The CONTACTOR™

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Piperazine – Why It's Used and How It Works

Piperazine has been used in gas treating as an additive, primarily with methyldiethanolamine (MDEA), for well over 20 years. Use of piperazine-promoted MDEA appears to have been first disclosed in U.S. Patent 4,336,233 issued June 22, 1982 with BASF Aktiengesellschaft as assignee. Since the patent's expiry in 2002, most solvent vendors now offer a piperazine-activated MDEA solvent under a range of trade names.

Over the years between 1982 and 2002, BASF's aMDEA® (for activated MDEA) solvent captured the lion's share of the market in ammonia synthesis gas purification and many other areas of application where deep CO_2 removal is the primary concern. There are other additives that can be used; examples include monoethanolamine (MEA) and diethanolamine (DEA) together with monomethyl-monoethanolamine (MMEA) as disclosed in U.S. Patent 3,622,267 also awarded to BASF (November 23, 1971). The main advantages of piperazine are (1) it's extremely reactive towards CO_2 and (2) being a diamine, it contains *two* reactive amine groups per molecule both of which can attach to CO_2, so it has exceedingly high CO_2 carrying capacity.

The second order reaction rate constants for a number of amines reacting with CO_2 are listed in Table 1 at 25°C. Piperazine is almost 10 times more reactive with CO_2 than any of the other common amines. This makes it an excellent promoter for the reactions that occur when CO_2 absorbs into MDEA. A good promoter reacts rapidly with CO_2 as soon as this gas dissolves into the liquid. It then shuttles the CO_2 (as carbamate) into the interior of the liquid where it dissociates back into the free amine and transfers the CO_2 to MDEA (Figure 1). The promoter diffuses back to the interface for more CO_2.

Table 1 Reaction Rate Constants With CO_2 of Common Gas Treating Amines

Amine	Reaction Rate Constant ($L \cdot mol^{-1}s^{-1}$)
MEA	6,000
DGA	4,500
DEA	1,300
DIPA	100
Piperazine	59,000
MMEA	7,100
MDEA	4

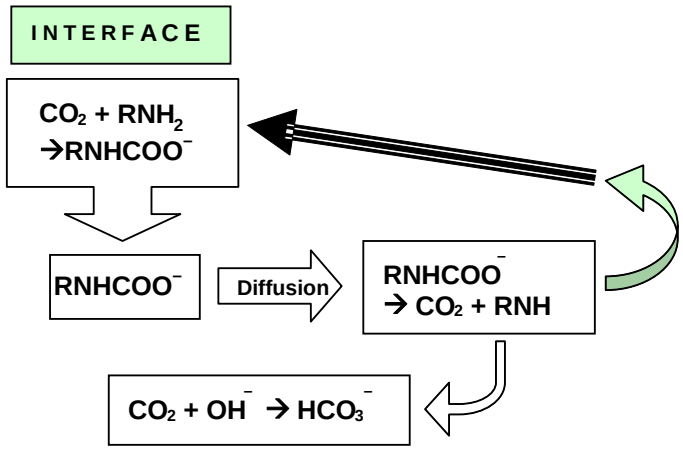

Figure 1 Schematic of Shuttle Mechanism

Piperazine very strongly binds with CO_2 so it does not readily release it to MDEA. This means that at the lean end (top) of an absorber the equilibrium partial pressures of CO_2 over the solution are very much lower than they would be with MDEA alone. In addition, however, at the very top of the column, CO_2 sees a lot of free reactive piperazine, it reacts quickly

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with it and is tightly held in solution by it—this is what allows very low (parts per million) treated gas CO_2 specifications to be achieved[†]. But towards the middle and bottom of the contactor, the piperazine is *almost* (but never quite) fully consumed by CO_2. The piperazine carbamate (and the dicarbamate) concentration, however, is high and its CO_2 can now be readily released to the MDEA. Newly freed piperazine travels back to the interface for more CO_2. This is called a 'shuttle mechanism'.

The reason piperazine-promoted MDEA is so successful is primarily because of its extreme reactivity. In addition, the fact of a diamine means that for a given molar concentration (which is the concentration unit in which one should think when dealing with amine strength, not weight percent) of piperazine, there is in fact twice the concentration of amine groups to react with CO_2. So piperazine gets a double thumbs-up.

In the following example, a 22-tray contactor is used to treat 1,160 psia, 77°F gas containing 30% CO_2. We will compare 50 wt% generic MDEA with 5%, 7% and 9% piperazine in a total 50 wt% amine mixture with MDEA, all at 1,150 gpm and 120°F. Although not shown in Figure 2, the simulation *using ProTreat* is of the entire plant including regeneration and heat exchange. Reboiler duty and all other process conditions were kept constant for all four cases. Key simulation results are shown in Table 2.

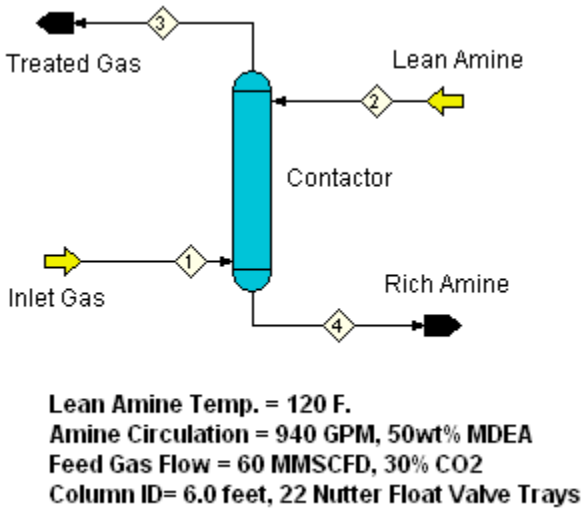

Figure 2 PFD and Process Conditions

Table 2 Effect of Piperazine on Treating

Wt% Piperazine	Treat (ppm CO_2)	Lean Load (mol/mol)	% Rich Equilib'm	Reflux Ratio
0 (22 trays)	85,300	0.0015	70	2.2
0 (50 trays)	48,300	0.0015	83	2.0
0 (100 trays)	48,000	0.0015	83	2.0
5 (22 trays)	51	0.016	91	1.2
7 (22 trays)	39	0.021	89	1.1
9 (22 trays)	10	0.026	87	1.0

The effect of piperazine on CO_2 treat is nothing short of stupendous—it allows promoted MDEA to reach a few tens of ppmv while MDEA alone cannot do better than 8.5% in the same equipment, and it cannot reach below 4.8 mol% CO_2 even with 100 trays in the column under otherwise identical conditions.

MDEA was developed as a solvent for selectively removing H_2S from gas streams down to parts per million, while *slipping* as much CO_2 as possible. *MDEA was never intended for CO_2 removal*. While it can be useful for bulk CO_2 removal, *it certainly cannot be used for deep removal*.

The commercial advantages of using piperazine promoted MDEA for CO_2 removal, especially deep removal, are twofold. Firstly, it needs considerably lower circulation rates compared with conventional reactive amines such as MEA and DEA. Second, as a result of the reduced circulation rate and the smaller heat of reaction, the reboiler energy requirements are significantly lower than conventional single amines.

Piperazine promotion of MDEA has probably been one of the most commercially-successful developments in gas treating since the concept of mixed amines was first applied.

ProTreat™ is the only commercial, publicly available simulation tool that allows you to model this process at all, and it does so with the same high degree of reliability as it does for more conventional single and blended amine systems.

[†] Parts-per-million CO_2 specifications **cannot** be achieved using generic MDEA in any contactor of reasonable height, no matter what the gas pressure is, or what your current simulator tells you.