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36. R.S.H. is funded by the Natural Environment Research Council, the Engineering and Physical Sciences Research Council, the Scottish Funding Council, the U.K. Energy Research Centre, and the Scottish Centre for Carbon Storage (SCCS) Industry Consortium. S. Brandani (Edinburgh Univ.) explained the Joule-Thomson effect, and J. Gibbins (Imperial College, London) discussed power plants. I thank all at SCCS for discussions, especially M. Wilkinson, M. Naylor, S. Gilfillan, and N. Markusson (Edinburgh Univ.); A. Todd and E. Mackay (Heriot-Watt Univ.); and M. Akhurst, M. Smith, and M. Quinn (British Geological Survey).

10.1126/science.1172246

PERSPECTIVE

Amine Scrubbing for CO₂ Capture

Gary T. Rochelle

Amine scrubbing has been used to separate carbon dioxide (CO₂) from natural gas and hydrogen since 1930. It is a robust technology and is ready to be tested and used on a larger scale for CO₂ capture from coal-fired power plants. The minimum work requirement to separate CO₂ from coal-fired flue gas and compress CO₂ to 150 bar is 0.11 megawatt-hours per metric ton of CO₂. Process and solvent improvements should reduce the energy consumption to 0.2 megawatt-hour per ton of CO₂. Other advanced technologies will not provide energy-efficient or timely solutions to CO₂ emission from conventional coal-fired power plants.

Existing coal-fired power plants in the United States have more than 300,000 MW of power capacity, providing about 50% of the total power generated nationally and representing more than 30% of CO₂ emissions. Any reasonable strategy for ameliorating anthropogenic climate change must reduce these emissions without closing these plants. Amine scrubbing is probably the only technology for postcombustion capture of CO₂ that is available to address this problem.

The history of flue gas desulfurization should teach us what to expect in the development and deployment of technology for CO₂ capture. Lime or limestone slurry scrubbing for flue gas desulfurization was first applied at two British plants in 1936 (1), and was identified as an effective technology as early as 1965 (2). However, it was deemed to have unacceptable capital cost, poor reliability, and poor environmental

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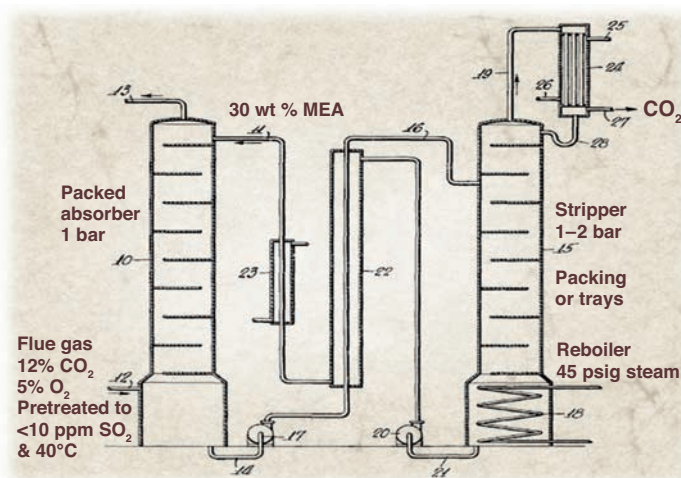


Fig. 1. The amine scrubbing process invented by Bottoms in 1930 (7).

performance, as well as being too commercial, and therefore was considered an unworthy candidate for government-funded research and development. Work on limestone slurry scrubbing continued, nevertheless, gaining increasing attention through the 1970s [e.g., (2, 3)] and beyond, and now it is the dominant technology for flue gas desulfurization.

Amine scrubbing, the technology of choice for CO₂ capture, was first evaluated in 1991 (4)

and—like flue gas desulfurization—was deemed to have unacceptable energy use and costs. It had been successfully applied to gas- (5) and coal-fired plants (6) on a small scale in the early 1980s, but was perceived to be too commercial and not worthy of government support. Since 2000, the U.S. Department of Energy has primarily supported R&D on other advanced technologies for CO₂ capture. However, amine scrubbing will probably be the dominant technology for CO₂ capture from coal-fired power plants in 2030.

CO₂ removal by absorption and stripping with aqueous amine is a well-understood and widely used technology. The basic process, patented in 1930 (7), is one in which CO₂ is absorbed from a fuel gas or combustion gas near ambient temperature into an aqueous solution of amine with low volatility (Fig. 1). The amine is regenerated by stripping with water vapor at 100° to 120°C, and the water is condensed from the stripper vapor, leaving pure CO₂ that can be compressed to 100 to 150 bar for geologic sequestration.

Hundreds of plants currently remove CO₂ from natural gas, hydrogen, and other gases with low oxygen. Four coal-fired plants with power outputs of 6 to 30 MW separate CO₂ from flue gas using 20% monoethanolamine (MEA). More than 20 plants use 30% MEA on gases with substantial O₂ content, including a gas-fired turbine with a flue gas rate equivalent to that of a 40-MW coal-fired power plant that produces flue gas with 15% O₂. More than 10 plants use a proprietary hindered amine, KS-1, with flue gases produced by combustion of clean fuels. Four other demonstration projects using MEA, KS-1, and another proprietary amine at coal-fired plants of 5- to 25-MW capacity will start up in Germany and Alabama, USA, in 2010 and 2011 (8, 9).



A reasonable schedule of process scale-up will permit widespread deployment on plants of 800 MW as early as 2018. This timing will require legislative cap-and-trade and other measures to provide incentive for the expensive, first-of-a-kind demonstration plants. However, limestone slurry scrubbing was demonstrated and deployed in less than 7 years, and amine scrubbing is understood far better than was slurry scrubbing at an equivalent point of its development. It should be possible to install amine scrubbing on an 800-MW plant that would be operational by 2013, if some institution would assume the financial risk and the extra cost of a hastily designed and constructed first-of-a-kind plant.

Economic design studies of scrubbing with aqueous MEA demonstrate both the feasibility of the technique and the uncertainties caused by the lack of experience with full-scale installations. Two studies of MEA scrubbing have been completed on a 450-MW plant (Table 1). In 2001, the design used 20% MEA. In 2006 (10), the study updated the costs from 2001 by employing 30% MEA and better energy integration. The new design reduced energy expended from 0.51 to 0.37 megawatt-hours (MWh) per metric ton of CO₂ removed and the cost of CO₂ removed from \$82 to \$51 per ton. The cost of CO₂ removal is sensitive to the value of replacement power, assumed in this case to be \$80/MWh. The actual cost of replacement power will be specific to the local power grid and is assumed to include the additional cost of CO₂ allowances. In the ERCOT (Electric Reliability Council of Texas) grid, for example, replacement power would be provided by combined cycle generation using natural gas, so the net CO₂ removal for the 2006 case would be 74% and the assumed cost would include any CO₂ penalty associated with gas combustion. Further development of this technology will provide more efficient systems to reduce energy cost, large single absorbers, heat exchangers, and compressors to reduce capital cost, as well as more robust solvents to reduce makeup costs and secondary environmental impact.

Improved solvents and process configurations are expected to reduce the parasitic power demand of CO₂ removal by amine scrubbing from the predicted values of 0.37 to 0.51 MWh/ton CO₂ (10) to 0.19 to 0.28 MWh/ton CO₂ (11, 12), equivalent to 20 to 30% of typical power plant output. The theoretical minimum work is 0.11 MWh/ton CO₂ (9), or about 12%. About half of that energy is low-temperature heat (steam) for the stripper reboiler. The other half is compressor work to provide CO₂ at 150 bar for transport and sequestration. Although no large plants have been built, the estimated energy use with optimized systems has decreased to 27% with 30% MEA (13) and 22% with KS-1 (14).

Large absorbers, extensive heat exchange requiring multiple parallel exchangers, and expensive compressor trains produce expected capital

costs of \$700/kW (10) to \$1000/kW (15) of treated capacity (\$106 to \$151 per ton of CO₂ removed over a year), but the cost of these units and other equipment that will be used in parallel should reduce those costs.

Reduced capital and energy costs will come with amines other than MEA, but there cannot be major improvement because the existing designs already provide about 50% thermodynamic efficiency. Concentrated piperazine (PZ) is a thermally resistant solvent with a high heat of CO₂ absorption that is claimed to reduce power loss to

absorber. Advanced amines such as KS-1, PZ (17), and ethyldiethanolamine (18) are resistant to degradation but are more expensive and will require more complex gas pretreating to avoid economic losses from process upsets and the effects of SO₂, NO_x, and fly ash. More expensive solvents, such as ionic liquids, will be more economically sensitive to process upsets and other impurities, even if they are otherwise stable.

Conceptual designs of amine scrubbing systems assume 90% CO₂ removal. Seventy to 95% removal probably represents the range where the cost of

Table 1. Economics of CO₂ capture by MEA scrubbing (10).

Year of design	2001	2006
MEA (weight percent)	20	30
Power used (MWh/ton)	0.51	0.37
@ \$80/MWh (\$/ton CO ₂ removed)	41	29
Capital cost (\$/ton CO ₂ removed per year)	186	106
@16%/year (\$/ton CO ₂ removed)	30	17
Operating and maintenance cost (\$/ton CO ₂ removed)	6	6
Total cost (\$/ton CO ₂ removed)	77	52
Net CO ₂ removal with power replaced by gas (%)	72	74

0.24 MWh/ton CO₂ by operating the stripper at 150°C (12). Vacuum stripping or the use of solvents with a lower heat of absorption will not get the full impact of solvent regeneration by heating to a higher temperature and will require more energy (11, 12). Solvents with greater capacity, such as KS-1, minimize sensible heat losses from heating and cooling the circulating solvent. Solvents with a faster rate of CO₂ absorption, such as methyldiethanolamine with PZ, allow for adequate absorber performance with more dissolved CO₂ in the rich and lean solvent, resulting in reduced energy use by the stripper (12).

Improved process configurations such as absorber intercooling, stripper interheating, flashing systems, and multipressure stripping will also provide reduced energy use, but at the expense of complexity and capital cost (11–13). However, solvent and process improvements are not additive, and we should not expect to do much better than 0.2 MWh/ton CO₂, or about 20% power loss. Claims of greater energy reduction for poorly developed processes must be based on poor understanding of process principles.

MEA is subject to oxidative and thermal degradation (16, 17), but it is the least expensive amine and its losses are expected to be less than \$5/ton CO₂. Impacts of SO₂, NO_x, and fly ash on solvent degradation will be minimized by efficient upstream equipment and including an alkaline scrubber to remove the residual SO₂. Oxidative degradation can be minimized by additives such as free-radical scavengers (16). Thermal degradation can be minimized by operating the stripping systems at lower temperature (e.g., 100°C). Volatile amine emissions in the clean gas are easily avoided by a water wash section at the top of the

CO₂ removal (\$/ton) is minimized. However, there are few fundamental barriers to greater removal.

Advanced separation methods such as membranes and pressure-swing adsorption are likely to be noncompetitive because of compression work. When the driving force for membranes or adsorption is provided by real, intercooled, adiabatic compressors, the expected work is about 0.21 MWh/ton CO₂ (11), with no driving force allowed for the separation itself. Therefore, it is unlikely that real membrane or adsorption systems will compete with advanced amine systems that provide CO₂ at higher pressure with a heat-driven, thermal-swing stripper.

Amine scrubbing is a flexible, tail-end technology that can be tested on existing power plants and applied in increments from 0.2 to 800 MW, as required by development needs and regulations. If the tail-end system is unreliable or lost power production is required to meet peak load demand, the scrubbing system can be turned off. Therefore, the capacity to meet peak demand will not be lost when these systems are retrofitted onto existing plants, although lost power production will have to be replaced from less efficient or more costly existing plants such as gas-fired combined cycles.

The development, demonstration, and deployment of oxycombustion and the integrated coal gasification combined cycle (IGCC) necessarily require and impact a complete power plant. As in the use of fluidized bed combustion and IGCC for SO₂ control, commercialization of these systems will be delayed by the financial, construction, and technical schedules of building successively larger, successful systems. Furthermore, like membrane technology, oxycombustion relies on

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mechanical compression to provide the work of separation and will not provide competitive energy consumption. In addition to separating oxygen for the production of CO₂, stoichiometric oxygen (about 20%) must be provided for hydrogen contained in the coal and for the excess required for adequate combustion (about 15%). Consequently, the estimated work for oxycombustion starts at 0.22 MWh. This estimate does not include the irreversibility of the exchangers and distillation columns in the air separation unit, nor does it include the irreversibilities of compressing the excess and leakage air along with the CO₂.

Amine scrubbing will be applied first on large coal-fired boilers with 12% CO₂. It would also be useful with boilers fired by biomass at 14% CO₂, cement plants at 25% CO₂, and steel works with 25% CO₂. It will be less attractive with gas-fired combined cycles at 4% CO₂ or gas- or oil-fired boilers or heaters at 7% CO₂. Amine scrubbing, in use for nearly 80 years, is a robust technique that is ready to be tested and used on a scale

appropriate for CO₂ capture from coal-fired power plants. Process and solvent improvements should reduce the energy use to 0.2 MWh/ton CO₂. Other advanced technologies will not provide solutions as energy-efficient or as timely to decrease CO₂ emissions from conventional coal-fired power plants.

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10.1126/science.1176731

PERSPECTIVE

Why Capture CO₂ from the Atmosphere?

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Air capture is an industrial process for capturing CO₂ from ambient air; it is one of an emerging set of technologies for CO₂ removal that includes geological storage of biotic carbon and the acceleration of geochemical weathering. Although air capture will cost more than capture from power plants when both are operated under the same economic conditions, air capture allows one to apply industrial economies of scale to small and mobile emission sources and enables a partial decoupling of carbon capture from the energy infrastructure, advantages that may compensate for the intrinsic difficulty of capturing carbon from the air.

Even if we could halt human carbon emissions today, the climate risks they pose would persist for millennia—assuming that we must rely only on natural processes to dissipate our carbon cycle perturbation and the resulting climate changes (1). The impact of carbon emissions persists longer than that of nuclear waste (2), the archetypal long-lived waste product. An immediate emissions halt is essentially impossible, however, and simple extrapolations of emission trends suggest that even with strenuous efforts to limit emissions, CO₂ concentrations in the atmosphere will rise beyond 450 parts per million before mid-century, passing the level commonly invoked as a ceiling above which the risk of dangerous climate change becomes unacceptably high. Moreover, the climatic response to elevated CO₂ concentration is uncertain, so a small risk of catastrophic impacts exists even at today's concentration, and that risk grows

monotonically as emissions continue to drive up the atmospheric CO₂ burden.

Technologies for decarbonizing the energy system, from solar power to the capture of CO₂ from the flue gases of coal-fired power plants, can cut emissions but they cannot reduce the climate risk posed by the carbon we have already added to the air. It may be possible to increase Earth's reflectivity, engineering a cooling that counteracts the CO₂-driven warming (3, 4). Although climate engineering may be important for managing climate risk, it cannot eliminate the long-term climate and geochemical risks posed by elevated CO₂. It is therefore in our interest to have a means to reduce atmospheric CO₂ concentrations in order to manage the long-run risks of climate change. Unless we can remove CO₂ from the air faster than nature does, we will consign Earth to a warmer future for millennia or commit ourselves to a sustained program of climate engineering.

Air capture is an industrial process that captures CO₂ from ambient air, producing a pure CO₂ stream for use or disposal (5, 6). It is one of an emerging set of technologies for remov-



ing CO₂ from the atmosphere that includes biomass energy with CO₂ capture, along with various means of accelerating geochemical weathering (7, 8).

Over the long run, the ability to remove CO₂ from the air should be viewed as an essential tool in our kit for managing carbon-climate risks. We therefore need, at the minimum, a serious long-term exploratory research effort to develop air capture along with other direct methods for removing CO₂ from the atmosphere.

In the near term, efforts to limit climate risk should focus on reducing emissions. Capturing CO₂ from the air, where its concentration is 0.04%, might well seem premature, given that there is still no power plant in which CO₂ is captured from the full exhaust stream. One might well conclude that there is little reason to develop and deploy air capture in the coming decades, before we can reduce emissions to the near-zero level where the ability to drive global emissions negative becomes relevant. The global energy system is marvelously diverse, however, and in

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