

Absorption as a Method for CO₂ Capture

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Introduction.

In light of the Kyoto protocol and the expected increase in power production world wide, development of economic and safe removal processes for CO₂ from power plants based on combustion of fossil fuels is of utmost importance. In particular the Norwegian scenario, where the establishment of gas fired power plants will lead to an increase in the inland CO₂ emissions unless recovered and safely deposited.

The conventional technology today for recovery of CO₂ from high to low pressure gases is absorption with various types of solvents. Typically, recovery at high partial pressures of CO₂, as found in cleaning of natural gas, would be performed using promoted MDEA (Methyl-diethanolamine) systems, or even physical solvents for very high pressures. At lower partial pressures, the more active amines like DEA(Di-ethanol amine) or MEA(Mono-ethanol-amine) are used in processes in operation today.

The amine systems, and in particular those applicable to low pressures, have inherent disadvantages like high heat of reaction, relatively high volatility and high rates of degradation. This makes them unattractive in use for CO₂ recovery from natural gas fired power plants, when considering energy efficiency, economics and environmental impact. For low pressure, exhaust gas, applications the absorption plants become very large and expensive. This leads to very significant financial costs in addition to the operating costs.

On the equipment side, there are three major parties involved today. Mitsubishi has focused on developing more efficient tower packing materials with low pressure-drops. So far there are no commercial installations of these tower packings, but large scale pilot testing has been performed.

Membrane absorber contactors are being developed by TNO in the Netherlands and by Kværner/Gore in Norway and Germany. TNO are using Polypropylene membranes and in contrast to the Kværner/Gore equipment, these membranes are limited in chemical stability. Conventional amine solutions can not be used and this has necessitated the development of a special chemical system called CORAL. The system is inorganic, and this an advantage as vaporisation losses are avoided. TNO also claims that it has improved stability towards oxygen, implying lower degradation rates, and better mass transfer properties than MEA. The energy consumption is, however, as for MEA.

Kværner Process Systems (see Falk-Pedersen (1999), Svendsen et. al (1999, 2000)) has, in collaboration with W.L. Gore, developed membrane absorber and desorber units that are much more compact than conventional towers. They can reduce the required pressure drop and have inherent properties that make them advantageous also from an operational point of view (no foaming, less transfer of undesired components like hydrocarbons or oxygen, and reduced

degradation rates due to limited contact between liquid and high temperature surfaces). The Kvaerner/Gore absorber units use PTFE membranes and can be used with all interesting solvents and solvent groups. These units show great promise in cutting the equipment costs, to reduce the plant size, and to simplify operational procedures.

There is also today a large research activity in developing new improved absorbents. Among the most active groups working on alternative solvents are Mitsubishi/Kansai in Japan (e.g. Mimura et. al.(1999)) and Professor Amit Chakmas group at the University of Regina (e.g. Chakma et.al. (1999)). Mitsubishi/Kansai have developed a range of new absorbents called KS1, KS2 and KS3. The composition of the systems is proprietary. Some properties of the KS1 system are shown in figure 1. They claim substantial improvements compared to a conventional MEA-based process. Up to 30% reduction in energy requirement can be achieved and 80-90% reduction in waste production. The first commercial installation with KS1 came in operation in late 2000. It is a small 160 tCO₂ /d plant operation on a slip-stream from a natural gas fired power plant in Malaysia.

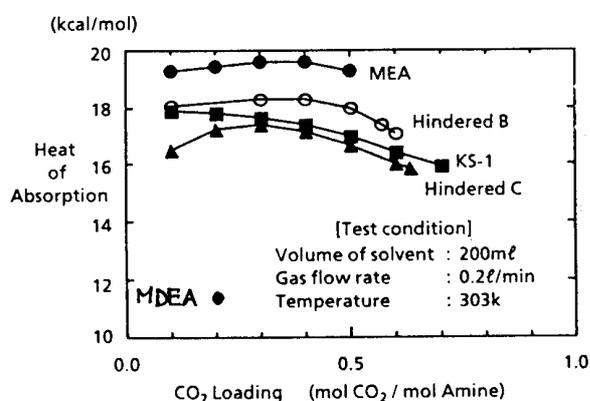


Fig. 2 Heat of Absorption of CO₂ with alkanolamine

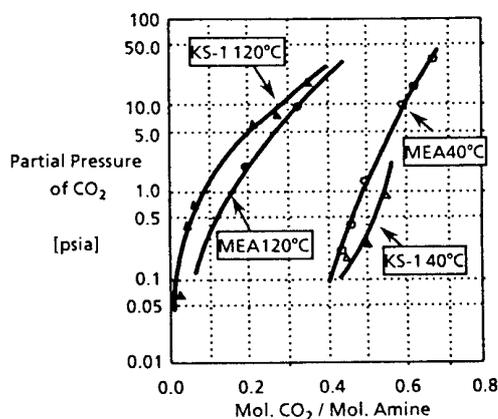


Fig. 3 CO₂-H₂O-Amine phase equilibrium

Figure 1. Heat of absorpton and equilibrium curves for KS1 compared to other amines.

The reduction in energy consumption is caused by the reduced heat of absorption compared to MEA, but, even more important, also by the larger temperature sensitivity of the equilibrium curve. This gives a higher cyclic capacity and easier CO₂ removal in the desorber.

The amine blends developed by Chakma and his group also give in the order of 30% energy reduction compared to MEA and low degradation losses. However, low energy requirements only come together with slow absorption kinetics, i.e. there will be a trade off between energy consumption and equipment size.

Our group at the Department of Chemical Engineering, NTNU, has been heavily involved in the Kvaerner/Gore project through the development of mathematical models for the membrane absorption process and through testing of the units in our laboratory. We also work with developing new and better solvent systems and with improved desorber design. These activities will be described in some detail in the following.

The Kvaerner/Gore membrane absorber process

An example of a low pressure design of the membrane absorber is shown in figure 2. The flow is combined cross- and counter-current. The liquid flows inside thin tubes, typically 0.7-3 mm ID. The tubes are held together in sheets and the structure is called "ribbon tubes". The flows between the sheets in thin rooms created by spacers. In contrast to conventional hollow fibre

modules, this construction directs the gas flow such that all surfaces are exposed to the gas. The membrane itself can be porous, as shown in figure 3, or covered with a very thin dense layer if needed. The material, PTFE, has excellent properties as it is hydrophobic and show very long term stability. The hydrophobic quality allows for a 0.5 bar overpressure on the liquid side without wetting of the membrane pores, and a liquid side overpressure is needed to avoid penetration of gas.

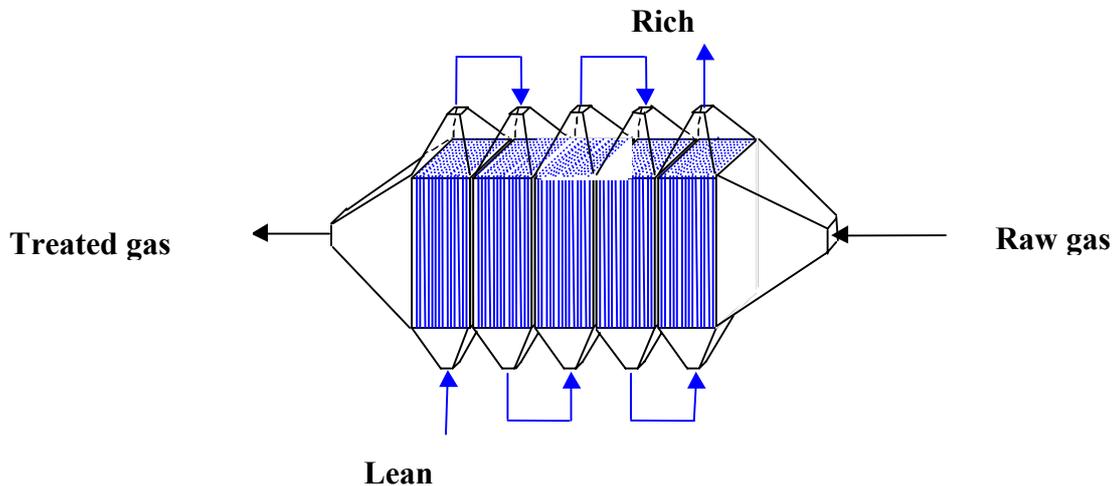


Figure 2. A five unit cross flow/counter-current flow low pressure membrane absorber

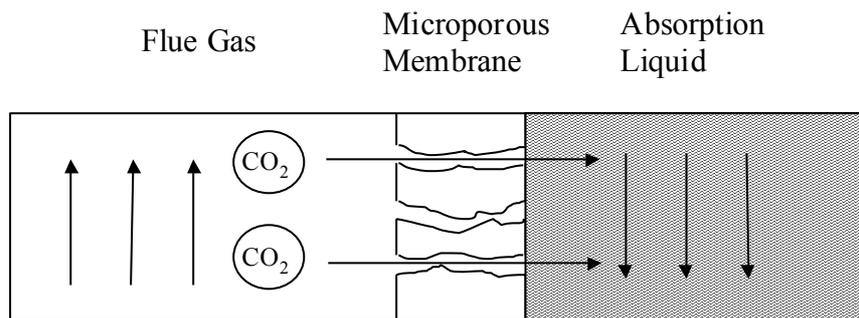


Figure 3. Schematic of porous membrane

The porous membrane itself has no selectivity, but adding a dense layer may provide also some membrane selectivity. The membrane separates the phases physically and enhances the operating conditions by avoiding gas liquid shear. This results in no foaming, no channelling and no liquid entrainment or flooding. This also means the gas and liquid flow rates can be varied independently of each other almost without limits. Very compact packing of the tubes can be achieved and specific contact areas of 500-1500 m²/m³ can be used. The units have also been tested for offshore applications, and size and weight reductions of 70% can be achieved.

Possible disadvantages lie in the membrane resistance, which for gas film controlled systems may become large, and the laminar flow pattern inside the tubes. However, the latter disadvantage has been turned into an advantage as lateral mixing in the tubes has been introduced by altering the ribbon tube geometry. Thus lateral mixing in the membrane units can be better than in regular absorber packings.

Model development

The mathematical model of the absorber is schematically shown in figure 4, see Hoff et. al.(2000). It assumes plug flow for the gas phase and either co-current or counter-current flow of the liquid phase. It has been assumed that the liquid flows in laminar flow inside the ribbon

tubes. With a tube diameter as given before and a linear velocity is in the range 0.5 -5 cm/s this gives Reynolds numbers for the flow well below 100-200. It has further been assumed that the flow inside the tubes is symmetrical and can be described by a Hagen-Poiseuille profile. Implicitly this assumes constant viscosity in the fluid. This is not completely correct as the viscosity of the used aqueous amine systems increases with increased CO₂ loading and will therefore increase towards the tube wall. CFD simulation have, however, confirmed that the effect of this is negligible. It is further assumed that the membrane is gas filled. This has been verified experimentally.

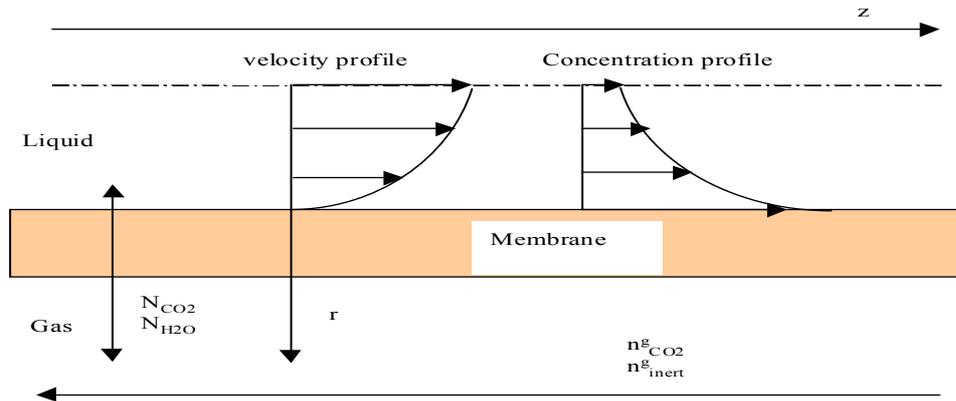


Figure 4. Membrane model concept.

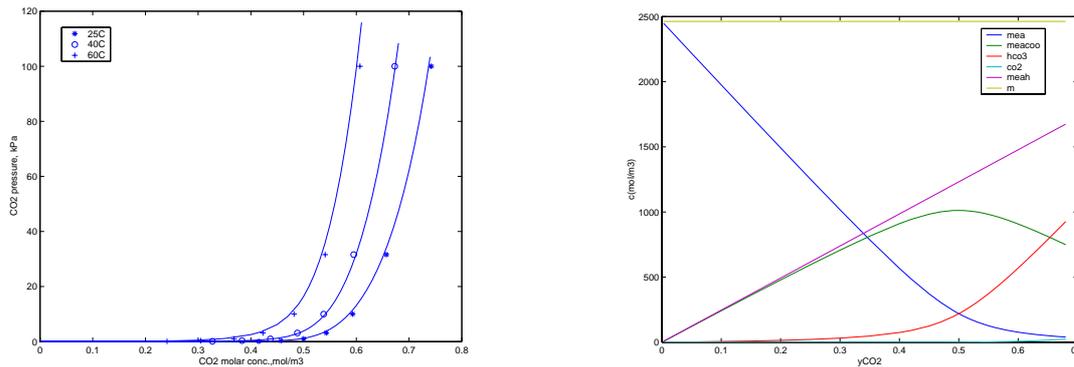


Figure 5. Equilibrium data for CO₂ in amine systems, and speciation of the components

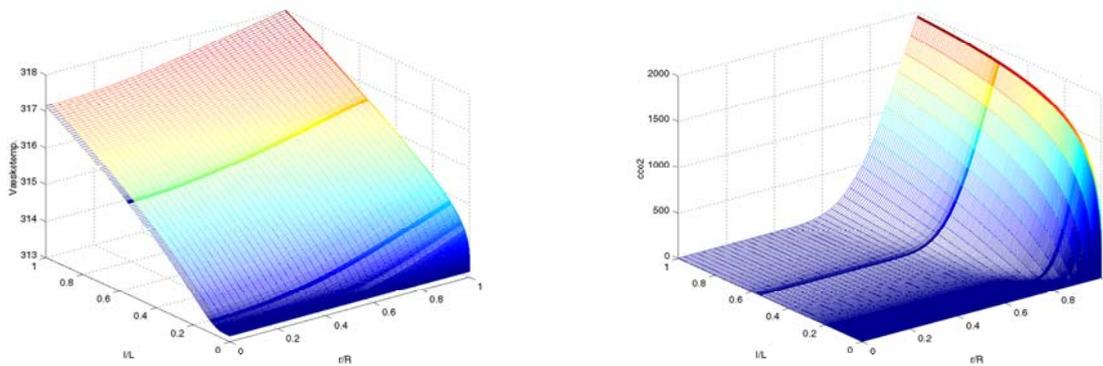


Figure 6. Temperature and bound CO₂ concentration profiles.

The liquid phase is modelled as a combined diffusion/reaction process and there is a need for sub-model for equilibrium, kinetics, and transport and thermodynamic properties. In figure 5a, an

example of the equilibrium model for MEA is shown. In order to use a rigorous kinetic model we need to know the concentrations (activities) of the various species involved. The equilibrium model must therefore not only predict the VLE data correctly, but must also provide correct values for all species. An example is shown in figure 5b. In order to achieve a satisfactory description of the equilibrium, rigorous models based on activity coefficients must be used. Our activity coefficients models are developed based on the combination of UNIFAC contribution method used for molecular interactions and the MSA (Mean Spherical Approach) used for ionic interactions. The Peng-Robinson equation of state is used for the gas phase.

The model is implemented in two versions, one in Matlab, and one in Fortran. The Matlab version is based on the Method of Lines and is discretised in the radial direction, using finite differences for calculating the numerical derivatives, and integrated in the axial direction using a Matlab routine, Ode15s. The Fortran version is based on a finite volume technique and discretised in both directions. A comparison of the models will be presented at ISCRE 17, next year, see Poplsteinova et. al. (2002).

Several systems have been implemented, including both chemical and physical absorbents. Underlying data are taken from own experiments and the open literature and no fitting is performed. Very good correspondence between experiments and simulation results is obtained.

New absorbents

The quest for new absorbents can be very laborious. A tremendous lot of experimental work has been done over the years on characterising the amines with respect to equilibrium, kinetics, transport parameters, and heats of absorption. We also run these experiments in our laboratory in equilibrium cells ranging for atmospheric conditions up to about 70 bar, and temperatures from ambient to 125°C. In addition we have kinetic cells, a wetted sphere apparatus and one membrane unit. Transport parameters can also be measured in these. A rapid experimental screening technique has also been developed where the absorption rate as function of loading can be obtained. This is a measure of the combined equilibrium-kinetic performance of a system and can be used as a first indication of the properties of a system.

Further, molecular modelling has just been taken into use for the rapid theoretical screening of amine systems. The hope is that one may be able to deduce chemical properties such as pKa values, heats of reaction and reaction rates from these simulations. A very initial example is given in figure 7.

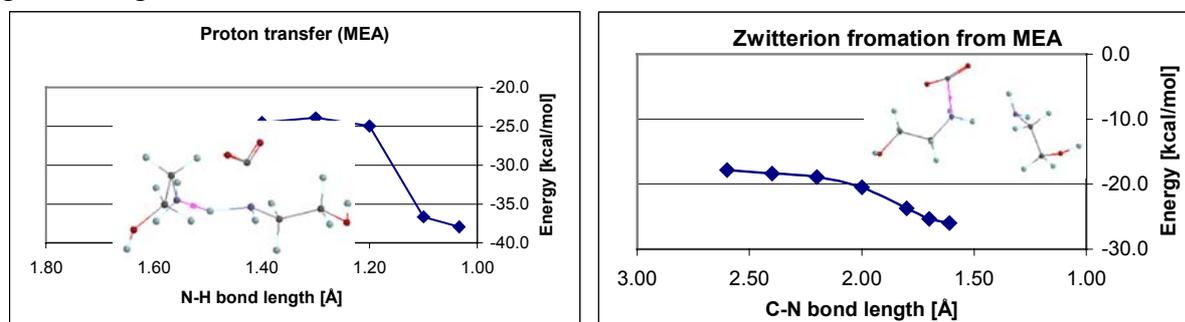


Figure 7. Energy as function of bond length for Zwitterion and proton transfer reactions

Assuming that the CO_2 reacts through a Zwitterion formation, followed by a proton transfer mechanism, the energy difference between the starting point of the blue curve on figure 7a, and the end on figure 7b, should be a measure for the heat of reaction. The

height of the highest point gives an indication of the reaction barrier, and thereby also of the rate. The simulations are for reactions in vacuum using a Hartree-Fock(HF 3-21g) calculation.

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