



## Post Combustion Carbon Capture — Is MEA the Best Benchmark?

For as long as post combustion carbon capture (PCCC) has been a subject of interest, the benchmark system has remained CO<sub>2</sub> absorption into MEA (monoethanolamine). Today, a host of technologies is being actively studied, ranging from chemical absorption such as CO<sub>2</sub> into amines and amino acids, membrane separations, precipitating systems, etc. Excellent and very thorough reports<sup>†‡</sup> are available that detail the assessment of these technologies.

The basis for comparison between various technologies is generally 90% CO<sub>2</sub> removal from the flue gas generated by coal-fired and gas-fired power plants. Chemical absorption still leads the list in terms of Technology Readiness Level (TRL), being at TRL9 compared to the lower TRLs of other technologies. Based on commercial CO<sub>2</sub> capture systems, with enhanced performance, 30 wt% MEA-based chemical absorption is no longer regarded as the only benchmark CO<sub>2</sub> capture technology. The cited works propose a PZ (piperazine) – AMP (2-amino-2-methyl-1-propanol) solution as the new benchmark (40 wt% total amine, 1:2 molar ratio of PZ-AMP). This is called CESAR1 and has energy requirements similar to CANSOLV and Aker S26. Still, MEA is always referenced.

Rather than a detailed comparison between MEA and the new benchmark for a single set of operating parameters, this issue of The Contactor™ points out some of the more interesting performance characteristics of PZ-AMP. The metrics reported both here and in the referenced reports were obtained using the OGT | ProTreat® simulator.

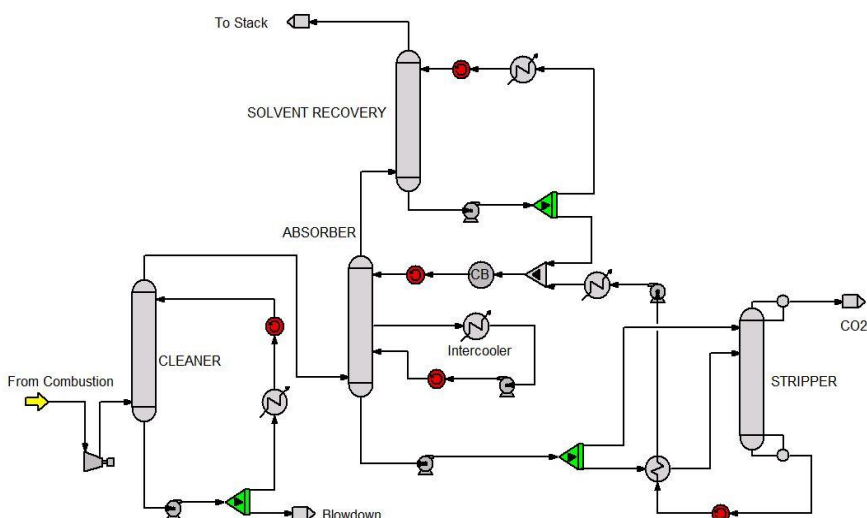
**Figure 1** shows a PFD of the plant, as simulated. The combustion gas is first quenched and cleaned to remove ash, then passes through the absorber where it is contacted with the PZ-AMP solvent. The absorber temperature bulge is controlled with an Intercooler that takes some of the heat of absorption out of the solvent and lowers the temperature

bulge in the column. The solvent feeding the absorber consists of the regenerated solvent from the Stripper plus the blowdown solvent from the Solvent Recovery column.

Piperazine and AMP in the solvent are volatile enough for solvent losses to present serious economic and environmental penalties if they are not recovered and kept within the System. This is done in the Solvent Recovery Column with a large recirculating water flow and a small slipstream passing to the absorber. These three columns all handle about the same gas flow so rather than three separate columns they could be combined into a single column containing three sections.

Stripper feed consists of a small slipstream from the main feed which is relatively cold upon entry at the top of the stripper (and captures water and amines from the stripper vapor) and the main feed itself which is preheated close to the stripper temperature at the feed point.

There is nothing radically different about this flow-sheet that would distinguish it from an MEA-based plant — and the principles are identical. What is different is the energy



**Figure 1 Post-combustion Carbon Capture Plant**

<sup>†</sup> Ashleigh Cousins, Paul Feron, Jenny Hayward, Kaiki Jiang, Rongrong Zhai, (2019) CSIRO Report EP189975, CSIRO, Australia.

<sup>‡</sup> IEAGHG, Further Assessment of CO<sub>2</sub> Capture Technologies for the Power Sector and Their Potential to Reduce Costs, 2019-09, September, 2019

consumption required for 90% CO<sub>2</sub> recovery by PZ/AMP vs. MEA. Cousins et al. report that PZ-AMP solvent offers a 22% reduction in energy consumption for coal-fired and 15% for gas-fired power plants over 30 wt% MEA. The specific reboiler duties for a coal- vs. as-fired plant were determined to be 2.46 and 3.0 GJ/t CO<sub>2</sub>. They propose 40 wt% PZ-AMP in a 1:2 Molar ratio as the new standard for PCCC.

### Why Piperazine and AMP

Although AMP is a primary amine, it is sterically hindered so it does not react with CO<sub>2</sub> to form a carbamate. Instead, it acts mainly as a sink for the hydrogen ions formed by the hydrolysis of CO<sub>2</sub> in water. Consequently, the heat of absorption of CO<sub>2</sub> into an AMP solution is considerably lower than for MEA; therefore, the heat needed to be supplied to the reboiler in a solvent stripping unit is much lower, too. On the downside, however, the rate of CO<sub>2</sub> hydrolysis is far slower than the rate of carbamate formation so the *absorption rate* of CO<sub>2</sub> into water is much slower than absorption into a carbamate forming amine such as MEA. To speed up the absorption rate when using AMP, piperazine is used, albeit in lower concentration than MEA (12wt% vs. 30 wt%). Because piperazine is a carbamate former (with very fast CO<sub>2</sub> reaction kinetics) it has a higher heat of CO<sub>2</sub> absorption than AMP so in part its presence negates part (but not all) of AMP's advantage. There is still a 15% to 22% advantage in gas- and coal-fired applications.

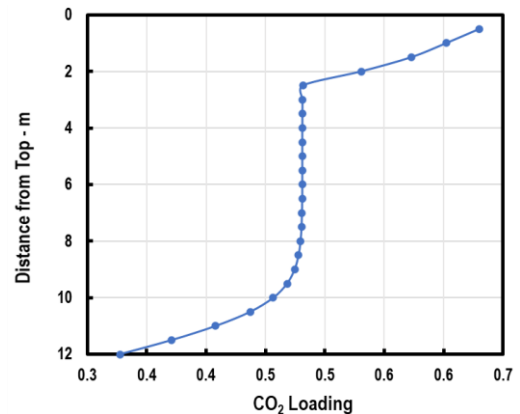
There are several bases on which to compare CCS processes including cost per tonne of CO<sub>2</sub> and cost per unit of plant production. It must be mentioned that on a per tonne of CO<sub>2</sub> basis, in a power plant, the cost is a very weak function of the solvent technology while in a waste-to-energy plant MEA is cheaper. This results in large part from solvent cost.<sup>§</sup>

### Achieving 90% CO<sub>2</sub> Capture

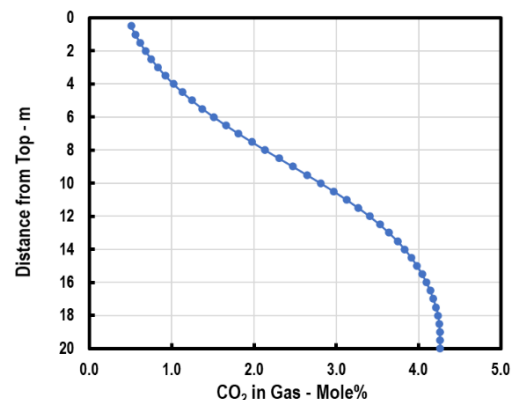
Piperazine is such a fast reactor with CO<sub>2</sub> that it is sometimes difficult to limit CO<sub>2</sub> capture to only 90%. Control over the extent of capture is achieved by limiting the degree of stripping, i.e., by controlling the lean solvent CO<sub>2</sub> loading through manipulating the reboiler energy supply. **Figure 2** shows how solvent CO<sub>2</sub> loading decreases along the height of the stripping column. The solvent remains heavily loaded through much of the stripper's height and only starts to drop off near the bottom of the column. In fact, about 50% the stripping takes place in the last few meters of packing, and 50% in the reboiler (recycled lean solvent has a loading of 0.187 mole CO<sub>2</sub> per mole of total amine). This does not bode well for mild steel metallurgy and a much more expensive stainless steel would be required. This is one of the significant differences from more conventional gas treating applications. The other significant difference is in the absorber behavior.

**Figure 3** shows the way CO<sub>2</sub> concentration in the

absorber gas changes with position along the absorber. As the absorber bottom is approached, absorption slows right down so that at the bottom itself absorption virtually stops altogether. The absorber has become pinched at the bottom. This is quite unlike conventional gas treating where a lean end (top) pinch is much more usual.



**Figure 2** Loading Profile in Stripper



**Figure 3** Gas Phase Profile in Absorber

### Conclusion

PZ-AMP solvent blends are now being used commercially in PCCC applications (e.g., 400-day campaign by RWE). Cousins et al. have suggested maybe it's time to replace MEA with PZ-AMP as the benchmark solvent, a suggestion that can make sense. There are numerous amine-based liquid solvents suitable for PCCC. The jury appears to be still out on which ones are the best, but MEA is no longer the sole contender.

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<sup>§</sup> Garcia, S., et al., ALIGN CCUS D1.4.3 Guidelines and Cost-drivers of Capture Plants Operating with Advanced Solvents, Project 271501, Jan 25, 2021