The CONTACTOR™

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CO_2 Capture from Flue Gas – Part 1: Solvents

Whether or not you personally subscribe to global warming as a reality and believe CO_2 emissions must be reduced, CO_2 capture (Carbon Capture and Storage—CCS) is here to stay. It is fostering a hunt for better technologies and turning the use of existing ones into a growing market. This is the first of a three-part note on CCS and provides a thumbnail sketch of both existing solvent-based methods and ones under development for the capture of CO_2 from power plant flue gases. Other technologies include combustion at high pressure to enable easier CO_2 removal from the combustion gas, and combustion with oxygen which produces essentially undiluted CO_2 suitable for direct sequestration. However, new combustion strategies are outside the scope of this note.

Solvents fall into one of two categories: reactive and physical. A typical physical solvent is the dimethyl ether of poly(ethylene glycol) (DMPEG) commonly marketed under the brand names AGR, SELEXOL® and Genosorb®. Cold methanol (Rectisol®) and N-formyl morpholine (Morphysorb®) are other examples of physical solvents. It seems very unlikely that any physical solvent can be used at reasonable circulation rates to remove the usual target of 90% of the CO_2 in the flue gas at atmospheric pressure. Almost of necessity, the solvent must be reactive towards CO_2 in order to have acceptable absorption capacity. Amines of various kinds (including ammonia which can be seen as just an amine without carbon) react with CO_2 or, in the case of tertiary amines such as MDEA, and the hindered amine AMP, at the very least provide an alkaline environment that promotes the water-hydrolysis of CO_2 to bicarbonate and carbonate ions.

In Part I we look at some of the ways in which CCS using amines differs from more conventional treating of sour natural and refinery gases. In Part II we will examine a variety of processing schemes aimed at minimizing the energy associated with the capture step of CCS. And in Part III we will look at how a variety of packings, both random and structured, perform in this type of application. CCS from power plant flue gases presents significant new challenges that don't exist in the natural gas and refining industries, not the least of which is the inherently low pressure.

Flue gases are generally at pressures measured in only a very few inches or centimeters of water column—extremely low pressures—and, consequently, the volumetric flows are enormous. This makes for absorbers of gargantuan proportions requiring a tremendous amount of power just to provide the additional few inches of water column needed to drive the flue gas through the contactors. Packed columns offer greater hydraulic capacity than trays, and only packing offers sufficiently low pressure drop to keep blower energy requirements feasible. Structured packings are far superior to random or dumped internals. There is simply no place in the CCS-from-flue-gas market for trays—their pressure drop is too high and column diameters are far too large even to contemplate installing trays.

CCS does not require deep CO_2 removal so discharging a gas containing on the order of 1% or so CO_2 is quite acceptable. This means contactors can be run severely rich-end pinched, and CO_2 lean loading is relatively unimportant so regenerators don't have to be run as hard as in a gas plant, for example. However, the amine should be as reactive as possible, otherwise enough CO_2 will not be removed in a contactor of reasonable height (50 feet, say) to meet the desired CO_2 recovery. The requirement of fast reaction with CO_2 pretty much eliminates all the alkanolamines except MEA, and possibly AMP and DGA®. Unfortunately, fast forward reaction rate and favorable phase equilibrium usually go along with more difficult regeneration requiring higher heat inputs. Reboiler energy is one of the greatest operating costs associated with CCS using amines.

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Mixed solvents containing more than one amine could be attractive for reducing reboiler energy needs except for the fact that the predominant amine would likely be MDEA which has less favorable CO_2 backpressures compared with primary amines. Even piperazine-promoted MDEA is easily outperformed by MEA in flue gas treating. Currently, research is being carried out by Dr. Gary Rochelle at the University of Texas at Austin in which the primary amine is replaced by potassium carbonate/bicarbonate and piperazine is used as a promoter.

In flue gas treating where only about 90% CO_2 removal is needed and solvent rates are minimal, temperature bulges tend to be large and to be located at the top of the contactors (see figure). This makes the exiting gas hot. Combined with the huge volumes of gas that must be processed at atmospheric pressure, this can lead to enormous solvent losses unless steps are taken to provide a high volume water wash at the top of the absorbers. Losses are caused by amine volatility so the ideal amine would have small, or even zero, volatility. Unfortunately, MEA is relatively more volatile than the other common alkanolamines, a property not in its favor.

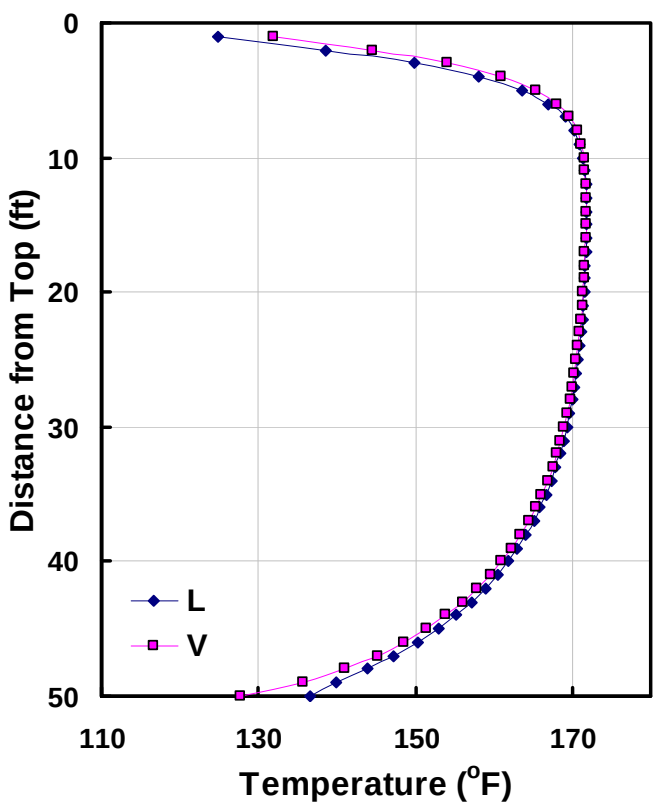

Figure 1 Contactor Temperature – 30 wt% MDEA and 13% CO_2 in Flue Gas

Another important factor affecting choice of solvent is the fact that flue gases always contain oxygen, which arises from the excess air used to burn fuels such as coal, oil, and gas. Alkanolamines are susceptible to oxidative degradation and MEA is no exception. Fortunately, both MEA and DGA can be thermally reclaimed, although a continuously operating reclaimer would add to the capital and operating costs.

Oxidation of the amine also produces highly corrosive degradation products so proprietary corrosion inhibitors must be used to deal with this problem, especially when the solvent is 30 wt% MEA.

Ideally, a highly suitable amine would (1) have fast reaction kinetics with CO_2, (2) exhibit low CO_2 equilibrium back pressures at absorption conditions (3) have easily reversible reactions at regeneration temperatures, (4) be nonvolatile and (5) resist oxidative degradation. It would also need to be available at low cost but the quantities used in a few full-scale CCS operations would quickly bring the solvent price into line.

Our attention has recently been drawn to a number of articles in the literature dealing with reaction kinetics and phase equilibrium of CO_2 with aqueous solutions of the sodium salt of glycine, an amino acid.

$$H_2N - CH_2 - COONa$$

Amino acids are already partly oxidized and so are less susceptible to further oxidation by the oxygen contained in flue gas. Their alkali metal salts are completely nonvolatile so vaporization losses would be essentially zero. Literature data indicate that the equilibrium partial pressure of CO_2 over sodium glycinate is at least a factor of 100 lower than over MEA. However, it reacts at only about 1/10th the rate that MEA does so absorption rates might be lower and a greater depth of packing may be needed.

The sodium salt of glycine is reminiscent of BASF's Alkazid® M process which uses the potassium salt of *N*-methylalanine for CO_2 removal, and to a lesser extent BASF's Alkazid DIK process which uses the potassium salt of *N,N*-dimethylaminoacetic acid (dimethylglycine) for removing CO_2 and H_2S. These amino acids found use in more than 50 plants between 1950 and 1976 and they (or their analogs) may find renewed use in CO_2 capture because of their non-volatility.

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