

Solvent Formulation for CO₂ Separation from Flue Gas Streams

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ABSTRACT

CO₂ separation using reactive solvents is considered to be a technically viable option for capturing of CO₂ from flue gas streams. However, the cost of CO₂ capture using conventional solvents such as aqueous solutions of monoethanolamine (MEA) is prohibitively high. Nearly half of the total cost is due to operational costs, of which about 70 to 80% can be contributed to the cost of regeneration of the solvent. In addition, the conventional solvents are rather corrosive and can be degraded by many of the contaminants present in the flue gas streams. Therefore, there is considerable incentive to develop solvents that require lower energy for regeneration and also induce less operational difficulties. This paper will provide a critical review of the chemical solvent based processes for the separation of CO₂ from combustion gas streams and describe the main parameters affecting the process performance.

INTRODUCTION

Currently, the desire to alleviate the problem of global warming has resulted in the environmental concern over a reduction of greenhouse gas emissions from industrial sources. The major greenhouse gases contributing to problem are methane (CH₄), carbon dioxide (CO₂), nitrous oxide (N₂O) and halogens such as chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs) (Ref. 1). Among these, CO₂ is the primary contributor to the problem due to its abundance, and is thus a major target for reduction. To reduce the excessive CO₂ emissions, there is great interest in capturing CO₂ and utilizing it as a flooding agent for enhanced oil recovery (EOR). Based on current technologies, the gas absorption with a chemical reaction process using amine is considered to be the most cost effective and has the best proven operability record. However, the cost of absorption using conventional solvents such as aqueous solutions of monoethanolamine (MEA) is still relatively high. A major reason for the high cost is that the conventional solvents introduce a variety of practical problems including: (i) a high energy consumption for the solvent regeneration; (ii) a high rate of corrosion of the process equipment; (iii) a fast evaporation rate causing high solvent losses; and (iv) a high rate of degradation in the presence of oxygen. All these problems translate into high capital and operating costs.

One way to reduce the process cost is use of the better solvents in the CO₂ separation process. These solvents should have higher CO₂ absorption capacity *as well as* faster CO₂

absorption rates. They should also have low vapor pressure, high degradation resistance, and low corrosivity. A number of energy efficient proprietary solvents have recently been developed that are based on either sterically hindered amines (Ref. 2,3) or formulated amines (Ref.4).

SOLVENT SELECTION

The essential elements of solvent selection criterion are feed gas characteristics (composition, pressure, temperature, etc.) and the treated gas specifications (i.e. the process requirements). These two elements provide a preliminary evaluation of the solvent working capacity which may, however, be influenced by several other elements such as solvent characteristics and operation issues of the separation process. The working capacity establishes the solvent circulation rate, which has a major impact on both plant investment and operating cost of the systems. The solvent circulation rate has a direct impact on the size of the absorber tower, piping system, circulation pumps, and size of the regenerator facilities. In general, 50 to 70% of the plant investment is directly associated with the magnitude of the solvent circulation rate. Obviously, there are advantages in employing the highest possible absorption capacity solvent as limited by solubility, precipitation and corrosion considerations.

The partial pressure of CO₂ in the feed gas to a first approximation determines the solvent circulation rate. In a countercurrent column, the feed gas contacts the fully loaded rich solvent at the bottom of the column. At a minimum, there must be, therefore, sufficient solvent to absorb all the CO₂ in the feed and provide a driving force for absorption at the bottom of the column. The partial pressure of CO₂ in the product determines the degree of regeneration required. The equilibrium partial pressure of CO₂ in the regenerated solvent must be lower than the partial pressure of the product gas. Otherwise, there will not be a positive driving force for absorption at the top of the absorber. Therefore, two most important cost factors - circulation rate and regeneration energy duty - are established to a significant extent by the CO₂ partial pressures in the feed and the product. In addition, a significant portion of the investment of a chemically reactive system is dependent on the regeneration energy duty.

SOLVENT CHARACTERISTICS

Mass-Transfer (Kinetics)

CO₂ absorption with a chemically reacting solvent involves mass-transfer with chemical reaction. The role of the chemical reaction is to speed up the mass-transfer rate as well as to provide greater solvent loading capacity at lower CO₂ partial pressure conditions. The reaction between dissolved CO₂ and amine is reversible and proceeds through a series of reactions. In general, the chemical reaction proceeds forwards in the absorption direction under low temperature and high partial pressure conditions and reverses in the desorption (regeneration) direction under high temperature and low partial pressure conditions. Ideally, higher reaction rate constants for both the forward and the reverse reactions are favorable, This will allow the absorption and regeneration to be accomplished within as short a time frame as possible.

The forward reaction is exothermic while the reverse reaction is endothermic. The extent of heat required to breakdown the carbamate complex during the regeneration stage depends partly on the heat of reaction. Solvents with lower heat of reaction require less energy for regeneration than those that have higher heats of reaction.

Solvents with higher reactivity as indicated by higher forward reaction rate constants also tend to have higher heats of reaction and therefore they require more energy for regeneration and are more difficult to regenerate. As such they tend to have higher residual solvent loadings (lean loadings) than the less reactive ones. It should be noted that the higher the rate constant, the greater the mass-transfer coefficient, thus the lower capital cost for the absorbers.

Thermodynamics and Absorption/Regeneration

In addition to the aforementioned parameter, the absorption characteristics of the solvent need to be ascertained from equilibrium solubility data. A comparison of the absorption characteristics of two hypothetical solvents A and B is demonstrated with the aid of a McCabe-Theile diagram in the schematics below (Figure 1). Solvent B has higher equilibrium solubility compared to Solvent A for a given partial pressure. For given solvent circulation rate, Solvent B will require fewer numbers of trays relative to Solvent A for a given CO₂ separation duty. It can also be shown that for a given column, Solvent B will require less solvent circulation rate to achieve the separation. Thus solvent B is the ideal candidate from absorption point of view.

Traditionally, there has been far more attention given to the absorption characteristics of a given solvent and less attention paid to the stripping characteristics. However, in an energy constraint design driven either due to a desire to lower the cost of operation or due to the availability of limited supply of regeneration energy, attention must also be paid to the stripping characteristics of the solvent. A solvent that requires more stripper trays for a desired lean solvent loading will require higher overhead reflux ratio. This will lead to a higher reboiler heat duty. Thus, the solvent should have easier stripping characteristics. The following schematic provides a comparison of two hypothetical solvents A and B with different stripping characteristics. Solvent A requires fewer trays for a given reflux rate or requires a lower reflux rate for a given column (Figure 2). Thus Solvent A is the ideal solvent from regeneration point of view.

Solvent Working Capacity

Figure 3 shows the equilibrium CO₂ loadings of three solvents under typical conditions for flue gas absorption. In this case it is assumed that a flue gas stream from a natural gas fired turbine containing 6% CO₂ is to be contacted with solvents in an absorber at a total pressure of 200 kPa. The corresponding CO₂ partial pressure is 12 kPa. Solvent C provides the highest equilibrium loading, followed by Solvent A and Solvent B.

Figure 4 shows the equilibrium CO₂ loadings under regeneration conditions typically found for the same three solvents. It is assumed that a CO₂ partial pressure is 1 kPa at the reboiler. Solvent C provides the lowest loading, indicating a better regeneration capacity than the other two solvents. Solvent B is a close second, while solvent A has the highest lean loading values.

From solvent capacity point of view, solvent C is clearly the best performing solvent requiring a lower solvent circulation rate. However, it would require the highest number of stages for a given separation.

Solvent Corrosiveness

CO₂ separation process using reactive solvents has never been considered to be a problem-free technology despite the fact that it has been in industry for over half a century. The process is constantly subject to a number of operational difficulties, of which the most severe is corrosion of the process equipment (Ref. 5). The corrosion takes place in many plant locations such as the absorber bottom, the rich-lean heat exchanger, the entire regeneration section and the overhead condenser. Based on the plant experiences, corrosion problems impact directly on the plant's economy as it can result in unplanned downtime, production losses, reduced equipment life and even injury or death (Ref. 6). The corrosion problems also can affect the plant's economy by limiting the operating ranges of the process. Let us consider, as an example, the impact of limited concentration for the amine solutions. Generally, use of highly concentrated amine solutions for CO₂ absorption can lower the energy required for solution regeneration. This suggests that higher solution concentrations would result in lower operating costs. However, in practice, operating the process beyond a typical concentration can cause a significant increase in the system corrosiveness. As a result, achieving additional economic benefits by increasing the solution concentration to reduce energy consumption of the process may not be practically feasible if corrosion cannot be reduced.

Solvent Stability

MEA based processes require the use of reclaimers for the removal of degradation products. A side stream of 1 to 5% of the total solvent circulation rate would normally be employed. However, this varies with the expected degradation rate of the solvent. In some cases, it may be desirable to treat as much as 10% of the total solution in circulation through the reclaimer. Assuming heat requirement rate similar to MEA, reboiler with a 5% slip stream would add 5% additional energy load for a MEA based system. Thus a solvent that does not require a reclaimer or requires only batch operation can potentially save up to 5% more energy than MEA.

IDEAL SOLVENT

Examining the previous comparative examples, it is clear that the favorable performance of an ideal solvent is very difficult to be achieved. The solvent that has superior absorption characteristics may not have similar stripping characteristics. By the same token, another solvent that might have higher solvent loading capacity may have poorer mass-transfer characteristics. Thus, the ideal solvent has to be designed by formulating different components having specific properties that contributes to the desired characteristics.

PSR - FAMILY OF SOLVENTS

The PSR solvent is a proprietary designer solvent that can be formulated to provide optimized separation of CO₂ from any gas streams. The first generation of PSR solvent was presented at the 2nd International Conference on Carbon Dioxide Removal in Japan (Ref. 4) and the 4th

International Conference on Greenhouse Gas Control Technologies in Switzerland (Ref. 7). One of the advantages of the PSR solvent is its flexibility. Its formulation can be optimized to meet the needs of specific tasks since it is composed of a number of ingredients. The key features of the PSR solvents are: (i) lower solvent circulation rate; (ii) lower regeneration temperature; (iii) lower solvent degradation rate and (iv) lower corrosion rate.

Lower solvent circulation rate is attractive because it lowers the energy for regeneration. PSR solvents require lower circulation rates due to their ability to maximize rich solvent loading, while achieving a leaner amine through maximum regeneration. Thus, the overall working capacity of the PSR solvents (mole of CO₂ removed/mole of solvent circulated) is higher than that of MEA, ranging from 20% to 80% (Table 1). Depending on the solvent type used, solvent circulation rate can be lowered by a wide range. PSR solvents are designed to achieve regeneration at lower temperature (5 to 10 °C lower) than MEA solvents, thus resulting in energy savings. This also leads to a better process integration by allowing low pressure steam to be used in the regeneration process. The relative energy requirements of PSR solvents are about 55% to 85% of these conventional amines.

The other side benefits of PSR are lower solvent degradation and corrosion rates. The PSR solvents are more resistant to the solvent degradation than MEA due to their ingredients and lower reboiler temperature. (As much as 70 to 90% lower than that of MEA). Apart from avoiding various operating problems due to solvent degradation, the other advantages are in the reduction of solvent replenishment costs and solvent disposal costs. Generally, corrosion accelerates when CO₂ loaded solvents encounter high temperature conditions such as in the reboiler. Since PSR solvents achieve lower lean loadings upon regeneration than MEA, they contain lower amounts of CO₂ when they enter the reboiler. In addition, if the reboiler temperature can be kept at a lower level, then again the corrosion rate will decline. Thus a combination of lower CO₂ loading and lower reboiler temperature helps the PSR solvents to keep corrosion rates under control. In general, the corrosion rates of PSR solvents are about 30% to 60% lower than those of MEA (Table 2).

CONCLUSIONS

The development of an ideal solvent that is energy efficient requires various considerations. The key factors are absorption and regeneration characteristics, solvent capacity, corrosion potential and solvent stability. Solvents that require less regeneration energy usually require large contacting surface areas. Also, solvents that are effective in the absorption process may be more difficult to regenerate. Designer solvents can be formulated by adding different components, each having various beneficial characteristics. Various additives can be added to enhance mass-transfer rates, reduce corrosion and increase solvent stability. Properly formulated solvents can reduce energy requirements by as much as 40% compared to conventional MEA solvents.

REFERENCES

1. Davis, M. L. and Cornwell, D. A. *Introduction to Environmental Engineering*: 2nd Edition, McGraw-Hill Inc., 1991
2. Suda, T., M. et. al., *Energy Convers. Mgmt.*, 33 (5-8), 317-324, 1992.

3. Mimura, T., S. Shimojo, T. Suda, M. Iijima and S. Mitsuoka, *Energy Convers. Mgmt.*, 36 (6-9), 397-400, 1995.
4. Chakma, A., *Energy Convers. Mgmt.*, 36 (6-9), 427-430, 1995.
5. Kohl, A.L, and Nielsen R.B, *Gas Purification*: 5th Edition, Gulf Publishing, 1997.
6. DuPart, M. S.; Bacon, T. R. and Edwards D. J. *Hydrocarbon Processing*, April, 75-80, 1993.
7. A. Chakma and P. Tontiwachwuthikul, "Designer Solvents for Energy Efficient CO₂ Separation from Flue Gas Streams", **Key-note paper on CO₂ Capture Technologies** at the 4th International Conference on Greenhouse gas Control Technologies", Interlaken, Switzerland, August 1998.

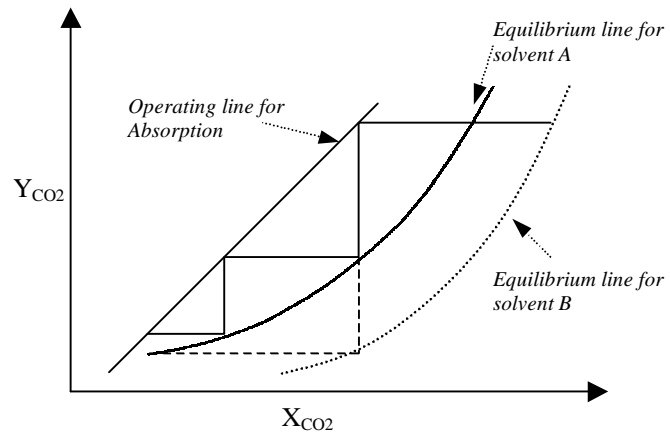


Figure 1: Operating and equilibrium lines under absorption operations.

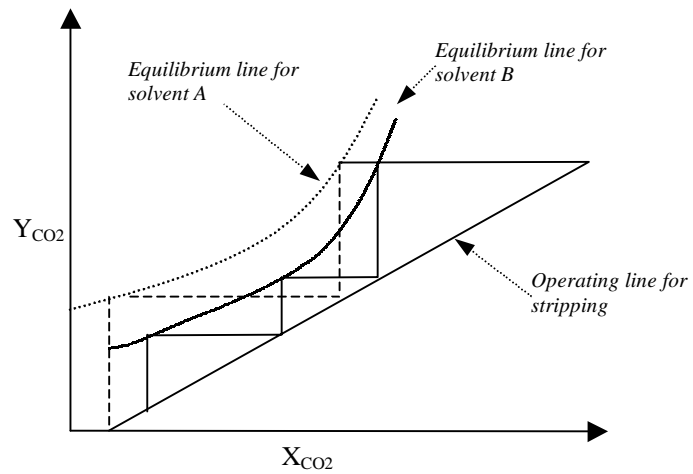


Figure 2: Operating and equilibrium lines under regeneration operations.

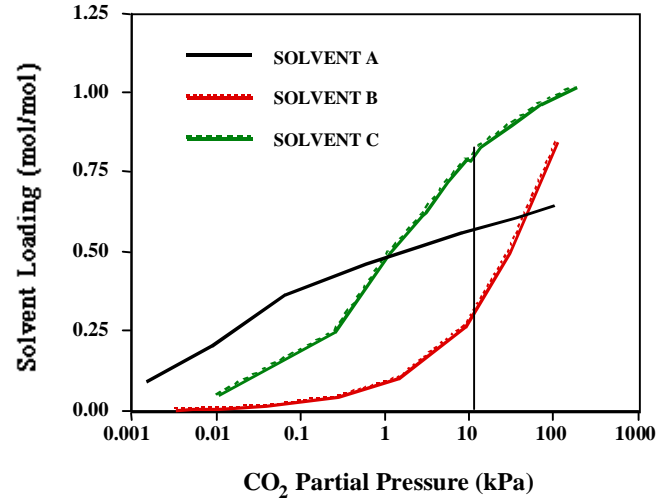


Figure 3: Solvent loadings as a function of CO₂ partial pressure under absorber conditions.

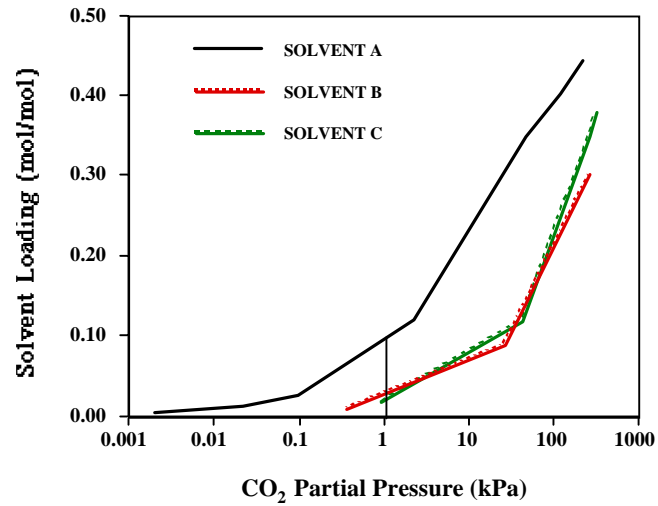


Figure 4: Solvent loading as a function of CO₂ partial pressure under regenerator conditions.

Table 1: Working capacities of conventional and PSR solvents.

Solvent	Lean loading (mol/mol)	Rich loading (mol/mol)	Working capacity (mol/mol)
MEA	0.22	0.53	0.31
PSR-1	0.06	0.60	0.54
PSR-2	0.16	0.61	0.45
PSR-3	0.19	0.59	0.40

Table 2: Comparison of corrosion rate.

Condition	MEA	PSR-1
Temperature (°C)	80	80
Pressure (atm)	1 atm	1 atm
CO ₂ content	Saturation	Saturation
Corrosion rate (mpy)	136	78