperatures with the base case CCS facility outlined above. Enzyme viability is calculated, in terms of residual activity in a continuous operating power plant for one year. Here five different stripper temperatures were used, 60 °C, 70 °C, 80 °C, 90 °C and above 100 °C. It was assumed that absorption is done at a lower temperature and enzyme activity loss is limited, therefore deactivation is only occurring in the stripper. The reduced deactivation at lower temperatures has been reported in scientific literature[2,3]. Figure 2 outlines trends over a time period of one year, from initial activity (100%). From this figure it can be observed that significant activity loss is found after a few minutes with the highest temperature (100 °C). However, some enzyme activity still remains after 1 year with the two lowest temperatures. In this model we have assumed a uniform temperature in the stripper unit. It was also tested if a non-uniform temperature model, where parts of the stripper were warmer and colder than the bulk solvent, would influence the outcome of the model. From this we see a slight decrease in stability, but the results follow the same general trends as the data in Figure 2 (data not shown).
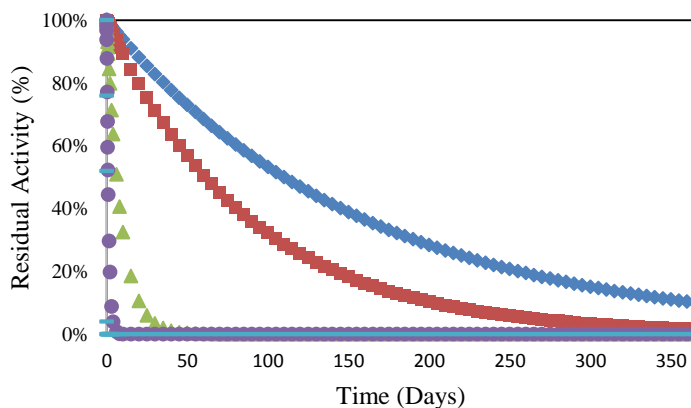

Figure 2: Residual enzyme activity after one year with five operating temperatures in the stripper: 60 °C (blue diamond), 70 °C (red squares), 80 °C (green triangles), 90 °C (purple circles) and over 100 °C (light blue dashes).

Furthermore, the use of an ultrafiltration unit was considered. Here the rich solvent will be passed over an ultrafiltration membrane where a limited amount of enzyme will pass through. The enzyme which does not pass through the membrane is then shuttled back to the absorption column with 10 % of the rich solvent. Figure 3). The stability of the enzymes of this process depends on the amount of enzyme which passes through the membrane and the temperature the enzyme is exposed to in the stripper.
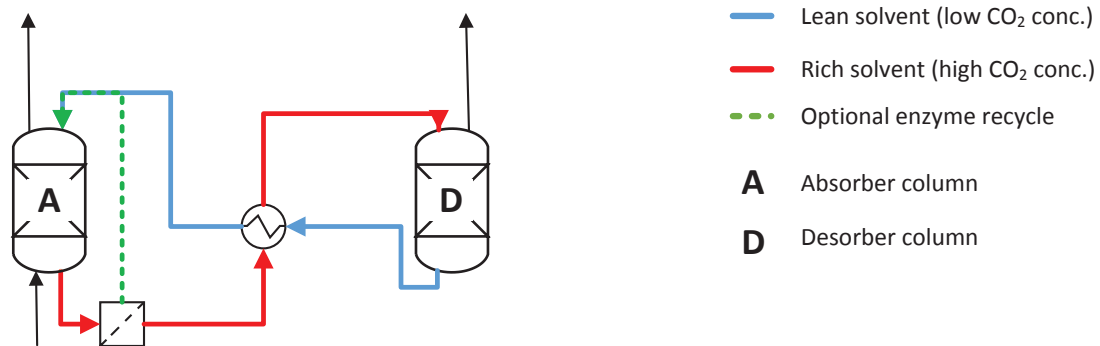

Figure 3: One possible set-up of an ultrafiltration unit in a CCS facility. The process is similar to that which is described above (Figure 1). However, the rich solvent will be passed through an ultrafiltration device where most of the solvent will pass through, and some of the rich solvent will be diverted back to the lean solvent with the enzymes, not passing through the desorber column.

Here three membranes with enzyme retentions of 99.9%, 99% and 90% are used for the calculations, and compared with soluble enzyme. The rate of deactivation of the enzymes which pass through the membrane and experience the conditions in the stripper unit are calculated using five different stripper temperatures 60 °C, 70 °C, 80 °C, 90 °C and above 100 °C. The comparison of the models can be found in Figure 4: a, b, c, d and e, respectively. It is observed that the efficiency of the membrane has a significant impact on the enzyme viability. The membrane with the poorest enzyme retention (90%) has only a small impact on enzyme viability for all temperatures above 70 °C. For stripping temperatures over 70 °C membranes with higher selectivity preform significantly better. The membrane with the highest selectivity (99.9% selectivity) preforms well at temperatures up to and including 90 °C. Finally, it was investigated if temperatures above 100 °C, where instant deactivation is assumed, is a viable option with the use of ultrafiltration. Without the use of ultrafiltration membranes all activity is lost within 1 hour of operation. Although the use of membranes, especially the membrane with the highest enzyme retention at 99.9% significantly increases the life span of the enzymes, high activity loss is still observed. 50% of the activity is lost after 1 month and after 6 months only 1% activity remains.
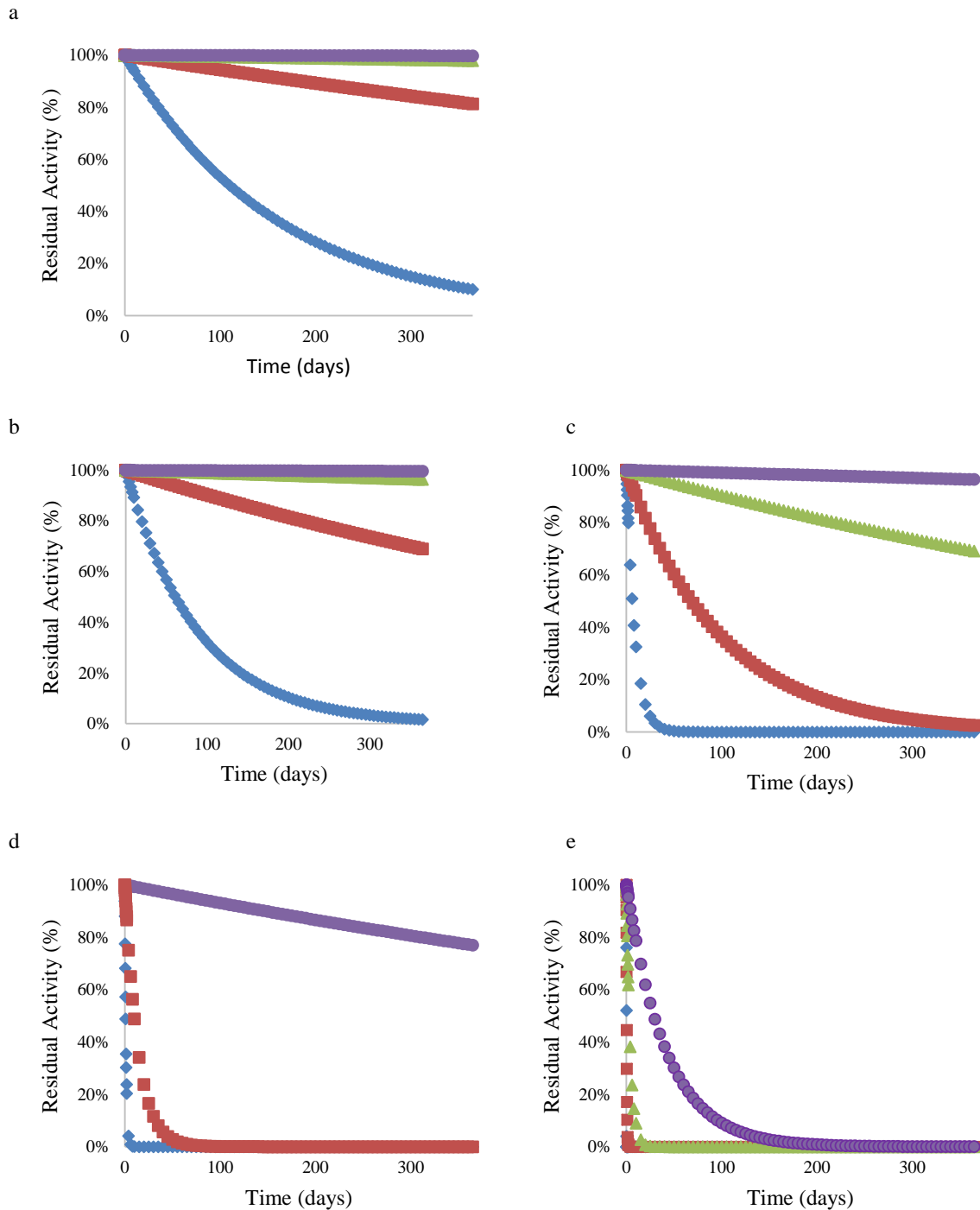
Figure 4: Effect of enzyme stability, measured by residual activity over time, of ultrafiltration enzyme separation with various stripper temperatures: (a) 60 °C, (b) 70 °C, (c) 80 °C, (d) 90 °C, (e) over °100 C (instant deactivation). Membrane retention for all figures: Blue diamond: No membrane, Red squares: 90% retention, Green triangles: 99% retention and Purple circles 99.9% retention.

Discussion

Enzymes can enhance the absorption rate of CO_2 into kinetically limited solvents, such as tertiary amines and carbonate salts[3,5,7]. However, enzymes are often limited in CCS applications due to thermal stability, which is problematic due to the high temperatures encountered in the stripper unit. We have therefore explored the use of ultrafiltration units in comparison to free enzymes in solution. There are two key issues that makes a CCS process challenging to operate compared to other applications where enzymes are used. Firstly, the scale of a CCS facility must be kept in mind. In the base case used in this paper the addition of only 1% enzyme would be 20 tonnes enzymes. Thus, the cost of the enzyme would be a significant contribution. Secondly, the number of cycles should be kept in mind. This base case has a 1 hour cycle time, which equates to almost 9000 cycles per year. Thus the addition of enzymes on regular intervals would significantly dilute the solvent, and would likely over time change physical properties of the solvent, such as the viscosity. Figure 2 indicates how such a process would look like with a solubilized enzyme without the use of any ultrafiltration units. With the deactivation rates indicated here, it was found that even with the lowest stripper temperature 60 °C, enzymes must be added 3 times a year to maintain an activity over 50% of initial activity. When the temperature increases this trend intensifies, such that at stripper temperatures of 80 °C, enzyme must be added 60 times in a year to maintain the same activity of 50% or higher. As discussed above this does not only add costs to the process, but it also poses a practical problem with solvent dilution, and increased enzyme concentrations.

One solution could be the use of an ultrafiltration membrane unit, which restricts the enzymes in one area of the process, the absorber, so the enzymes does not enter the high temperature areas of the stripper. This means enzyme deactivation is minimized. Here, calculations have been carried out with 3 enzyme retentions, 90%, 99% and 99.9%. Operated at the same five stripper temperatures as outlined above from 60 °C to above 100 °C. In the scenario described here, 10% of the rich solvent stream is diverted while the majority of the enzymes are diverted back to the lean solvent, thus not being regenerated. The non-retained enzyme, will pass through the stripper column and deactivate at the same rate as the soluble enzyme. It should be noted that such a set-up poses several disadvantages. Firstly, 10% of the solvent is not regenerated, thus the capacity of each cycle and the overall capacity of the facility is reduced by 10%. Furthermore, the kinetic penalty of such a set-up is likely to be higher than 10%, since the reaction rates in the absorber decreases with loading.

Our calculations show that the 90% enzyme retention membrane works well up to 70 °C, with temperatures above that more stringent requirements set for the enzyme retention capacity. Furthermore, it was found that ultrafiltration is only suitable when a deactivation process is taking place. In the calculations above 100 °C, where instant deactivation was, even the 99.9% membrane is not suitable for long term use, without replenishing enzymes. This is due to the high number of cycles in such a process as discussed above. Practically, this means that primary amines, such as monoethanolamine, frequently used as solvents in CCS, may not be suitable solvents with enzyme enhanced CCS, since stripper temperatures above 120 °C are used for this type of enzyme retention. Nonetheless, using other methods such as enzyme immobilization in the absorber column, might still be attractive. Furthermore, it indicates that the use of a conventional reboiler in a set-up as described here might be unsuitable, shown in Figure 1. One could rather envision using a stripper set-up with vacuum, steam or a combination of the two. Indeed such setups has been applied in practice with success in enzyme enhanced CCS[8].

It is clear from the results in Figure 4, that the use of a membrane with a higher enzyme retention has a better performance with respect to retention of enzyme activity. However, increased enzyme retention often comes at a cost. The capital costs of such membranes are likely to be higher, and it would be expected that they are more difficult to produce and maintain at a high level of perfection, since any tear/leak would be detrimental to enzyme activity at higher stripping temperatures. In addition the flux of the membranes should be considered, since it will influence the membrane size needed for such a setup. Table 4 indicates the membrane size needed to maintain the target flux of two commercial membranes. In addition, for an efficient ultrafiltration, it is needed to operate with a higher pressure, here a pressure of 4 bar has been used. In fact, it has been stated the cost of cross-flow ultrafiltration is dominated by membrane replacement and pumping[9].

Table 4: Required membrane sizes of ultrafiltration membranes used in this study, operated at 4 Bar, with a flux of $2.1*10^6$ L/h.

Type	Selectivity	Water permeability $(L/m^2*h*bar)$	Membrane size (m^2)	Source
Commercial	90	50	10600	Alfa Laval
Commercial	99,9	400	1330	Alfa Laval

The calculated membrane sizes are relatively high. However such setups are uses commercially in other industries such as the water purification industry. Where numerous membrane units are connected in series. As such the membrane sizes estimated here would be feasible for such a set-up.

Conclusion:

The use of ultrafiltration in enzyme enhanced CCS was evaluated. A model using three different enzyme retention membranes was used in combination with five different stripper temperatures. It was found that to retain over 50% activity for one year an ultrafiltration unit was required in all cases tested here. With higher the stripper temperatures the requirement for the membrane selectivity increased. For the highest temperature, where instant deactivation was assumed, the most selective membrane with 99.9% enzyme retention, did not meet the requirement. Thus, the use of enzyme enhanced CCS might be restricted to temperatures below 100 °C, or temperatures the enzyme can with stand for shorter time periods, if the use of ultrafiltration units are in use.

Acknowledgements

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