

Introduction: Carbon Capture and Separation

Carbon capture and sequestration (CCS) is the only available technology that can reduce the emission of CO₂ into the atmosphere due to burning of fossil fuels.^{1–3} Our addiction to fossil fuels started with the Industrial Revolution. It is clear that the Earth temperature has a direct dependence on the CO₂ concentration, and an increase in the average global temperature has been registered since the beginning of the 1900s. A rise of a few degrees Celsius is expected to significantly affect the climate. At present, we already see the evidence on the Earth landscape that such changes are already happening.⁴

CCS is a technology that can only be used on stationary sources (power plants and industrial applications), which accounts for 50% of the total emissions. The other half of the emissions is related to transportation. The reason that we are not yet performing CCS on a large scale is related to its costs. At present only a few countries have a price associated with the emission of CO₂, and as long as we can emit CO₂ for free, there is little if any economic incentive for CCS. In addition, the large-scale storage of CO₂ in geological formation raises concern about the safety of this process for the public at large.

At present, the energy penalty paid for the processes aimed to carbon capture and sequestration, or CCS, is high. The current estimate is that one needs a carbon tax of ca. \$70–100 per ton of CO₂ to recover the costs. Among the three steps constituting the CCS process (capture, transportation, and geological storage), capture constitutes the most energetically demanding, accounting for about 70–80% of the total cost. For example, in a coal-fired power station, this penalty is estimated to be 25–40% of the energy produced.⁵ Of this penalty about 30% is the energy required to compress CO₂ and 70% of the energy is used for the separation of CO₂ from flue gases. The costs of the CCS process can be reduced significantly if there are breakthroughs in the capture field. Being the amount of CO₂ emitted yearly in the atmosphere of the order of gigatons, it is evident that any improvement on this side can be greatly beneficial.

Carbon dioxide separation is a multisized problem because of the number of processes it has to be applied to.⁶ This issue covers different aspects of carbon capture, with particular attention to processes needing the most urgent improvement in the short to middle term, that is postcombustion capture and natural gas sweetening. In the long term, precombustion and the costly air capture processes require consideration. Postcombustion technology is particularly appealing because it can retrofit existing power plants, such as, for example, coal-fired ones that represent the most important anthropogenic CO₂ sources.

Aqueous organic amine-based technology is the most mature one for postcombustion capture, as it is based on the same technology that is currently used to remove CO₂ from natural gas (natural gas sweetening). The carbon capture process involves an absorber in which the flue gas is bubbling through an amine solution. The amines selectively remove the CO₂ from the flue gas. The CO₂ rich solution is subsequently pumped to the stripper where steam from the power plant is used to heat the CO₂ rich amine solution. As this steam cannot be used to generate electricity, it is this step that contributes the most to the

energy penalty. In addition, power is needed to compress the pure CO₂ to 150 bar, which is the typical pressure for geological storage.⁷

Although feasibility studies indicate that it will remain competitive in the future, this technology suffers from many problems, such as high cost, toxicity, degradation, and evaporation of the solvent. Yang et al.⁸ discuss the use of quantum mechanical methods to model the reactions at the basis of CO₂ capture by aqueous amines, pointing out the merits of the different mechanisms. A critical review of the influence of the simulation parameters and solvent models on the accuracy and reliability of the results is also presented to give a perspective on the capability for in silico design of more effective systems.

Water as solvent remains the weakest point of these systems. The large heat capacity of water is at the origin of the huge energy penalty paid for their regeneration by heating. It is intuitive that substituting water with low heat capacity organic solvents can allow a significant gain in efficiency. Heldebrant and co-workers⁹ focus on the use of concentrated organic “water-lean” solvents, or even nonaqueous solvents, bearing or solvating N-based species. Solvents technologies are surveyed, covering aspects from the atomistic description of the capture phenomenon to bench-scale testing, with the aim to assess the viability of water-lean solvents for postcombustion CO₂ capture. The high solvent viscosity and boiling-off are the main issues related to these systems.

Ionic liquids, ILs, possess a further improvement with respect to the two previous classes of systems. These organic ionic compounds, although liquids, are characterized by a large nonvolatility coupled with a high structural designability. By tuning their properties by varying the anionic and the cationic parts or by introducing functional groups, ILs reach outstanding performances in different fields. Zeng et al.¹⁰ review the use of ILs for carbon separation. Their inclusive overview covers the atomistic description of the sorption phenomenon as well as process design. The effect of the material constituents on the CO₂ affinity was thoroughly discussed along with the points on which the research need to be focused. Studies on IL-based solvents and IL-based membranes were also considered. The importance to simplify the synthetic protocol and upscale their production is highlighted as one of the crucial steps in order to lower ILs cost and make their implementation realistic.

Metal–organic frameworks (MOFs) are a class of materials whose structure is obtained by assembling metal oxides/metal units by organic linkers. The number and spatial orientation of unsaturated coordination of their constituents determine their topology, whereas their physical chemical activity is governed by their nature. The flexible structure of these materials is combined with the benefit of dealing with solid materials instead of liquids, eliminating their typical weaknesses, namely viscosity and solvent boiling-off. Most MOFs are characterized by a crystalline structure, which makes the interplay between computational predictions and experiments more appealing than for other

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classes of materials. MOFs design has allowed their successful implementation in many different fields, including CCS. Yu et al.¹¹ survey the literature of CO₂ adsorption and separation in MOFs, in its multipronged complexity. The strategies for enhancing CO₂ capture rely on the hallmark of MOFs, their structural modularity. Factors pivotal for the practical implementation of MOFs for CCS, easily extendable to other classes of materials, are also extensively discussed.

A challenge in the implementation of all the carbon capture technologies is the presence of impurities in the gas stream that can poison or even damage the absorber. All the reviews reported in this issue deal with the problem of material durability, a key quality for a realistic use of these systems. As an example, gasification of coal and biomass causes the conversion of the sulfur contained in these resources into sulfuric acid. The H₂S present in the flue gases can strongly bond and even react with the sorbent materials, significantly affecting the lifetime of the scrubbing systems. Research dealing with sour gas sweetening has to include H₂S removal, often present in significant amounts. Shah et al.¹² focus on materials and processes for the selective removal of H₂S, considering all the processes reported in the state-of-the-art literature: adsorption, absorption, membranes, and cryogenic distillation.

Finally, implementation of carbon capture and separation facilities would increasingly make available gigatons of CO₂ that must be disposed of. Sequestration, the last step in CCS, involves CO₂ long-term storage in a subterranean or submarine site. As an alternative, recycling of CO₂ in valuable chemicals, such as, for example, fuels, would have the double benefit to avoid the cost associated with the sequestration step and to valorize CO₂ as chemical feedstock. Álvarez et al.¹³ detail the latest progress in heterogeneous catalysis for carbon dioxide hydrogenation. They also provide an overview of the green route for H₂ production, one of the crucial points in the economical feasibility of these technologies. The different technological readiness level of the processes for the methanol, DME, and formate/formic acid production is discussed, evidencing which factor among the catalyst design, CO₂ purity, and cost is limiting their implementation.

The importance of the economical aspects of a technology proposed for carbon capture has been discussed in all the contributions. The reviews of this issue cover different aspects of carbon capture and separation, highlighting the importance of diverse approaches to foster the development of a carbon neutral society. The presence of a section on process design in each review confirms the maturity of the field and gives the important message that CCS is a technology that can be implemented tomorrow in a world for which reducing CO₂ should be one of the highest priorities.

We hope that readers will benefit from the information presented in this volume, allowing a further and decisive development in this societally relevant field. We thank all authors for the excellent contributions, as well as thank the editorial staff of *Chemical Reviews* and, in particular, Prof. Sharon Hammes-Schiffer and LeeAnn Pannebaker for their invaluable support.

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Notes

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Biographies



Jenny G. Vitillo received her Ph.D. in Materials Science in 2005 from the University of Torino (Italy). She had a postdoctoral appointment at the same University from 2005–2013 and 2016–2017. Funded by a FIRB project (Italian starting grant), in 2013 she moved to the Department of High Science and Technology of the University of Insubria, Italy. At present, she is a Post-Doctoral Associate at the Department of Chemistry of the University of Minnesota. Her research focuses on environmentally relevant problems by using experimental and computational approaches. Carbon dioxide capture, utilization, and storage (CCUS) represents one of her main research subjects. In this respect, she is author of a recent review on CCUS, covering different aspects of this topic.



Berend Smit received an M.Sc. in Chemical Engineering in 1987 and an M.Sc. in Physics both from the Technical University in Delft (The Netherlands). He received in 1990 a cum laude Ph.D. in Chemistry from Utrecht University (The Netherlands). He was a (senior) Research

Physicists at Shell Research from 1988–1997 and Professor of Computational Chemistry at the University of Amsterdam (The Netherlands) from 1997–2007. In 2004, Berend Smit was elected Director of the European Center of Atomic and Molecular Computations (CECAM) Lyon France. Since 2007 he has been Professor of Chemical Engineering and Chemistry at U.C. Berkeley and Faculty Chemist at Materials Sciences Division, Lawrence Berkeley National Laboratory. Since 2014 he has been Director of the Energy Center at EPFL. Berend Smit's research focuses on the application and development of novel molecular simulation techniques, with emphasis on energy related applications. Together with Daan Frenkel, he wrote the textbook *Understanding Molecular Simulations* and, together with Jeff Reimer, Curt Oldenburg, and Ian Bourg, the textbook *Introduction to Carbon Capture and Sequestration*.



Laura Gagliardi is a Distinguished McKnight University professor at the University of Minnesota. She obtained her Ph.D. from the University of Bologna, Italy, in theoretical chemistry. After a postdoctoral appointment at Cambridge UK, she began her independent career as an Assistant Professor at the University of Palermo, Italy, in 2002. She then moved to the University of Geneva, Switzerland, in 2005 as Associate Professor. Her move to the University of Minnesota came in 2009, where she is now Distinguished McKnight University Professor and Professor in the Department of Chemistry. Her research interests are in the area of theoretical and computational chemistry, with special focus on sustainable energy challenges. She is a fellow of the American Physical Society and the Royal Society of Chemistry. In 2004 she won the annual award of the International Academy of Quantum Molecular Science to scientists under 40, and in 2016 she won the Bourke Award of the Royal Society of Chemistry UK. She is currently the Director of the Energy Frontier Research Center named Inorganometallic Catalyst Design Center, based at the University of Minnesota. She has coauthored more than 260 publications.

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