Carbon capture and storage (CCS): the way forward


Carbon capture and storage (CCS) is broadly recognised as having the potential to play a key role in meeting climate change targets, delivering low carbon heat and power, decarbonising industry and, more recently, its ability to facilitate the net removal of CO2 from the atmosphere. However, despite this broad consensus and its technical maturity, CCS has not yet been deployed on a scale commensurate with the ambitions articulated a decade ago. Thus, in this paper we review the current state-of-the-art of CO2 capture, transport, utilisation and storage from a multi-scale perspective, moving from the global to molecular scales. In light of the COP21 commitments to limit warming to less than 2 °C, we extend the remit of this study to include the key negative emissions technologies (NETs) of bioenergy with CCS (BECCS), and direct air capture (DAC). Cognisant of the non-technical barriers to deploying CCS, we reflect on recent experience from the UK’s CCS commercialisation programme and consider the commercial and political barriers to the large-scale deployment of CCS. In all areas, we focus on identifying and clearly articulating the key research challenges that could usefully be addressed in the coming decade.
1 Introduction

This paper is the third installment in a series of publications over several years in Energy & Environmental Science. The first (published in 2010) provided an introduction to CO\textsubscript{2} capture technologies, with an overview of solvent-based chemisorption (amines and ionic liquids), carbonate looping, oxy-fuel combustion technologies, CO\textsubscript{2} conversion and utilisation (CCU) and multi-scale process engineering of CCS. The second installment presented an update on developments in amine scrubbing, ionic liquids, oxy-combustion and calcium looping. New topics added in this second paper include chemical looping combustion, low temperature adsorbents, direct air capture technologies, flexible CCS operation, CO\textsubscript{2} transport and storage, and a historical overview of the UK and EU CCS policy and legislation.

Distinct from the previous installments, this third paper sets out to comprehensively review the state-of-the-art developments in CCS, whilst also providing a holistic perspective on the role of CCS technologies in mitigating anthropogenic climate change. We first discuss the current status of CCS development and highlight key CCS technologies that are near commercialisation phase (Section 2). Then in Section 3 we contextualise CCS technology by considering its representation and utilisation in integrated assessment models (IAMs), challenging the view that it is a "bridging technology", likely to be relevant for only a few decades. We then go on to quantify and qualify the role and value of CCS at a more granular level by evaluating the way in which CCS interacts with national scale electricity systems. This in turn helps us address the question of what service CCS provides to the electricity system, with whom is CCS competing and what technologies does CCS complement.

We then move on to consider the utility of CCS in decarbonising the industrial sector, with a focus on the key emitters – the production of iron and steel, cement and oil refining and petrochemicals. Throughout, we aim to challenge the perception that industrial CCS is uniquely costly, showing that, for example, the cost of decarbonising the refining sector is essentially "lost in the noise" of market fluctuations of the end use sectors.

Section 4 of the paper considers key post-combustion CCS technologies in detail. The purpose of this paper is not to enumerate the panoply of technologies that are available for capturing CO\textsubscript{2}. Rather, we focus on solid- and liquid-phase sorbents, and attempt to specify key research questions that need to be address in these areas. We then select three particularly promising alternative technologies for CCS in Section 5: chemical looping combustion, membranes and ionic liquids.

It is well known that the thermophysical and kinetic properties of the sorbents used for CO\textsubscript{2} capture dictate both the capital and operating cost of the processes in which they are used. For this reason, there is a concerted effort to rationally design new sorbent materials, with the bulk of the effort in the development of liquid sorbents, where available theories are more readily applied. Thus, we present an assessment of SAFT-based approaches to model and design new materials in Section 6, with a focus on how efforts at the molecular and process scales might be linked.

Before CO\textsubscript{2} can be safely and reliably sequestered, it must be transported from source to sink. Whilst the majority of studies assume pipeline transport, ship and rail transport are potential alternatives; these other transport options are discussed in Section 7. Similarly, despite the fact that CO\textsubscript{2} transport by pipeline is exceptionally mature, the impact of capturing CO\textsubscript{2} from a diverse set of power and industrial sources on the quality of CO\textsubscript{2} being transported is sufficiently important to warrant careful consideration.

The typical fate of CO\textsubscript{2} is to be sequestered, either in a saline aquifer or, potentially, used for enhanced oil recovery (EOR). The various challenges of operation, monitoring and verification of CO\textsubscript{2} storage are discussed in Section 8, whereas Section 9 discusses CO\textsubscript{2}-EOR. A potential alternative to the storage of CO\textsubscript{2} is its re-use – the valorisation of CO\textsubscript{2} to produce marketable compounds. The argument is sometimes made that this can both contribute to climate change mitigation and provide an attractive revenue stream. Section 10 discusses the potential for CO\textsubscript{2} conversion and utilisation (CCU), also its merits and challenges are presented and considered.

In light of the global commitment achieved in Paris in December, 2015, we have extended this paper to include key negative emissions technologies (Section 12); bioenergy with CCS (BECCS) and direct air capture of CO\textsubscript{2} (DAC). These areas are of particular importance owing to their potential importance and their controversy.

Despite the fact that there are currently 37 CCS projects at various stages in the Americas, Europe, Middle East and Asia-Pacific, CCS continues to languish as an "orphan technology". With decades of technical experience across the entire value chain, it is clear that it is not a lack of technical expertise that is inhibiting the commercial deployment of CCS technology. Thus, we have devoted a section of this paper to consider "what needs to happen" from a commercial perspective (Section 13), drawing upon experience developed as part of the UK’s most recent CCS commercialisation programme. Having provided this perspective from the private sector, we...
then complement this with an international analysis of the political economy of CCS (Section 14). Section 15 then concludes with a proposed approach to evaluate the utility of a “novel technology” and feasibility of particular targets by identifying limitations that might prove to be showstoppers.

2 Current status of CCS development

Carbon capture and storage is expected to play an important role in meeting the global warming targets set by the IPCC and at COP21. There is a suite of technologies being developed for the capture, transport, storage, and utilisation of CO2. Typically, technology development will progress in a series of scale-up steps: (i) bench or laboratory scale, (ii) pilot-scale, (iii) demonstration scale, and lastly (iv) commercial scale. Fig. 1 summarises the current development progress of different CCS technologies on the TRL scale. As illustrated by Fig. 1, there is congestion of technologies at the TRL 3, TRL 6 and TRL 7 development phases. The progression of a technology beyond TRL 3 requires further research funding, whereas advancing technologies beyond TRL 5 and TRL 7 needs significant financial investment and/or commercial interest (e.g., in the case of polymeric membranes). Further detailed discussion on the technical development of the individual CCS technologies is presented in the following sections of this paper. Here in this section, we highlight the key CCS technologies that have reached (or close to reaching) the commercial phase of development.

CO2 capture

Chemical absorption (e.g., using aqueous amine solutions) has been used to remove CO2 from natural gas for decades, thus, it is considered to have a TRL of 9. This technology has been utilised in two commercial-scale post-combustion capture facilities in coal-fired power plants, Boundary Dam and Petra Nova. Recent developments in polymeric membranes have enabled the technology to successfully achieve demonstration scale (TRL 7). The Polaris membrane is now available commercially and has been used for CO2 separation from syngas. Air Products are licensing a polymeric membrane developed at NTNU, which can be applied to coal-fired power plants and other combustion processes (still under development). Thus, The first “commercial-ready” direct air capture (DAC) plant recently opened in Hinwil, Switzerland on May 2017, with the support of cost contributions from the Swiss Federal Office of Energy. The plant supplies 900 tonnes of CO2 annually to a nearby greenhouse. Capture technologies that have also reached TRL 7 (demonstration) (e.g., oxy-combustion coal power plants, adsorption) could also potentially reached commercial status in the near future. In contrast to post-combustion capture, integrated gasification combined cycle (IGCC) with CCS has been less successful with the Kemper County IGCC Project being suspended recently.

Southern Company’s decision to halt the project came after encountering a series of problems, these include failure to meet the delivery deadline, severe technical issues and being majorly over budget.

CO2 transport

The technologies for CO2 transport are well established. There are >6500 km of CO2 pipelines worldwide (both on-shore and off-shore), most of which are associated with EOR operation in the United States. The technology for CO2 transport with ships is also relatively mature. As these transport technologies are currently being used in commercial applications, all have a TRL of 9.

CO2 storage

As many commercial-scale CCS projects already use CO2-enhanced oil recovery (EOR), 13 of the 17 operating commercial-scale CCS projects, there is a significant amount of existing experience and knowledge, which has enabled CO2-EOR to reach TRL 9. Similarly, saline formations have been used for CO2 storage at commercial-scale project, including Sleipner CO2 Storage, Snolhvit CO2 Storage and Quest (on-shore and off-shore). In contrast, CO2 storage by enhanced gas recovery (EGR) and storage in depleted oil and gas fields have not reached operation at commercial-scale, thus, both are still at the demonstration phase (TRL 7). Ocean storage and mineral storage are still in the early phases of development.

CO2 utilisation

There are a number of facilities that utilise CO2 for various applications. These commercial CO2 utilisation processes are TRL 9 as they are mature technologies. Most are in the food and beverage industry and some in chemical production (e.g., urea, methanol). Several projects utilise CO2 for mineral carbonation, for example, Searles Valley plant (US). In Saga City, Japan, CO2 capture from waste incineration is utilised for the cultivation of crops and algae. The CO2 for each project is mainly sourced from industrial processes (e.g., fertiliser production, ammonia production, ethylene glycol plants), but some projects capture the CO2 from power plant flue gas.

Commercial-scale CCS projects

Deployment of large scale CCS projects has been slow. Of the 37 major large scale CCS projects, 17 of these are in operation, in construction and the remainder are in varying stages of development. As shown in Fig. 2 and 3, the majority of the commercial large-scale CCS projects are located in the United States. In terms of the project life cycle (i.e., identify, evaluate, define, execute and operate), the US also has the greatest proportion of projects in operation. For all but one of these projects, enhanced oil recovery is the primary storage for the captured CO2. Furthermore, the projects in the US have the largest CO2 capture capacity compared with projects in the rest of the world: Century Plant captures 8.4 MtCO2 per year, whereas Shute Creek Gas Processing Facility capture 7 MtCO2 per year.

Although China has the second highest number of projects, only one of these is in the execute phase (Yanchang Integrated CCS Demonstration), and most are in early stages of development (e.g., pre-feasibility, FEED studies). The CO2 capture capacity of the
projects in China range between 0.4–2 MtCO₂ per year. Europe has the third highest number of large-scale projects, with two operational projects in Norway: the Sleipner CO₂ Storage Project captures 1 MtCO₂ per year, and Snøhvit CO₂ Storage Project 0.7 MtCO₂ per year. Of the five projects in Canada, three are in operation: (i) Great Plains Synfuel Plant and Weyburn-Midale Project (3 MtCO₂ per year), (ii) Boundary Dam CCS Project (1 MtCO₂ per year), and (iii) Quest (~1 MtCO₂ per year). There are also operating CCS projects in Brazil, Saudi Arabia and United Arab Emirates with CO₂ capture capacities ranging from 0.8–1 MtCO₂ per year. A fundamental requirement for the success of CCS projects in all of these projects is the availability of safe geological storage for the capture CO₂. Furthermore, other factors that can help bring CCS projects into operation phase include secure financial funding, as well as supportive policy and legislative frameworks.

### 3 Role and value of CCS

#### 3.1 Climate change mitigation

Integrated Assessment Models (IAMs) have been at the heart of the Intergovernmental Panel on Climate Change's (IPCC) assessment of pathways towards keeping average global warming to less than 2 °C within this century. They provide a means to...
explore the future role of particular technologies in meeting climate targets such as renewables or nuclear.

CCS is one of the very attractive options in the IAMs mitigation portfolios, as it has a number of advantages. First, CCS can be integrated into existing energy systems without requiring large amendments to the system itself. Clearly, renewable technologies become more expensive at high penetration rates as a result of the need for the infrastructure to accommodate intermittency.\(^2^9\) Furthermore, CCS is a viable option for the decarbonisation of emission-intensive industries such as cement production (specific industrial CO\(_2\) capture costs are given in Section 3.3).\(^3^0\) And finally, CCS can be combined with low-carbon or carbon-neutral bioenergy (BECCS) to generate negative emissions, \(i.e.\) while the cultivation of the feedstock biomass sequesters about as much CO\(_2\) as is generated during the process of producing energy (bio-electricity or biofuels), additionally capturing the latter leads to a withdrawal of CO\(_2\) from the atmosphere.\(^3^2\) BECCS has the double benefit of mitigating emissions and generating energy, making it attractive from the cost-optimisation perspective of an IAM.

### 3.1.1 CCS in integrated assessment models (IAMs)

Based on the model intercomparison study by Koellbi \textit{et al.},\(^3^3\) some general statements on the implementation of CCS in IAMs can be made. In some cases, CCS is modelled as a lump-sum add-on cost to the technology it is combined with, while other models separate capture costs and transport \& storage and a few separate all cost items. The latter modes obviously give more detail about the CCS supply chain, which enables modellers to also test the sensitivity of results to individual cost components. All IAMs include at least the power sector for CCS and many also cover industry and liquid fuels/hydrogen/gas production. At least 1 sector is also eligible for BECCS (in- and excluding liquid fuels), but many IAMs cover up to 3 sectors with BECCS. There is quite a divergence with respect to the assumption about CCS lifetimes, ranging from 30 to 60 years (partially depending on the technology), though most of the models assume around 40 years. It is also interesting in this light that there are some models not allowing early retirement of CCS plants. Almost all of the IAMs of the model intercomparison assume that CCS investment costs develop according to an exogenous constant (often declining); only two have endogenous learning.\(^3^4\)

\(^3^4\) Endogenous learning occurs through learning curves in these models, \(i.e.\) cumulative capacity determines the cost reductions, while other models assume cost reductions according to an exogenously given factor.
Finally, concerning storage, while many models have a regional differentiation of storage capacity, only a few models allow for international trade in storage capacity. The maximum capacity ranges between 3500 GtCO₂, cumulative, and unlimited storage. Transportation and storage cost (excluding capture cost) varied between 10–300 US$ per ton CO₂, depending on model and storage type. All of the models considered transportation and storage costs at the lower end of this range. Models that also considered high transportation and storage cost include the POLES model (upper range value of $300 USD) and the GRAPE model (upper range cost of $262 USD). The higher values for storage cost are associated with options that were offshore, enhanced coal bed methane (ECBM) and at greater depths (e.g., 2000–3000m).

The IAMs thus differ widely in their deployment of CCS, yet the model intercomparison, which is the basis for the numbers cited above, could not explain the divergence of results on the basis of model type, model assumptions or the way in which CCS has been modelled. So either these are not the drivers of the difference or their impact is confounded by other factors via system effects. Individual model studies find that CCS contributes 50% more to mitigation if technological learning is included (Riahi et al. cumulative storage of 150–250 GtCO₂) and that the contribution of CCS is sensitive to its cost in 2050 but not in 2100.

3.1.2 Current status of CCS deployment. Even though CCS thus plays a central role in IAM decarbonisation scenarios, deployment has barely reached the levels indicated by the projections of IAMs and roadmaps by the International Energy Agency. Looking into the future, only a few of the Intended Nationally Determined Contributions (INDCs), which countries pledged at the climate negotiations in Paris, feature CCS as a priority area.

More specifically, a recent report on CCS by the IEA reviews the progress of the past 20 years and concludes that the current rate of progress is falling short of what is required to achieve climate goals. This is further underlined in the analysis of the INDCs by Spencer et al. national and global scenarios based on the Paris pledges both show little deployment of CCS, with a share of CCS in electricity generation of only 3% in 2030 for the USA, China, Japan and the European Union. This is further exacerbated by the opposition against CCS, which is motivated by perceived uncertainties concerning its safety and the fear that it will serve to prolong the dependence on fossil fuels and be a barrier to greater utilisation of renewable power.

The next section will present the current state-of-the-art knowledge on the role of CCS – and by extension BECCS – in IAMs. The review will first focus on an model intercomparison exercise of 18 IAMs (EMF27) and then widen towards the low stabilisation pathways in the IPCC’s Fifth Assessment Report (AR5). Secondly, an investigation of the scenarios consistent with the more ambitious 1.5 °C climate goals adopted at COP21 in Paris (UNFCCC 2015), serves to underline the main insights on CCS and puts specifically BECCS into the spotlight.

3.1.3 Integrated assessment modelling: the role of CCS in meeting targets

State-of-the-art scenarios focusing on the 2 °C target. This subsection draws on the results of the model intercomparison presented in Koelbl et al. as it is the most recent and most comprehensive assessment specifically targeted at the role of CCS in long-term climate change mitigation scenarios. The study itself draws on the output of the 27th Energy Model Forum (EMF), to which 18 IAMs contributed, thus providing an excellent opportunity for a systematic comparison of results with respect to the role of CCS. Koelbl et al. find that CCS plays an important role in all of the models’ mitigation portfolios that were investigated. While the range of CO₂ captured varied widely between models (up to 3050 GtCO₂ cumulatively until 2100 in some instances), none of them captured less than 600 GtCO₂. Table 1 shows the ranges across scenarios with different stabilisation targets and renewable penetrations by model type** based on Koelbl et al. While the authors cannot easily explain the large range across models by looking at individual model assumptions (see Section 3.1.1 and Table 1), the fact that models consistently capture a minimum of 600 GtCO₂ cumulatively until 2100 – which would be more than half of the required emission reductions consistent with a 2 °C pathway†† – does give a sense for the magnitude and importance of the role of CCS in IAMs.

Furthermore, the authors do not find a decreasing role for CCS over time. On the contrary, the CCS share in primary energy is mostly higher in the second half of the century compared to the first. In particular, the ranges for capture rates in Koelbl et al. are 5–23 GtCO₂ per year in 2050 and 8–50 GtCO₂ per year in 2100. This undermines the reputation of CCS as a bridging technology and further underlines its importance in IAMs, which seek to achieve ambitious climate targets. The importance is further enhanced under pessimistic assumptions about technological development of renewable energy for a given climate target, indicating little flexibility for the cost-optimal deployment of alternatives.

† It has to be noted, however, that in most cases, results were only available for the full time horizon and scenarios considered for 12 models out of the 18 ones that participated, thus the authors conclude that more research is needed to substantiate some of the more detailed findings, which this section will not go into.

** The technology-focussed models are engineering-based models which consider a large number of energy technologies. They are typically used to calculate the least cost approach to meet a given demand (e.g., emission reduction target). In contrast, macro-econometric models consider production costs at an industry level, offering more economic detail but lack structural detail. A hybrid model combines both technology-based and macro-economic approaches.

†† To ensure global warming stays below 2 °C, the cumulative emissions from 1870 must remain less than 3650 GtCO₂. Of this quota, the total remaining emissions from 2017 is estimated to be around 800 GtCO₂. At current emission rates, global emissions is expected to exceed the 800 GtCO₂ budget within 20 years.

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Finally, the use of BECCS‡‡ in the models' CCS fuel portfolio increases with the stringency of the target. This is mostly connected to substitution for coal and natural gas over time. In response to the concerns with respect to large-scale cultivation of biomass for BECCS and the reservations concerning CCS discussed above, the EMF models also produced a whole array of scenarios limiting the use of both biomass and CCS. Although these scenarios achieve the same target, they are consistently characterised by higher costs, which is consistent with earlier findings by e.g. Azar et al.⁴⁹ and later confirmed by the results of the IPCC's AR5.⁶

In the absence of CCS, the total cost of climate change mitigation increased by 138%, whereas limited bioenergy availability increased cost by 64%.$$⁶ The integration of CCS into an energy system provides a significantly greater reduction in CO₂ emissions compared to wind technology.⁵⁰ With limited CCS and biomass availability, the deployment of nuclear, intermittent solar/wind, interconnection and gas-fired power needs to increase, consequently leading to higher total system cost.⁵¹ The increase in mitigation cost is associated with the delay in technology deployment (e.g., more time to establish infrastructure), use of more expensive technologies (nuclear), and maintaining grid stability (e.g., intermittency requires the addition of "back-up" capacity and part-load/flexible operation).⁵⁰

In particular, the IPCC scenarios associated with a more than even chance of achieving the 2 °C target are characterised by average capture rates of 10 GtCO₂ per year in 2050 and 25 GtCO₂ per year in 2100 and cumulative storage of 800–3000 GtCO₂ by the end of the century.⁷ With respect to finding more expensive mitigation strategies when CCS is not available, it is important to note that under these circumstances, there are actually a significant number of IAMs, which do not find a feasible solution at all: Riahi et al.⁵² conduct a model intercomparison, where a third of the IAMs do not find a feasible solution at 450 ppm without CCS under optimal circumstances. If there is further delay in mitigation, this share drops to a fifth. In other words, the target is not just more expensive to reach, but not reachable at all, given the current parameterisation of the models.

In addition, the AR5 scenarios have been under scrutiny for their deployment of CCS in conjunction with bioenergy. The 101 out of 116 scenarios leading to concentration levels of 430–480 ppm CO₂-equivalent (CO₂eq.) (considered to be consistent with a 66% probability of limiting warming to below 2 °C) require global net negative emissions between 2050 and 2100. About 50% of the scenarios feature BECCS exceeding 5% of primary energy supply.³¹

While these aspects of the IPCC scenarios have caused some people to doubt the feasibility of achieving the 2 °C target (e.g. Peters³¹), the role of CCS and particularly BECCS become even more important in light of the increased level of ambition following the 2015 Paris COP.⁵⁴

Towards 1.5 °C. What is currently available in terms of 1.5 °C IAM scenarios is much less than what is presented above on 2 °C from the IPCC's AR5. This subsection draws on work from Rogelj et al.⁵₅ and Luderer et al.,⁵⁶ which offer an assessment of what is currently available on 1.5 °C.¶¶

The most outstanding feature that systematically distinguishes the 1.5 °C from the 2 °C IAM scenarios examined in Rogelj et al.⁵₅ is that there is not a single pathway with a 50% probability of achieving the target without overshooting it until 2100. That is, the average global temperature increase will at some point exceed 1.5 °C, before returning to this level at the end of the century.

This implies that much of the CO₂ emitted in the first half of the century will need to be removed from the atmosphere again. In other words, emissions have to be negative at some point. Indeed, the analysis in Rogelj et al.⁵₅ shows that there are no feasible 1.5 °C scenarios without negative emissions. In particular, the cumulative negative emissions are between 450 and 1000 GtCO₂ until 2100. This is in stark contrast to some 2 °C scenarios, which do manage to reach their target without carbon removals. Luderer et al.⁵⁶ point out that energy efficiency improvements can have this effect for 2 °C scenarios.

In the current IAMs, these negative emissions are primarily achieved by the deployment of BECCS.¶¶ This has triggered a discussion reflecting on large concerns not only about CCS (cf. discussion in Section 3.1), but also with respect to the implications of the large amounts of biomass that would be needed to achieve sufficient scales to reach the level of negative emissions needed for ambitious climate change mitigation. In an ex-post assessment of the amounts of negative emissions through BECCS in the IPCC's AR5, Smith et al.⁶¹ estimated the

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Model type</th>
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<tbody>
<tr>
<td>1</td>
<td>Hybrid</td>
</tr>
<tr>
<td>1</td>
<td>730–2411 GtCO₂</td>
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<tr>
<td>2</td>
<td>653–2962 GtCO₂</td>
</tr>
<tr>
<td>3</td>
<td>625–2447 GtCO₂</td>
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Table 1 Cumulative storage for three scenarios of (1) a stringent concentration target, (2) less stringent concentration target, and (3) stringent target with lower penetration of renewables (based on Kooi et al.⁵⁵). The three model types considered are the hybrid models [synthesis of the technology and macro-economic approaches], macro-economic focused models, and technology focused models.

‡‡ It has to be noted that these scenarios are characterised by different probabilities than the 2 °C scenarios reviewed above, which means that the focus here should be on the qualitative results and not a direct comparison of numbers.

¶¶ There are a few that also consider large-scale afforestation, i.e. CO₂ is sequestered in additionally grown vegetation.
Table 2  Other negative emissions technologies not included in IPCC AR5 scenarios, without claiming to be exhaustive

<table>
<thead>
<tr>
<th>Technology</th>
<th>Description</th>
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<tr>
<td>Direct air capture (DAC)</td>
<td>Chemicals (e.g. amines or sodium hydroxide) are used to absorb CO₂, which is then mineralised for solid storage, or is stored in geological formations.</td>
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<tr>
<td>Soil carbon sequestration (SCS)</td>
<td>Carbon soil sequestration is enhanced by increasing inputs or reducing losses (see Smith).</td>
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<tr>
<td>Biochar</td>
<td>Through pyrolysis, biomass is made more resistant to decomposition and then added to the soil to store embedded carbon (see Smith).</td>
</tr>
<tr>
<td>Enhanced weathering (EW)</td>
<td>Minerals like olivine that naturally absorb CO₂ are ground and spread out to increase their surface area and make them absorb CO₂ more rapidly.</td>
</tr>
<tr>
<td>Ocean fertilisation (OF)</td>
<td>Iron can be used to make ocean phytoplankton absorb more CO₂ through photosynthesis, and then sink to the deep ocean and sequester carbon after their death.</td>
</tr>
<tr>
<td>Indirect ocean capture</td>
<td>Oceanic carbon uptake represents the largest sink for anthropogenic CO₂, absorbing about 40% of CO₂ emissions from the atmosphere since the start of the industrial era.</td>
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The range of land area, costs, water and nutrients footprints and biophysical effects. They find that, indeed, the areas of land which would be needed, are large (380–700 Mha by 2100).***

Relating the primary energy of the biomass (in EJ) used in BECCS to the amount of CO₂ stored geologically is complex. This relationship strongly depends on the choices made in the cultivation, harvesting, transport and utilisation of the biomass throughout the BECCS supply chain. Assuming that all of the CO₂ sequestered by the biomass is assumed to be released in the flue gas upon combustion, the amount of CO₂ sequestered per MJ of biomass would then depend on the capture rate applied at the BECCS facility, the biomass carbon content, the biomass heating value and the biomass carbon footprint. Considering a capture rate between 60% and 90%, a biomass carbon content between 45%dry and 50%dry, an HHV dry between 18 and 20 MJ kg⁻¹ (dry mass) and biomass carbon footprint between 0 and 36 gC₉₋₁ M⁻¹, the amount of CO₂ sequestered would be found to be between 14 and 92 gC₉₋₁ MJ⁻¹. One EJ of biomass could thus capture between 14 and 92 MtC per year, resulting in an annual requirement of between 130 and 860 EJ by 2100 to capture 12 GtCO₂ per year, however, the total primary energy supply in 2100 is expected to grow to 1300–1800 EJ.

Smith et al.61 also point to other negative emission technologies, which could complement BECCS to alleviate the pressure on land that is also needed to feed a growing population, host biodiversity and many other ecosystem services. The dominance of BECCS in the current scenarios may be due to the fact that other options (see Table 2) are not included in the models. Incorporating other negative emission technologies could potentially lead to a lower uptake of BECCS, assuming that these other technologies are cost-competitive in comparison to BECCS, especially in scenarios limiting CCS and/or biomass use.

3.1.4 Outlook: the future of CCS in IAMs. As the IAM community is moving towards producing input for the Special Report on 1.5 °C – upon invitation from the UNFCCC – in order to inform climate negotiations at COP23 in 2018 (and eventually the sixth assessment cycle), there are two developments, which could alter the role of CCS in their models.

The first is related to the above-mentioned concerns with respect to the high share of BECCS in low-stabilisation portfolios. More research along the lines of Smith et al.61 and Fajardy and Mac Dowell63 will help to shed light on the implications for other policy goals such as ensuring food security, as well as biodiversity and other ecosystem services. In addition, as can be seen in the adopted outline for the Special Report,63 climate change mitigation is closely embedded into a broader context of sustainable development, indicating that the new scenarios will also be designed to reflect a wider set of policy objectives.

The second development is the growing body of knowledge on other options for negative emissions and their interplay with what is currently included in the IAMs. There are already some IAMs that are experimenting with the integration of enhanced weathering66 and direct air capture (DAC) is also an important candidate for integration into the IAMs despite current uncertainty on technical performance and cost.67

The main CCS research priorities in IAMs include:

- More within-model studies to understand better the interactions between CCS characteristics and modelled deployment/cumulative storage, which are difficult to discern in model intercomparisons.33
- Update parameterisation with new insights from CCS research and demonstration.
- Within-model studies also to better understand system dynamics.
- Complement with geographically explicit techno-economic engineering approaches and geological suitability analysis to identify key areas for deployment and more realistic potentials.2,68
- Explore scenarios considering technology choice depending on institutional barriers and social acceptance.
- Include other negative emissions options (e.g. direct air capture, soil carbon sequestration, enhanced weathering) in addition to BECCS to decrease competition for storage capacity, and biomass (also other side effects, such as competition for land and water63).
Clearly, as ambitions become higher and action is further delayed, CCS will continue to play an important role in mitigation pathways. Broadening the portfolio of energy options to include CCS would improve the affordability of a near-zero emissions energy system.\textsuperscript{86,87} This is especially true in the case of combining it with bioenergy to generate negative emissions. Yet, especially with respect to negative emissions, many research gaps remain, which will need to be urgently addressed to keep this window of opportunity open.\textsuperscript{70}

\subsection{3.2 Integration of CCS into the electricity system}

The following modelling assessment has been conducted in the context of the UK electricity system (i.e., uses data for the UK). There are a number of similar studies on the UK energy system which evaluate different scenarios.\textsuperscript{50,51,71–74} Also, energy systems in the context of other countries have been evaluated, for example, the US,\textsuperscript{75,76} Greece,\textsuperscript{77} Poland,\textsuperscript{78} or for Europe in general.\textsuperscript{79}

\subsubsection{3.2.1 Background.} The UK is aiming to decarbonise the electricity system.\textsuperscript{86,88} To meet decarbonisation targets, the Committee on Climate Change (CCC) recommends that grid intensity in 2030 should be no more than 50 g kWh\textsuperscript{–1} to 100 g kWh\textsuperscript{–1}.\textsuperscript{83–85} This will allow the partial decarbonisation of the heating and transport sectors via electrification. The UK has also adopted the 20–20–20 targets proposed by the European Commission.\textsuperscript{86} This requires approximately 30% of electricity to come from renewable sources by 2020 to achieve the UK's overall target of 15% of primary energy from renewable sources, e.g., solar, wind and biomass, however, excludes nuclear and CCS.\textsuperscript{86,87} This has led to a suite of policies that have subsidised the production of electricity from renewable sources.

A significant proportion of this has come from intermittent sources such as wind and photovoltaic (PV). In financial year 2014/15, more than 50 TWh (representing 15% of the 340 TWh generated) was from intermittent renewable energy sources (IRES).\textsuperscript{88}

It has been proposed that the UK could generate a very high proportion (if not all) its energy from IRES.\textsuperscript{89–91} However, there are a number of issues that are likely to arise that could be expensive to solve or could ultimately limit the penetration of IRES. The three main factors that may constrain IRES deployment:

1. IRES technologies do not displace firm capacity on a one for one basis, nor do they typically provide ancillary services such as inertia, frequency response, or reserve capacity;\textsuperscript{50}

2. Their intermittent output and the relatively unpredictable element of their output demand more of these ancillary services from the grid than conventional plants;\textsuperscript{50,51}

3. The highly correlated nature of the wind and sun across the UK means that at high penetration level, IRES output is weighted towards periods of surplus and away from times of system shortages. Consequently, the surplus causes wind output to be curtailed and become increasingly lower in value (market cannibalisation).\textsuperscript{92}

Many studies have considered some of the costs that arise from integrating IRES.\textsuperscript{93} However, in addition to cost, it is vital to include the above issues and consider the need to balance energy, whilst also considering the margin of firm capacity over peak demand and the provision of response, reserve and inertial services. Using the BERIC model,\textsuperscript{94} we provide some new analysis of these issues here.

\subsubsection{3.2.2 Modelling the system.} Input data on technology costs were based on the nth of a kind (NOAK) “medium” costs published by Parsons Brinckerhoff (PB) on behalf of the former Department of Energy and Climate Change (DECC).\textsuperscript{55} The Department of Energy and Climate Change (DECC) is part of the Department for Business, Energy and Industrial Strategy (BEIS). In July 2016, the Department of Energy and Climate Change (DECC) merged with the Department for Business, Innovation and Skills (BIS) to form the Department for Business, Energy and Industrial Strategy (BEIS).

The carbon price was set at £70 per t\textsubscript{CO2} for most runs described here, except for some sensitivities run at £100 per t\textsubscript{CO2}. Captured carbon had a total burial cost of £19 per t\textsubscript{CO2} to cover all downstream costs as in the reports by PB.\textsuperscript{95,96} Other commodity costs were gas at 75 p per therm and biomass at £23.23 per MWh thermal HHV basis, making biomass-fuelled power plants slightly more expensive than a combined cycle gas turbine (CCGT) at full load.

Taking these inputs gave a full load cost of nuclear of £87 per MWh which compares well with Hinkley’s nth of a kind strike price of £89.50 per MWh.\textsuperscript{97–98} Onshore wind would need £81 per MWh which again compares well with payments under the Renewables Obligation (RO) which came out at an average of £84 per MWh in 2015/16.\textsuperscript{99} Note that the reported strike price for CCS varies from £90 per MWh (gas-CCS in 2030) to £100 per MWh (coal-CCS in 2030).\textsuperscript{100} However, if technology learning is taken into account, the cost of CCS may reduce to be £85 per MWh, enabling CCS to be competitive with other forms of clean energy.\textsuperscript{101}

The availability profile for wind was based upon the generation reported to Elexon during 2012 which, of the five years examined, had the most typical characteristics.\textsuperscript{102} PV availability was simulated using a curve rising from zero at sunrise to maximum at noon back to zero at sunset. This was randomly scaled by a factor between zero and 1 to represent the daily variability of insolation, and scaled again to give the expected

\begin{itemize}
  \item Market cannibalisation refers to the effect of decreasing market price that occurs with increased production of intermittent renewable energy. The reduction in market price is due the following reasons: (i) highest production of wind and solar energy does not coincide with the peak electricity demand, and (ii) market value tends to reduce with increased market share.
\end{itemize}

\begin{itemize}
  \item In July 2016, the Department of Energy and Climate Change (DECC) merged with the Department for Business, Innovation and Skills (BIS) to form the Department for Business, Energy and Industrial Strategy (BEIS).
  \item The agreed strike price of 89.50 per MWh has been fully indexed to the Consumer Price Index. It also includes a price reduction benefit, which is based on the assumption that EDF Energy will distribute the first of a kind costs of the reactors across the Hinkley Point C and Sizewell sites. However, if EDF decides not to invest in Sizewell C, the strike price for Hinkley Point C alone will be 92.50 per MWh.\textsuperscript{97,98}
  \item Examination of the profiles for the last five years showed that the profiles for 2012/13/14 were very similar in shape. However, 2011 had significant fluctuations (more peaks) and 2010 had substantially lower load factors. Thus, 2012 was chosen to represent a typical availability profile.
\end{itemize}
profile for monthly energies as predicted by the JRC online PV tool\textsuperscript{105} for Birmingham.

Demand data was based on 2012 outturns corrected for the small proportion of wind which is embedded and assumed to generate in line with the majority of the portfolio. This calculated consumer demand was then scaled to match the peak energy demand for 2030, derived from the National Grid’s Slow Progression scenario,\textsuperscript{104} which gave an annual energy demand of 317 TWh.

**Scenarios.** The main modelling explored a matrix of scenarios covering all combinations of 9 levels of nuclear penetration (0–40 GW), 8 levels of wind (0–56 GW) and 7 levels of CCS (0–30 GW). For other technologies, capacities were set at levels in National Grid’s “Gone Green” scenario for 2030.\textsuperscript{104} Further sensitivity analysis looked at varying the capacity of each of the 17 technologies in the model one by one away from the central scenario. In all cases unabated gas-CCGT was treated as the “slack variable”, its capacity being adjusted to retain the same derated capacity margin over demand.

**Methodology.** BERIC is a linear program (LP), whose objective function is to minimise short run costs at each scheduling point in the scenario run.\textsuperscript{94} A sample set of 220 half hour “points” are scheduled independently from each other. The model is constrained to stay within the following bounds:

1. Energy demand must be balanced exactly by generation. Demand is given by the 2012 shape scaled to meet peak energy demand of the 2030 Slow Progression scenario.

2. There must be sufficient reserve to meet the requirement at all times. BERIC meets a reserve demand that represents the requirement for frequency response and faster reserve products covering timescales of seconds and minutes. Wind and PV generation creates a demand for reserve cover at a rate of 17% of output (similar to typical values used by National Grid).\textsuperscript{94}

3. There must be sufficient inertia to meet the requirement at all times. It is assumed that inertia levels will be allowed to drop from the current minimum level of 150 GW s down to 90 GW s following recent changes to the grid code that improved tolerance to a higher Rate Of Change Of Frequency (ROCOF).

Generation is scheduled in fleets according to type, so the fleet of CCGTs is scheduled as one, all wind turbines as another etc. However, the solver has freedom to assign any proportion of the fleet to one of four operating states (i) off, (ii) minimum stable generation, (iii) optimum level for providing spinning reserve, and (iv) full capacity. In effect, there are no quanta associated with individual units.

### 3.2.3 Decarbonising the electricity system

**The effect of renewable energy.** Fig. 4 shows the carbon intensity of the grid as a function of wind and nuclear capacity. Following the top blue line where no new nuclear (or CCS) is built, it can be seen that even with 56 GW of wind, CO\textsubscript{2} emissions have only dropped to around 180 g kWh\textsuperscript{-1}. The curvature of the line indicates that further wind build suffers from diminishing returns as emissions reduce – i.e., the available output of wind is increasingly ineffective at replacing fossil generation. This is due to curtailment when low carbon output exceeds demand. The ideal situation would be to have sufficient storage and/or demand side management to be able to make use of all curtailed output.\textsuperscript{51,74} This is represented by the dotted blue line that is tangential to the initial blue curve. Even without output curtailment, CO\textsubscript{2} intensity is 133 g kWh\textsuperscript{-1} at 60 GW wind capacity, greater than the 50–100 g kWh\textsuperscript{-1} target by CCC,\textsuperscript{83–85} which is needed to enable decarbonisation of other sectors through electrification.

The lower curves represent 5 GW increments of new nuclear build. It can be seen that with 20 GW of new nuclear then 100 g kWh\textsuperscript{-1} can be achieved with around 11 GW of wind. The National Renewable Energy Action Plan (NREAP) targets a wind build of 28 GW by 2020 (combined onshore and offshore capacity).\textsuperscript{105} It can be seen that if this is accompanied by about 15 GW of nuclear then 100 g kWh\textsuperscript{-1} is achievable. It should be noted that other firm low carbon plant (such as biomass and CCS) could achieve similar results, albeit with slightly higher capacities to account for their residual emissions.

**Need for low carbon firm capacity.** Fig. 5 shows the carbon intensity with different levels of nuclear, CCS and wind in the grid mix. The two surfaces represent the target of 50 g kWh\textsuperscript{-1} recommended by CCC for deep decarbonisation\textsuperscript{82} and the UK’s Department of Business, Energy and Industrial Strategy (BEIS) central estimate of 100 g kWh\textsuperscript{-1}.\textsuperscript{72} Meeting either of these targets would mean the solution would have to lie on the visible side of the surface. For example, point A is the pure nuclear solution meeting 50 g kWh\textsuperscript{-1}, which corresponds to 31 GW of new nuclear. In the absence of gas-CCS at point C, 56 GW of wind is required, scaling back nuclear build to 18 GW. Adding gas-CCS is less effective at reducing emissions (it was modelled with 91% capture), so 30 GW will only displace 18 GW of nuclear build and achieve the same target grid intensity. This highlights the importance of considering the residual CO\textsubscript{2} emissions. As decarbonisation targets become more stringent, there is the potential need for CO\textsubscript{2} capture of 95% or more (Fig. 5), i.e. minimise/eliminate residual CO\textsubscript{2} emissions.

Table 3 summarises the various technology adoption pathways that will meet the CCC targets for CO\textsubscript{2} intensity (based on results in Fig. 5). Adopting the weaker 100 g kWh\textsuperscript{-1} target\textsuperscript{2,83–85} means a pure CCS (no wind, no new nuclear) solution is possible within the bounds modelled, at just 27 GW of gas-CCS. However, even with 56 GW of wind ("maximise wind" scenario), a significant amount of firm low carbon capacity is required, either 11 GW of new nuclear or 19 GW of CCS.

### 3.2.4 The role of CCS

**Inherent storage and flexibility of the capture plant.** Carbon capture plants of nearly all designs have some additional opportunities (over an unabated plant) to store energy by time shifting energy intensive processes.\textsuperscript{106} For post-combustion, the amine regeneration could be scheduled at times of excess power enabling output to be boosted when required,\textsuperscript{107–113} which could provide reserve, response or firm capacity services.
Fig. 4 The CO₂ emissions in 2030 as a function of wind and nuclear build when unabated CCGT is used as flexible back-up.

Fig. 5 The CO₂ emissions as a function of nuclear, CCS and wind build. The surfaces show the technology deployment requirements in order to meet the CCC targets for CO₂ emissions of 100 g kWh⁻¹ and 50 g kWh⁻¹.
Similarly for oxy-fuel or pre-combustion capture, an oxygen buffer would allow the air separation unit (ASU) to run independently of generation so energy was not sapped at times of high export value (e.g., operate ASU during off-peak electricity demand).\(^{114,115}\)

In a system with a growing proportion of generation from low running cost options, such as IRES, the value of energy is likely to decline, and the supply of some grid services and firm capacity is likely to be limited whilst demand for them grows. Therefore, it is important to consider the balance between IRES and different services (firm capacity, reserve etc.) at the design stage so the full value of a CCS plant can be accessed.

**Value of CCS, nuclear and wind.** Many studies focus on the cost of technologies that can help decarbonise a system and often divide a discounted cash flow with a discounted energy output to give a levelised cost of electricity (LCOE) in £ per MWh. Although this approach has value for the comparison of a homogeneous set of thermal technologies providing a similar service (energy, firm capacity, reserve, response, inertia, etc.), it is no longer relevant when comparing technologies that deliver only a selection of these services, and nor does it account for the effects seen here where the effectiveness of a technology is strongly dependant on the existing grid mix.\(^{50,51,71,94,116}\)

An alternative metric that works for all technologies is the value of technology addition (VOTA), also referred to as system value.\(^{51,116}\) VOTA is defined here as the reduction in annualised total system cost with the deployment of a technology and is in units of £ per MWh of capacity deployed in a given year. Fig. 6 illustrates VOTA of various energy technologies for a number of different scenarios in 2030. For a higher carbon price, the value is generally higher (Fig. 6b, d and f), as might be expected. It can also be seen that the VOTA profiles have a similar shape, following a path of continuous additions of a technology eventually leads to an accelerating decline in the VOTA. If the system already has a significant amount of another low carbon technology, the drop-off in the VOTA will start earlier and decline faster. This has also been observed in some recent work by Heuberger *et al.*\(^{51}\) The value of CCS is less affected by the addition of wind to the system than nuclear plant is (Fig. 6c–f). This is due to CCS having lower capital cost and greater flexibility compared to nuclear.

**Competitor technologies.** Fig. 7 shows all the generation technologies that were modelled, starting with a 2030 system that meets 85 g kW\(^{-1}\) by incorporating 10 GW of new nuclear, 5 GW of gas-CCS, 28 GW of wind and 20 GW of PV. The trajectories for each technology represent the addition of more capacity. The left direction of Fig. 7 represents a reduction in emissions, whilst moving upwards corresponds to an increase in total system cost. Most technologies curve more steeply upwards as capacity is added (e.g. marine, PV, offshore wind), indicating the addition of cost whilst becoming increasingly less effective at reducing emissions. To achieve CO\(_2\) emissions of 50 g kW\(^{-1}\), it would take an additional 28 GW of offshore wind, with an addition to total system cost of more than 25%. Adding nuclear would require 6 GW, whereas the addition of gas-CCS requires 10 GW, which results in an additional cost of 3–4%. Biomass moves directly left, indicating CO\(_2\) emissions reduce at no additional cost.

The prediction of which technologies are cheapest is of course entirely dependent on the cost assumptions used. Although the absolute cost of a technology varies with the assumptions used, the curves have been independently shown to exhibit the same functional form. This demonstrates that there is a law of diminishing returns,\(^{94}\) and that this effect tends to be more pronounced for intermittent technologies than firm capacity as with increasing deployment the former delivers energy during increasingly congested periods.\(^{51,74,94}\) In summary, the three classes of technologies that can make significant reductions in emissions with only a small increase in total system costs are: (i) CCS, (ii) nuclear, and (iii) bioenergy.\(^{51,74,94}\)

**3.2.5 What next for system integration?** The decarbonisation of the energy sector will inevitably increase the average cost of electricity generation. The selection of different technologies has a significant impact on the overall CO\(_2\) intensity, value of technology addition and total system cost. It is increasingly recognised that decarbonisation targets (for both 50 and 100 g kW\(^{-1}\) grid intensity) cannot be achieved solely via the deployment of intermittent renewable energy (e.g., PV, wind). To balance the use of IRES in the system, firm capacity technologies are necessary for reliable low/neutral carbon electricity. The modelling of the UK system has shown that only fossil CCS, nuclear or bioenergy could take on this essential role. Some other systems will have additional options such geothermal, reservoir hydro power or even solar + energy storage in a predictably sunny climate. It is these low carbon technologies that will compete with CCS to provide firm capacity and not IRES technologies, which operate in a different market.

The value added to the system by a certain technology is dependent on the existing energy mix and the services that the
technology can provide (e.g., inertia, reserve, firm capacity). Thus, a single number such as the LCOE cannot be used to characterise the performance of a technology. Similarly, value assessment of a single technology in isolation is inadequate. A whole systems approach to valuing technologies and their impact on total system cost would recognise the role of low-carbon technologies in balancing demand and cost. Such an approach would enable better characterisation (e.g., availability, controllability, economic benefit) of different generation technologies within a given energy mix.

3.3 Industrial CCS

A significant proportion of GHG emissions can be attributed to industrial processes,\(^6\) contributing 25% of the global CO\(_2\) emissions.\(^{119}\) Thus, decarbonisation of the industrial sector will be essential to meet the CO\(_2\) emissions targets by IPCC.\(^6\) Some key industrial sectors that have been the focus of CCS studies include cement, petroleum refining, iron and steel manufacturing, and pulp and paper,\(^{120,121}\) with iron and steel, cement and refining being especially “high-emitting”;\(^{119}\) together consuming 38% (43 EJ) of total industrial energy consumption.\(^{122}\) CCS is regarded as a cost effective option to reduce CO\(_2\) emissions from industrial processes.\(^{119,123}\) The physical properties, composition and gas volume flows are different for each industrial process.\(^{124}\) Thus, the suitability and selection of a CCS technology would depend on these stream properties, e.g., CO\(_2\) concentration, moisture content.\(^{125–127}\) The challenge for the industrial sector will be maintaining international competitiveness with the implementation of technologies that reduce CO\(_2\) emissions, but increase costs.\(^{128}\)

3.3.1 Decarbonisation of the iron and steel industry. The industrial sector with the largest CO\(_2\) emissions is the iron and steel industry, accounting for 31% of all industrial emissions.\(^{123}\) Steel production generates high levels of CO\(_2\) emissions due to: (i) being energy intensive, (ii) the dependence on using coal, and (iii) the significant volumes of steel being manufactured.\(^{118}\) The two main steel manufacturing processes are:

- Integrated steel mills, which uses the blast furnace-basic oxygen furnace (BF-BOF) process. Coke is used to reduce the iron ore in the blast furnace to form “pig iron”, which is then converted to liquid steel in the basic oxygen furnace (with an addition of ~ 30% scrap steel).\(^{118}\)

- Mini-mills using an electric arc furnace process and a feedstock consisting of scrap metal, direct reduced iron (DRI) and cast iron.\(^{118}\)

The larger integrated steel mills are the main source of emissions and on average emit 3.5 Mt of CO\(_2\) annually, whereas the smaller mini-mill plants each emit <200 kt of CO\(_2\) annually.\(^{120,121}\) The average CO\(_2\) emissions from a typical steel mill is about 1.8 t\(_{\text{CO}_2}\) per tonne of crude steel, where the major carbon sources are from coal and coke (1.7 t\(_{\text{CO}_2}\)) and limestone (0.1 t\(_{\text{CO}_2}\)).\(^{117}\) Fig. 8 shows that there are multiple sources of the CO\(_2\) emissions within a steel mill process. Of these, the stream from the blast furnace contributes the greatest direct CO\(_2\) emissions (69%).\(^{117}\) However,
this flue gas is not directed to a stack, but instead, the energy in the gas is recovered in the on-site power plant.\textsuperscript{118}

The cost of CO\textsubscript{2} capture in the iron and steel industry is dependant on the type of technology and the location within the process. Most of the research has focussed on applying CO\textsubscript{2} capture in the blast furnace. Post-combustion capture from the BF has been estimated to cost between $65.1–119.2 per tonne of CO\textsubscript{2} avoided, capturing 50–55\% of emissions.\textsuperscript{129–131} A top-gas recycling blast furnace using post-combustion capture can capture 65\% of emissions at $54–88 per tonne of CO\textsubscript{2} avoided.\textsuperscript{132} The mean cost to capture 65\% of total emissions from the blast furnace is $76.6 per tonne of CO\textsubscript{2} avoided. Post-combustion capture from the coke oven will cost an average of $86.4 per tonne of CO\textsubscript{2} avoided (27\% of total emissions).\textsuperscript{121}

In the short term, minimising energy consumption and improving energy efficiency is the most cost effective approach to reducing CO\textsubscript{2} emissions.\textsuperscript{133–137} Some of the measures used to improve energy efficiency include heat loss reduction, heat recovery of waste energy, and efficient process design.\textsuperscript{133,137} Over the years, there have been efforts to reduce CO\textsubscript{2} emissions from the overall production process, such approaches include increased recycling of steel scrap, use of biomass or renewable energy, utilisation of by-product fuels to reduce the use of coke and coal.\textsuperscript{118}

The implementation of CCS technologies could further significantly reduce CO\textsubscript{2} emissions. In integrated steel mills, it is possible to capture CO\textsubscript{2} from the flue gas exiting the lime kiln, sinter plant, coke oven plant, stove, blast furnace and basic oxygen furnace. In the case of mini-mills, the main source of CO\textsubscript{2} would be the electric arc furnace.\textsuperscript{130} Post-combustion capture technology can be applied to these gas streams without affecting the iron and steel making process. Alternatively, an “in-process” capture process could be employed, merging the iron/steel making and the CO\textsubscript{2} capture processes.\textsuperscript{117,138} One such strategy is to use oxy-combustion conditions in the BF to produce flue gas of high CO\textsubscript{2} concentration, which would enhance CO\textsubscript{2} capture efficiency.\textsuperscript{117} Some commercial iron and steel facilities employ CO\textsubscript{2} capture and removal as part of the production process, however, the CO\textsubscript{2} is currently flared. For example, CO\textsubscript{2} is captured as part of some DRI facilities,\textsuperscript{118} the Saldanha steel plant in South Africa,\textsuperscript{139} the Finex process (South Korea)\textsuperscript{140} and HIsarna process (Germany and Australia).\textsuperscript{141,142} To prevent this CO\textsubscript{2} from being emitted to atmosphere, integration of CO\textsubscript{2} storage would be necessary.
In November 2016, the world’s first large-scale application of CCS in the iron and steel sector commenced operation as part of the Emirates Steel Industries (ESI) CCS Project (Phase 1 of the Abu Dhabi CCS Project). The system uses an amine-based absorption process with a capture capacity of 0.8 Mt of CO₂ per year. The CO₂ is subsequently transported through a 43 km onshore pipe to be injected for enhanced oil recovery (EOR) and stored.

3.3.2 Decarbonisation of the cement industry. After clean water, mankind produces a greater volume of concrete than any other product, and considering that each tonne of cement used within it causes the emission of around 880 kg of CO₂ (depending upon the method of production, between 600 and 1000 kg), it is unsurprising that more than 5% of global CO₂ emissions are caused by its manufacture. Approximately 60% of CO₂ emissions from cement production arise from the calcination of limestone (CaCO₃) to form CaO (the main precursor for cement production), with the remaining emissions from the process being from the fuel used to heat the kiln and effect the clinkering reactions. Both sources of CO₂ can be treated at the same combined stack. The intrinsic emissions of CO₂, which are part of the production process, mean that in order to make the scale of emissions cuts necessary to limit anthropogenic warming to 2 °C, CCS is a prerequisite.

There are a number of different CCS technologies that are applicable to cement production; there are several variants of post-combustion CO₂ capture, including solvent scrubbing or the use of solid sorbents, calcium looping, oxy-fuel and “direct capture”. In this context, the most obvious difference between cement production and power generation is that pre-combustion technologies are not applicable. This is because of the large quantity of process-related emissions from calcination of limestone that are not captured when pre-combustion is applied. The technologies are in general (with the exception of direct capture) conceptually similar to their counterparts in power generation, though it is notable that calcium looping utilises one of the feed stocks for cement production (CaO) as its main sorbent; this leads to significant synergies between the cement process and Ca looping. Direct capture has no obvious analogue; it utilises indirect radiative heating of the limestone-containing raw meal feed to the system to “directly” produce a pure stream of CO₂. Both direct capture and oxy-fuelled systems have the potential for efficiency gains within the system, owing to either thermodynamic benefits (direct capture) or a reduction in the total amount of thermal “ballast” in the system by eliminating the nitrogen from air.

The key issue for cement CCS is to ensure that the quality of the product remains the same after the CCS system has been applied. This is the main advantage for a scrubbing system based on post-combustion capture using alkanolamines (or other sorbent-based system). Unfortunately, cement plants are not in general endowed with sufficient low-grade heat to (without the addition of a CHP plant) allow capture of more than around 50% of the CO₂ produced in a cement plant.
One of the first references to a zero emission oxy-fuelled kiln was made in 2006.\textsuperscript{150} The European cement research association has identified oxy-firing of a kiln to be the most potentially beneficial process for the cement industry, and a long-term project has been working towards commercialisation of the process, starting in 2007 with basic literature review, followed by techno-economic feasibility studies. Initially, it was thought that the change in the kiln environment (from air/CO\textsubscript{2} to O\textsubscript{2}/CO\textsubscript{2} etc.) might change the volatilities of minor species within the process. Basic laboratory tests were conducted by the European Cement Research Academy (ECRA).\textsuperscript{151} No significant variations were found in cements produced under oxy-fuelled conditions as opposed to standard cements. Such findings were confirmed recently as part of a G8 project investigating the application of oxy-firing on cement.\textsuperscript{152}

Similar to the conclusions above, minimal changes to cement quality have been observed when simulating at a laboratory scale the application of calcium looping to cement production.\textsuperscript{147,153,154} No changes to cement quality would be expected using solvent-based post-combustion capture. Potential changes to cement chemistry from direct capture have not been tested yet; it is a stated aim of the current EU LEILAC project to conduct such tests.\textsuperscript{155}

The cost of CO\textsubscript{2} capture on cement plants has been studied by a number of researchers, though (as with all other industrial processes) nowhere near as comprehensively as costs for the application of CCS on power generation.\textsuperscript{***120,121} There is a broad consensus in the literature that amine scrubbing is likely to be more expensive than the two other most studied technologies, oxy-firing the kiln and calcium looping. Some recent work by Leeson et al.\textsuperscript{120,122} found that, when adjusted to a consistent year and currency basis, costs for calcium looping were between $20 and $75 per tonne of CO\textsubscript{2} avoided (central estimate $40), oxy-fuel was around $60 (only one estimate was found in the academic literature) and amine scrubbing was significantly higher, between $65 and $165 with a central estimate of $106. The single study referenced in Leeson et al.\textsuperscript{120} was conducted by Mott-MacDonald (with input from Whiteholmean and the British Cement Association) and was a comparison between post-combustion and oxy-fuel capture.\textsuperscript{157} Importantly, this study only considered “partial” oxy-firing, of only the pre-calciner, the sealing of the large rotating kiln, heat transfer changes within the kiln, etc., being considered to be sufficiently challenging that deployment in the “near future with moderate risk” was unlikely. However, it was stated that no “showstoppers” were found in the potential future deployment of a fully oxy-fired system, though this was an area for basic R&D. Post-combustion capture using amine scrubbing was shown to be nearly three times more expensive. This is because of two main issues – the requirement to protect the amines from NO\textsubscript{x} and SO\textsubscript{2}, the clean-up of which necessitates a selective catalytic reduction and wet scrubbing system, respectively; and the heavily increased fuel-burn, owing to the paucity of low-grade heat in the system. One point of note is that because the kiln would not be converted to oxy-firing in the above study, the amine scrubbing system captured significantly more CO\textsubscript{2} (74% vs 61%). It was also noted that integration of a cement plant with a nearby power plant would significantly reduce the costs for post-combustion capture (allowing the transfer of steam from the power station to effect the regeneration of the amines), though presumably similar benefits would accrue if an oxy-fuelled plant were located next to an oxy-fuelled power station with an oversized ASU. A recent paper\textsuperscript{158} examining the application of calcium looping to cement manufacture found that calcium looping had a high avoided CO\textsubscript{2} (94%) in comparison to an partially oxy-fuelled plant modelled (76%); the same group has modelled the integration of a calcium looping system with a power plant and export of the spent CaO to a cement works;\textsuperscript{159} this yields some of the lowest potential costs seen for CO\textsubscript{2} avoidance in cement manufacture, though the fuel-based emissions in the cement plant are not fully addressed. The minimum cost of CO\textsubscript{2} avoided in the combined system was approximately 27 £ per tonne. Of course, such integration would require the co-location of the two plants, which may be geographically challenging.

It was noted in Barker et al.\textsuperscript{157} that building a plant in a far-eastern location would be significantly cheaper (more than 50% cheaper) than building it in a European location. Another study\textsuperscript{160} investigating the application of post-combustion solvent scrubbing to cement production in a similar location (China), but for a retrofit, found a cost of $70 per tonne of CO\textsubscript{2} avoided (in this case, a CHP plant was used to make up for the lack of low-grade heat to regenerate the amines). This paper was one of the first to make the case for “carbon capture readiness” for the cement industry. This subject was also explored by Hills et al.\textsuperscript{145} who also considered the technology readiness levels (TRLs) for different CCS technologies applied to the cement industry. The TRLs for amine scrubbing, calcium looping and partial oxy-fuel were assessed to be at or near to 6, with full oxy-fuel being a little lower (4) and direct capture somewhere in between. This work also made it clear that because cement-plant renovation and capture plant construction are likely to take similar lengths of time, it would likely save time and money to synchronise these. Discussions with cement manufacturers\textsuperscript{161} similarly have underlined the long lifespans of cement plants and the razor-sharp margins in this industry; it has also long been known that some form of tariff is required to maintain a level playing field between regions with regulated CO\textsubscript{2} emissions and those not subject to such controls.\textsuperscript{123,162}

There is a renewed drive to apply CCS to industrial processes. Norcem (in collaboration with its parent company, Heidelberg Cement and the ECRA) has led the way\textsuperscript{163} in terms of testing amines on real flue gases (Aker Solutions) and are also testing solid sorbents (RTI International), and a membrane (DNV and others). As a part of the same test programme, Ca-looping (Alstom) will be tested at IFK, Stuttgart. A 1.9 MW\textsubscript{th} Ca-looping pilot plant is integrated with a cement works at ITRI (Industrial Technology Research Institute), Taiwan,\textsuperscript{164} and has demonstrated capture > 85% in a 7 hour long test; the stated

\*\*\* This is in contrast to activity on commercial deployment of large-scale CCS, where the vast majority of operational projects are in the industrial sector,\textsuperscript{119,156} 15 of the 17, and only two are in the power sector.\textsuperscript{9}

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aim is to progress to a 30 MWth pilot plant. The LEILAC project, headed by Calix Europe is a 21 million euro, 5 year project aiming to demonstrate the direct capture process. Regarding oxy-fuel combustion, ECRA has a current stated aim to develop a 500–1000 tpd pilot plant to be operational by 2019, with a cost between 40 and 60 million euros. The key extra cost component was stated to be the oxygen production facility.

3.3.3 Low carbon petrochemicals and oil refining. The first and most important point to make about the petrochemical sector is its strong underpinning expertise in many aspects of the individual elements and the whole system associated with CCS. This comes about through expertise in managing geological formations and reservoir engineering, offshore technologies, high pressure systems and safety, pipeline design, construction and operation and management of large, multi-partner, multibillion dollar projects with cross-party risk. This is complemented by the large balance sheets, access to low cost finance and comprehensive value chain relationships. Hence, one could argue that any large scale deployment of CCS would most likely be done in partnership with major players in this sector. Ten companies in the sector have recently established the oil and gas climate initiative (OGCI) in recognition of their capabilities and responsibilities in this area.

The sector is responsible for approximately 6% of total global CO2 emissions and these are distributed across the value chain from exploration and production, refining and downstream petrochemical production. Although in this analysis we are excluding the downstream use of the products, it is worth noting that the use of the industry’s products in power generation, heating and transport is responsible for approximately 50% of global emissions.

The relevant experience of this sector is broad, with a comprehensive understanding of relevant issues to CCS: geology, licensing, site operation, safety, high pressure operation/transport, and offshore engineering. Particularly, the oil and gas industry has considerable experience in upstream processing, which involves gas sweetening and produced CO2, as well as CO2-enhanced oil recovery (CO2-EOR) with the associated CO2 transport and injection infrastructure.

An interesting macroeconomic feature of this industry sector is the large swings in crude oil price (e.g. between approximately $40 to $140 per barrel) and that the price differentials that the industry must manage are considerably lower than the marginal cost of CCS applied to different elements of the value chain discussed below. For the sake of argument, assuming that approximately 17.2% of the feedstock is used as internal energy in the process for production, conversion and logistics (assuming an energy return on investment of 11:1 and a refinery efficiency of 91% and a very conservative decarbonisation cost of $200 per metric ton of CO2, the additional cost per barrel of crude oil would be $13, a figure easily contained within the recent price fluctuations, which in turn have been well borne by the end-use sectors.

The downstream sector of the oil and gas industry was particularly challenging to decarbonise, while contributing around 4% of global CO2 emissions. Oil refineries offer a particular challenge here owing to their large, integrated nature, the heterogeneity of these facilities in general and finally the potentially large number of point sources in any given installation (e.g. heaters, furnaces, boilers, crackers and utilities), which themselves have the potential to be diverse in terms of flow rate and composition and which may need innovative concepts in retrofit and exploring trade-offs between aggregating flue gas sources for centralised capture and aggregating CO2 streams.

There are some point sources of CO2 at a refinery that are relatively easy to mitigate, such as catalytic crackers – decarbonisation of these units should be a high priority. It was further noted that decarbonising a complex refinery might require the use of more than one capture technology. A report produced for the UK Government in 2015 estimated that a new, efficient refinery exploiting CCS where most economic could have CO2 emissions which are 36% of a 2012 baseline.

Refineries also benefit from locations favourable to CCS such as being near coasts and/or industrial hubs and therefore should have ready access to CCS infrastructure should it arise. Examples of such locations in Europe include Grangemouth and Rotterdam.

A variety of technologies for carbon capture have been considered for refining, including classical post-combustion capture (e.g. Andersson et al., who explore how excess waste heat can be exploited), oxy-combustion (e.g. Escudero et al., who consider utility boilers and find that it is an economically viable technology under certain scenario assumptions) and chemical looping combustion (CLC). The latter is interesting because the refinery light gases are suitable CLC fuels and from an engineering point of view, refinery designers and operators have experience of engineering and controlling hot solids looping processes in terms of fluid catalytic cracking.

One obvious quick win is the hydrogen production plant (mainly used for fuel upgrading) which by its nature produces a relatively pure stream of CO2 which would require basic post-processing prior to compression and transport.

An important factor to consider is whether the end-use emissions would grow with an increase in hydrocarbon production (considering both conventional and unconventional oil and gas and in particular the scope for increased gas production), and how these emissions can be mitigated at source. This can for example be based on-site hydrocarbon reforming to produce hydrogen with simultaneous storage of the associated CO2 which may have the potential to be a more cost-effective option than the production of hydrogen and the subsequent capture and storage of CO2. Australia and Japan are planning such a supply chain, using Australian coal as the primary resource (initially without CCS) and shipping liquid hydrogen to Japan. More generally, while it is relatively commonplace for countries to produce and distribute CH4 in the future gas exporting countries might reform the CH4 as a matter of course, exporting the resulting H2 and using the CO2 for enhanced oil or gas recovery. This would have the effect of removing concern about CO2 – enhanced hydrocarbon recovery; if the carbon is being immediately returned to the subsurface, then there can be no subsequent CO2 emission when the hydrogen is being used for heat, power or transport.
4 Post-combustion capture technology

This section discusses capture technologies that have been demonstrated at pilot plant scale or higher (i.e., at TRL of 6 or greater).

4.1 Liquid-phase chemisorption technology

The classic chemical absorbent for CO₂ separation applications is 20–30 wt% aqueous monoethanolamine (MEA). It was proposed in the original patent from 1930 for an amine process to separate acid gases and has found widespread use in industry. MEA is particularly suited to low CO₂ partial pressure applications and as a consequence has become the benchmark amine for CO₂ capture from electricity generation. In a standard CO₂ separation process applied to flue gas (10–15 kPa CO₂) at 40 °C, and using 30 wt% MEA and 90% CO₂ removal, typical minimum stripper reboiler duties are ~3.6–4.0 GJ per tonne CO₂ captured. This value has been validated at small to medium pilot scale in a number of studies. The reboiler energy requirement is not the only metric that defines the performance of an absorbent, but reducing this value is the primary goal of much chemical absorbent research, and new absorbents are typically benchmarked against the value for 30 wt% MEA. Rates of mass transfer, stability in the presence of oxygen and elevated temperature, solids formation, toxicity and biodegradability and price are also important in real world flue gas applications. New absorbents are also benchmarked against MEA in terms of these characteristics. MEA has good rates of CO₂ mass transfer, is low cost and readily corrosive when used at higher concentrations.

Research and development of new absorbents for flue gas applications has been ongoing for a number of decades. These new absorbents perform better than MEA in some or all of these characteristics. This suggests it may be time to move on from MEA and choose one of the new generation of absorbents for benchmarking purposes. As an example the formulation of aqueous piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) has been extensively studied. This blend has achieved ~3 GJ per tonne CO₂ captured at pilot scale and also has favourable mass transfer and stability properties. Commercial solvent technologies are also potential benchmark solvents, e.g. Econamine FG+, KS-1, and Cansolv. These advanced solvents contain proprietary blends of amines and have been selected for use in commercial-scale projects.

In the following sections state of the art amine-based and multi-phase chemical absorbents will be discussed. These will be limited to absorbents that have been characterised in detail and progressed from the lab scale at least to small pilot scale testing. The reason being that this is the critical step where absorbents that have performed well in the lab can suffer from unforeseen issues that limit their utility. When numbers for reboiler duty are quoted for amines these will be based on a standard absorber/stripper process configuration without absorbent specific or other process improvements (complete list provided in Table 4). By their very nature multi-phase absorbents require process modifications which makes the comparison less clear-cut.

4.1.1 Single amine absorbents. A large number of amines have been assessed for their individual CO₂ capture performance. Often this assessment is only partial in nature, such as mass transfer or absorption capacity only. Primary and secondary amines react with CO₂ to form a carbamate or bicarbonate reaction product. Which product forms depends upon the stability constant of carbamate formation and the protonated amino group pKₐ. The rate at which the products form is similarly influenced. These chemical properties are a function of the molecular structure. Tertiary amines are unable to form a carbamate as the amino group is saturated and unable to make an additional nitrogen-carbon bond. The overall reactions for carbamate and bicarbonate formation are shown in reaction (1) and (2), respectively. Typically reaction (1) is kinetically faster than reaction (2), however this can depend upon the underlying microscopic reaction steps and is not always the case. It is the extent and kinetics of these reactions, coupled with the viscosity of the absorbent that defines both the rates of mass transfer and the absorption capacity.

\[
\begin{align*}
\text{CO}_2 + 2\text{R}_3\text{NH} & \leftrightarrow \text{R}_3\text{NCOO}^- + \text{R}_3\text{NH}_2^+ \quad (1) \\
\text{CO}_2 + \text{R}_3\text{NR}_3 & \leftrightarrow \text{HCO}_3^- + \text{R}_3\text{NH}_2^+ \\
& \text{(where } \text{R}_3 = -\text{H or } -\text{CR}_a\text{R}_b\text{R}_c) \quad (2)
\end{align*}
\]

Piperazine (PZ) is a cyclic diamine that has been used as a low concentration (<10 wt%) additive to increase the rates of absorption in aqueous solutions of the tertiary amine methyl-diethanolamine (MDEA) by BASF since the 70’s (BASF’s activated MDEA). However, Xu et al. was one of the first investigations to tease out the specific impact of PZ on mass transfer in activated MDEA. Since then, it has been investigated extensively and concentrated PZ has been proposed as an absorbent in its own right at up to ~40 wt% by Freeman et al. and Rochelle et al. Piperazine is of limited solubility unless some CO₂ is present. It reacts very rapidly with CO₂ resulting in fast mass transfer, and being a diamine its capacity for CO₂ absorption is large. It has also been found to resist oxidative and thermal degradation, which allows for higher temperature stripper operation. In pilot scale testing it was able to achieve a 15% reduction in reboiler duty compared to 30 wt% MEA, giving a similar value to PZ/AMP formulations. The main challenges are the potential for precipitate formation and nitrosamine formation.

Aqueous ethylenediamine (EDA) has also been extensively evaluated as an absorbent. It is analogous in structure to MEA but with the hydroxide group replaced by a second amino group. Similarly to PZ, it is a diamine, however both of the amine groups are primary, rather than secondary. The kinetics of the reaction between EDA and CO₂ are slightly faster than MEA, but not as fast as PZ. As would be expected for a diamine its absorption capacity per molecule is larger than MEA, and it has a large enthalpy of CO₂ absorption resulting in elevated CO₂ pressures at stripping conditions. Its thermal...
and oxidative stability have been shown to be similar to MEA limiting stripper temperature to 120 °C. A drawback of EDA is that the replacement of the hydroxide group by an amino group results in larger volatility which will increase the demands on the washing sections during process operation and results in elevated absorbent losses. Pilot plant trials saw reductions in reboiler energy requirement of ~8–11.5% relative to 30 wt% MEA.

Lastly, MEA has itself made a resurgence. Advanced MEA processes are also being developed where MEA is used at concentrations greater than 30 wt%, and additives are used to control degradation and corrosion. For example, if MEA can be used at 40 wt% and other issues controlled via additives the reboiler energy demand can be reduced to 3.1–3.3 GJ per t CO2.

In terms of new amines that are progressing through lab scale bench studies amines containing heterocyclic functionality (that is the amine group incorporated into a ring structure) are of particular interest. PZ is the first heterocyclic amine that has been investigated extensively, however other heterocycles (in particular piperidines) are also being investigated due to the inherent stability of cyclic structures, and the combination of steric hindrance furnishing large CO2 absorption capacities while retaining fast reaction with CO2.

4.1.2 Amine blends. A number of new amine blends have been developed, characterised and tested at pilot scale. The blends of two amines are formulated such that the amines have complimentary characteristics. This formulation is both in terms of the selection of amines and the amount of each (i.e., blending proportions).

The blend of PZ and AMP is probably the best known and well characterised of new absorbent formulations. AMP is a very similar molecule to MEA, but with two additional methyl groups located at the α-carbon position. AMP is a sterically hindered amine highlighted in the work of Sartori and Savage. Being sterically hindered, it has greater absorption capacity than sterically unhindered primary and secondary amines, but it suffers from low rates of CO2 mass transfer at low CO2 loadings. Steric hindrance affects the absorption capacity of an amine by reducing the stability of the carbamate species formed either by crowding of the reactive site and/or electronic effects, resulting in increased bicharbonate formation. However in the case of crowding (which is the case for AMP), it may also affect mass transfer by reducing the intrinsic rate of reaction between CO2 and the amino group. Seo and Hong proposed the addition of PZ and so developed a PZ/AMP formulation. They demonstrated that the addition of PZ increased the rates of mass transfer significantly. Yang et al. then went on to show that the blend of PZ and AMP retains a large absorption capacity for CO2. In terms of stripper reboiler duties, this blend achieves values around ~3.0 GJ per t CO2 or ~20% lower than 30 wt% MEA. Being a blend, there is some variability in these results depending upon the actual composition used. Typically the larger the PZ/AMP ratio, the faster mass transfer is, while the smaller the ratio the lower the reboiler duty. To avoid precipitation the total amine concentration for this blend is limited to about 40 wt% and the contribution of PZ to 10 wt%.

As mentioned previously PZ has been used as an additive to aqueous MDEA to increase CO2 mass transfer for decades. More recently, but in a similar approach, MEA has been assessed as an alternative rate promoting MDEA additive. MEA and MDEA are both well characterised independently. As a blend the overall CO2 absorption capacity is reduced relative to MDEA alone, but is improved at partial pressures relevant for flue gas capture compared to either MEA or MDEA. This blend can also match the rates of CO2 mass transfer determined for aqueous MEA alone. It does not suffer from the potential precipitation issues of PZ/AMP but does suffer from greater rates of oxidative degradation than either MEA or MDEA in isolation.

In pilot scale testing using a synthetic flue gas, a reduction in reboiler duty of ~6–12% was seen relative to 30 wt% MEA. However, in the same work when using real power station flue gas this benefit was lost. This was attributed to the accelerated degradation of the MEA/MDEA mixture in the harsher flue gas environment and highlights the importance of good chemical stability.

No other blends to-date have had the detailed results of trials at pilot scale published in the public domain. However a range of new blends are progressing through bench scale
testing and assessment including ternary blends. These blends are generally constituted by amines that have first been investigated on an individual basis, as this is necessary to identify potential candidates for a blend.

### 4.1.3 Multi-phase absorbents

Two main classes of multi-phase absorbents are under development. The most mature of these are absorbents that undergo a liquid–solid phase transition upon CO₂ absorption. However, liquid–liquid phase separation absorbents are also being investigated. These absorbents undergo phase separation behaviour as a function of CO₂ content. Dual-phase systems reduce the energy requirements in comparison to single-phase absorption systems. The advantages of liquid–solid systems include increases to CO₂ absorption capacity and energy efficiency in the stripper. In the case of liquid–liquid systems, energy consumption reduces due to: (i) the decrease of the liquid amount sent to the stripper, and (ii) a reduction of the desorption temperature (characteristic of biphasic solvents).

#### Liquid–solid separation systems

Aqueous ammonia (NH₃) is the most advanced of the multi-phase absorbent processes. At room temperature NH₃ is a gas and aqueous NH₃ solutions are solutions of a dissolved gas. In aqueous solutions NH₃ reacts with CO₂ to primarily form ammonium and bicarbonate ions and has a number of favourable properties: it does not thermally degrade or oxidise; it is low cost and readily available; it is non-corrosive; it has a good CO₂ absorption capacity; and a low reboiler energy demand for stripping (2–3 GJ per tCO₂). The challenge is the high NH₃ vapour pressure and how losses and emissions to the environment can be controlled, and the formation of precipitates. Commercial technology vendors have been investigating chilled NH₃ processes where absorption is carried out at 0–10 °C. The purpose of the low temperature is to increase the aqueous solubility of NH₃ and concomitantly CO₂, however the low temperatures reduces rates of mass transfer and results in solids formation (ammonium carbamate/bicarbonate) and a multi-phase process. In addition, the low reboiler duty must be considered alongside the additional complexity of liquid–solid processes (changes in design to gas–liquid contactors and heat exchangers and the introduction of liquid–solid separation equipment) and the cooling demand of chilled absorption.

Aqueous potassium carbonate (K₂CO₃) solutions have the advantage of being less volatile, non-toxic, less corrosive, lower cost and more resistant to oxidative degradation compared to amines. Other important advantages of K₂CO₃ is that absorption can occur at high temperatures, also it has a low heat of absorption (CO₂ absorption in K₂CO₃ is 600 kJ kg⁻¹), whereas MEA is 1900 kJ kg⁻¹, reducing the thermal energy requirements of the regeneration process. However, the major challenge is the low reaction rate of K₂CO₃, resulting in poor CO₂ mass transfer. Pilot plant tests using an unpromoted 30 wt% K₂CO₃ solution could only absorb between 20–25% of the CO₂ from the flue gas. To improve CO₂ mass transfer, K₂CO₃ requires the addition of a promoter or catalyst. The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) have developed and optimised the K₂CO₃ processes for post-combustion and also pre-combustion capture of CO₂. The optimised K₂CO₃ technology, named UNO MK 3, can achieve a low regeneration energy of 2–2.5 GJ per tCO₂ (much lower than conventional MEA). These promising results have led to the scale-up and commercialisation of this process by UNO Technology Pty Ltd.

Amino acids, which are amines that also contain carboxylic acid functionality, have also been investigated as CO₂ absorbents. They have favourable characteristics in terms of vapour pressure as they are ionic in their neutralised form and they are resistant to oxidative degradation. Amino acids undergo the same chemistry with CO₂ as amines, with the amino group being the reactive centre. A challenge to their use is they are often of limited solubility and may form precipitates. To-date pilot plant trials of single phase amino acid based systems have not produced favourable results. As a consequence, amino acid based liquid–solid processes are also being developed. In this case the precipitate formed can be either the neutral amino acid or CO₂ containing products depending upon the amino acid used. Similarly to aqueous ammonia reboiler duties are estimated to be in the 2–3 GJ per tCO₂ range, but again the process complexity is increased and there is an additional heat duty to redissolve the precipitates for CO₂ stripping. Commercial technology vendors are also pursuing amino acid based processes.

#### Liquid–liquid phase separation systems

Though they are yet to reach pilot scale, liquid absorbents that undergo a phase separation upon reaction with CO₂ are being investigated. Three types of dual-liquid systems exist: (i) low critical solution temperature (LCST), (ii) mutual solubility type, and (iii) extraction type. In LCST systems, the absorbent solution separates into two phases at a certain temperature range, providing opportunities to reduce energy consumption. However, years of technology research and development reveal that the lower phase absorbs most of the CO₂ and has higher CO₂ loading, however, the total amount of CO₂ absorbed is very low. Thus, the performance of LCST systems is not as promising as anticipated.

Mutual solubility systems consists of at least two amines, where the reaction products of one amine has a solubility limitation with CO₂ in the other. As the reaction progresses, the CO₂ loading and concentration of reaction products simultaneously increase, which drives the formation of two phases. A large range of mixtures exhibit this behaviour, for example the mixture of 2-(dimethylamino)-ethanol (DEEA) and 3-(methylamino)ethanol (MAPA) forms a single phase when CO₂ free but two phases when CO₂ is absorbed. The CO₂ product is concentrated in the lower phase and the upper phase remains mostly DEEA. This formation of a phase concentrated in CO₂ means only this phase need be sent to the stripper reducing the flow rate and sensible heat requirements. It is estimated this could yield reboiler duties of ~2.1–2.4 GJ per tCO₂. The third dual-liquid system is the extraction type, originally proposed by Zhang. Extraction dual-liquid systems can use either one amine or a mixture of amines. The separation
into two phases occurs during regeneration, when the CO₂-rich liquid has been heated to a specific temperature. The two phases formed are an upper organic phase and a lower aqueous phase. The organic phase acts as a solvent, extracting regenerated amine and driving the equilibrium towards desorption, which reduces the regeneration temperature to ~80 °C. Solvent regeneration for extraction type systems only consumes ~2.5 GJ per tCO₂ (MCA + DMCA + AMP). However, the additional extraction step, which involves further heating to recover solvent, consequently leads to a total energy requirement of 3.5 GJ per tCO₂ for the whole process. Unlike the chilled ammonia and amino acid phase separation processes, which have additional cooling and heating duties respectively, along with other process modifications to deal with solids, these phase separation processes only require the introduction of a phase separation unit to the CO₂ capture process.

4.1.4 Outlook for chemisorption solvents. Many new absorbents are under development at the bench scale, however very few have progressed to small scale pilot plant studies outside of the cloistered halls of technology vendors. This testing in a complete process is a critical step for the development of absorbents. Issues that may not be apparent in a laboratory environment come to the fore. For example the hydrodynamics, volatility and degradation behaviour when exposed to high shear gas flows, pumping through pipework and continuous heating and cooling for extended periods is difficult to replicate in any one laboratory experiment. So it is critical that new absorbents that show promise using the traditional metrics of capture performance are moved on to testing at pilot scale. Only this will allow the development of a more complete understanding of the critical factors that ultimately lead to success and failure.

In terms of developing the perfect amine for CO₂ capture, this is a challenging task. The most common approach to-date has been to assess the performance of existing amine molecules. As a consequence of the knowledge gained doing this, there is now considerable understanding of the relationship between chemical structure and absorption performance and stability. The next generation of amines will be less a product of discovery and more a product of targeted task specific molecular design and synthesis, with multiple amine groups having complementary properties contained in single molecules. A few studies have started down this path with initial results looking promising. There is growing interest in water-lean solvents (e.g., ionic liquids, non-aqueous organic amine blends), which exhibit lower reboiler duty and higher mass transfer properties compared to aqueous formulations. However, water-lean solvent tend to be more expensive and testing has been limited to lab-scale (~3 L). As expertise in the relevant synthetic chemistry increases, and these task specific molecules become available in larger quantities and at lower cost, they are likely to outperform and outlast the current suit of amines.

4.2 Adsorption processes for CCS
Adsorption processes were first considered in the early 1990’s as an alternative to solvent processes for carbon capture. Since those initial studies, there has been a growing and sustained effort to develop adsorption technology for CO₂ capture. By far, the greatest research efforts have been directed at developing improved adsorbents with higher working capacity for CO₂, better selectivity, and better tolerance to impurities. New CO₂ capture adsorbents are reported almost daily. The classical adsorbents (carbons, aluminas, silicas, zeolites) and modifications thereof have all been explored for their potential in CO₂ capture applications and new adsorbents (metal organic frameworks, hydrotalcites, amine supported adsorbents, polymers, high temperature metal oxides) have all been explored for their application in a range of areas.

Leaving aside developments in adsorbents, important as they may be, there have also been important developments and progress in adsorption processes for CO₂ capture over the last three decades. A large variety of cyclic processes have been developed, in which regeneration is accomplished by temperature, pressure, vacuum, steam or moisture, or combinations thereof. These processes have been comprehensively reviewed. Novel adsorbent structures and gas-adsorbent device geometries have been proposed and evaluated, such as hollow fibres, monoliths, radial beds, fluidised and moving beds. Hybrid adsorbent technologies have been investigated in which adsorption is coupled with other separation or reaction technologies either as a distinct unit operation or an integrated unit. The application areas for adsorption process have expanded from post and pre-combustion flue gas to process streams (e.g., food and beverage, cement, steel, petrochemical, pulp and paper, and natural gas industries) and direct capture of CO₂ from air.

4.2.1 Advantages of adsorption for CCS. Adsorption is an attractive technology for a number of reasons. It can be retrofitted to any power plant should the adsorption column be optimised to ensure acceptable footprint and cost. In addition, it can cover a wide range of temperature and pressure conditions so that low, medium and high temperatures adsorbents can be used and adsorbents for both pre- and post-combustion settings can be designed – here we focus on low temperature adsorbents for post-combustion (i.e., <200 °C). It is worth noting that adsorption is particularly well-suited for air capture as it involves very low CO₂ concentrations. However, this is beyond the scope of this section. Air capture is discussed in Section 12.2 and further information on air capture using adsorption is available in other papers. While there is no direct and fully comprehensive way to assess the economics and energetics of adsorption compared to those of absorption, many indicators points to the cost reduction enabled by adsorption. Another strength of adsorption is the potentially minimal environmental footprint vis-à-vis amine-based solvents, which tend to decompose and form toxic and/or corrosive compounds. The use of waste materials as adsorbents could
potentially enhance the sustainability of the process, though life cycle assessment would be needed to confirm that aspect. 276

Considering the aforementioned strengths, pilot-scale CO 2 adsorption projects have been proposed and implemented, enabling the community to acquire the knowledge, skills and expertise needed to improve the technological maturity of CO 2 adsorption. Among them, there is the CO2CRC H3 capture project based at the International Power plant in Australia which operated from 2009 to 2011. 277 Besides adsorption, the project also investigated the potential of absorption and membrane processes for CO 2 capture from a coal-fired power plant. Publicly available information on the adsorbents used suggests they were provided by Monash University. The “CO 2 Ultimate Reduction in Steelmaking Process by Innovative Technology for Cool Earth 50” (or COURSE 50) project was launched in Japan in 2008 at an industrial CCS to capture CO 2 from the blast furnace stream at JFE Steel’s West Japan Works. 278,279 The capture system employs PSA and captures 3 ton per day of CO 2 while also evaluating a number of zeolites and activated carbons as adsorbents.

4.2.2 Molecular and process scale challenges. Worldwide projects deploying CO 2 adsorption technology at a large-scale are few compared to those that employ absorption technologies. This gap is particularly striking given the ~120 reviews on carbon capture (including CO 2 adsorption) in the past five years. 2,280–288 One plausible reason for this gap is that the number of possible adsorbent materials is enormous and the task of synthesising and testing them all is daunting. This is particularly so for the case of ‘designer sorbents’ such as metal organic frameworks (MOFs), which counts thousands of compounds already synthesised and millions more that are possible. High-throughput simulation techniques therefore have a key role in quickly screening for successful CO 2 adsorbing structures. One interesting approach uses a global approach to screen thousands of zeolites and MOFs for CO 2 capture solely based on their parasitic energy demand. 289 This methodology is limited however to crystalline adsorbents and does not take into account aspects such as materials robustness to cycling or competitive adsorption with other flue gas components.

The complexity of the screening challenge arising from the multitude of adsorbents is magnified by the plethora of performance criteria to be considered when designing an adsorbent. These criteria have been reviewed recently and are summarised in Table 5. 282 In addition to the criteria detailed in Table 5, we add the energy required for regeneration (linked to OPEX) and chemical and thermal robustness. Although many adsorbents have been tested for CO 2 capture, the focus has only been on their CO 2 uptake, selectivity and recyclability; these criteria are insufficient for the technical confidence needed to move to higher technology readiness levels. Fortunately, researchers have started to combine experimental data with molecular simulation and process-scale modelling. Thus, incorporating multi-objective optimisation enables quantitative comparison of adsorbents against a number of process performance criteria (e.g. purity, recovery, energy consumption, productivity). 290–296 For these studies, one needs to specify the process options, i.e. TSA, PSA or others, and rely on molecular simulation to provide sorption isotherms validated by experiments. It is interesting to note that while the challenge related to the numerous potential sorbents and performance criteria also exists when designing CO 2 capture solvents (absorption), the complexity in the case of solid sorbents is increased because data on mass-transfer resistance and diffusion limitations are scarce, yet are required to model a full adsorption process.

Adsorbents also face a number of process-related challenges. For instance, a pre-treatment step might be required as flue gas impurities, including water, can impair the performance of some adsorbents. In fact, this could be performed by a multi-layer adsorbent bed, as proposed in the CO2CRC H3 project. 277 Heat effects in the adsorption beds poses an additional complication in adsorption process schemes because the inherent exothermic nature of adsorption implies potentially high bed temperature rises (especially in the case of chemisorption). These effects must be quantified, managed and possibly exploited in clever process schemes. 297,298 Studies towards better heat integration are therefore of paramount importance. 297–299 Another challenge pertains to the manufacturing of new adsorbents and the ability to develop new manufacturing processes that enables to strike a good balance between reducing particle size, to enhance good intra-particle diffusion kinetics, and increasing the particle size to limit pressure drop.

4.2.3 Developments in cyclic adsorption processes. There are major engineering obstacles associated with the application of adsorption for CO 2 capture. The advances in cyclic processes improve the commercialisation potential of adsorption technologies, these developments are discussed below.

Pressure vacuum swing adsorption. Cyclic adsorption in fixed beds is now a relatively mature technology and all of the various modes of adsorbent regeneration have been applied to carbon capture. For post combustion flue gas at atmospheric pressure, vacuum swing adsorption (VSA) (also sometimes referred to as Pressure Vacuum Swing Adsorption (PVSAs) since the feed stream might be slightly pressurised) is the logical choice amongst the pressure regeneration modes since the feed stream is mostly nitrogen. A large number of studies of VSA have been carried out, most typically using activated carbon 300–302 and 13 x zeolite

| Table 5 | List and description of adsorbent evaluation criteria as defined in Bae and Snurr 282 Note: y is the molar fraction in the gas phase. Subscripts 1 and 2 refer to CO 2 and N 2, respectively. Superscripts ads and des mean adsorption and desorption conditions, respectively |
|-----------------|-----------------|-------------------|-----------------|
| **Criterion** | **Unit** | **Symbol, equation** |
| Uptake under adsorption conditions | mol kg⁻¹ | \( \Delta N_1 \) |
| Working capacity | mol kg⁻¹ | \( \Delta N_1 = N_1^{\text{ads}} - N_1^{\text{des}} \) |
| Regenerability | % | \( R = \frac{N_1^{\text{des}}}{N_1^{\text{ads}}} \times 100 \) |
| Selectivity under adsorption conditions | — | \( \frac{y_2}{y_1} \times \frac{N_1^{\text{ads}}}{N_1^{\text{def}}} \) |
| Sorbent selection parameter | — | \( S = \left( \frac{y_2}{y_1} \right)^{\frac{2}{12}} \frac{\Delta N_1}{\Delta N_2} \) |
adsorbents\textsuperscript{303--306} and a large number of adsorption cycles have been proposed and tested.\textsuperscript{307,308} The consensus is that if only a single VSA stage is used, significantly deep vacuum levels are required (at least 10 kPa) to achieve specification CO\textsubscript{2} product purity (> 95\%) necessary for acceptable CO\textsubscript{2} recovery using the popular 13\times adsorbent. More exotic adsorbents, such as metal organic frameworks (Mg-MOF 74,\textsuperscript{309} UTSA-16\textsuperscript{202}), may be able to improve this situation in the future but these MOFs are unlikely to be available at large scale in the near term. This has led researchers to examine two stage PVSA systems,\textsuperscript{300,310,311} in which different adsorbents can be used in each stage and there is scope for considerable integration. Of course, the penalty here is a substantial increase in cost. It is also worth pointing out that most PVSA studies have assumed a dry flue gas since the 13\times adsorbent suffers severe CO\textsubscript{2} capacity deterioration in the presence of water although Li et al.\textsuperscript{312} have shown that multilayer beds with 13\times can be used (although at a significant energy penalty) to handle wet gas streams.

The energy demand of the VSA process is frequently cited as being considerably less than conventional amine processes. This is not correct. A range of specific energies from 100 kWh per t\textsubscript{CO2} to more than 1000 kWh per t\textsubscript{CO2} have been reported – the exact number depending greatly on specifics of the process. Most of these quoted numbers rely on unrealistic equations for vacuum pump energy consumption. In one of the few studies in which an experimental energy consumption of 340–580 kWh per t\textsubscript{CO2} was reported,\textsuperscript{305} it was found that theoretical calculations significantly underestimated the true energy required. Reliable reported energies seem to fall between 1.5 to 3 GJ per t\textsubscript{CO2} (electrical). This converts to about 4.5 to 9 GJ per t\textsubscript{CO2} thermal, substantially more than conventional amine solvent processes (reboiler duty of 2–4 GJ per t\textsubscript{CO2}, shown in Table 4). Overall, VSA and PSA appears to be more suitable for smaller scale operation and it is difficult to see these fixed bed processes being extended beyond the 50 MW scale for post-combustion capture unless multiple trains are installed, losing economy of scale. Applications for VSA and PVSA are more likely to be in IGCC,\textsuperscript{311} petrochemical, and steel and cement processes where the gases have higher CO\textsubscript{2} partial pressures and lower volumetric flow rates.

\textit{Temperature swing adsorption.} A more attractive and scalable regeneration option for post combustion capture is temperature swing adsorption (TSA). Generally, both PSA and TSA are considered mature technologies and have been employed for a number of applications in industrial gas separation.\textsuperscript{266,301,314--316} Temperature swing adsorption has been used for removing trace amounts of CO\textsubscript{2} and water from air in Air Separation Units and natural gas dehydration prior to liquefaction. Its application to bulk CO\textsubscript{2} removal is however, in its infancy. Numerous studies have been reported from the groups of Mazzotti,\textsuperscript{317,318} Webley,\textsuperscript{319} and others (Korea,\textsuperscript{320,321} and RTI,\textsuperscript{322,323}), which have highlighted the performance and obstacles of this approach. Joss et al.\textsuperscript{318} developed improved cycles for TSA operation attaining comparable regeneration energies to solvent based processes. In their study, additional purge and recycle steps as well as intermediate heating was used to produce very high purity CO\textsubscript{2} (> 99\%) at high recovery (> 95\%). As their adsorbent was 13\times zeolite, which strongly adsorbs water (thereby reducing its CO\textsubscript{2} capacity), there was a need to dry the flue gas stream prior to their TSA. This adds 2–3 GJ per t\textsubscript{CO2} to the energy requirement (already comparable to amine-based processes).

Pre-drying the flue gas stream is therefore not a feasible option for large scale adsorption based CO\textsubscript{2} capture, which suggests water tolerant adsorbents (in fact, water non-adsorbing adsorbents) may be needed. The voluminous work on amine-based sorbents fills this requirement.\textsuperscript{324}

Conventional TSA run in packed beds incurs the significant penalty of long cycle times due to long heating and cooling requirements. To overcome these limitations, fluidised bed configurations are popular for TSA.\textsuperscript{325,326} The strong mixing enables rapid heat transfer but intense mixing and co-current gas-solid flow leads to lower average CO\textsubscript{2} loadings (the adsorbent is at equilibrium with the gas leaving the fluidised bed). Pirngruber et al.\textsuperscript{327} has estimated a lowest heat of 2.1 GJ per t\textsubscript{CO2} (thermal) for ideal adsorbents under isothermal conditions. More realistically, an energy of 3.2 GJ per t\textsubscript{CO2} is likely. Sjostrom et al.\textsuperscript{328} recently developed and tested a supported amine sorbent in a circulating fluidised bed with adsorption using entrained flow, regeneration \textit{via} a temperature swing with an option for a sweep gas, gas/solids separation, and cooling. A CO\textsubscript{2} removal of 90\% was achieved.

One important variant of the fluidised bed process is the SARC (swing adsorption reactor cluster) process,\textsuperscript{329} in which multiple fluidised bed adsorbers (each one consisting of several counter-current beds, similar to amine absorption) are cyclic through adsorption, evacuation, regeneration (by heating) and cooling. The evacuation step removes nitrogen from the beds (vented to atmosphere) prior to the regeneration step in which the carbon dioxide is recovered. Heat pumps recover heat generated by adsorption and return it to the beds for regeneration. A process integration study of the proposed SARC process in a large-scale pulverised coal (PC) ultra-supercritical (USC) power plant was performed and showed an energy penalty of 9.6\% points for the base case with ammonia as the heat pump working fluid.\textsuperscript{329}

In a process designed to mimic solvent systems (e.g. counter-current flow), moving beds have been investigated in temperature swing modes.\textsuperscript{297,330} The major challenge associated with large scale moving bed processes is that the gas velocity must be kept low enough to prevent the solids from becoming fluidised. This translates to beds with impractically large diameters, not to mention the mechanical difficulties in handling solids in large scale unit operations. Novel structured adsorbents (described in Section 4.2.4) may provide some solutions to these problems.

\textit{Steam, electrical and moisture regeneration.} Many of the TSA systems described above rely on indirect heating or heating with hot gas for regeneration. If low-pressure steam is available, this is the preferred option for TSA implementation. Clearly, water tolerant adsorbents are required and functionalised adsorbents (e.g. amine-based sorbents) are ideal for this application.\textsuperscript{331}
These adsorbents suffer from degradation at very high temperature and poor kinetics at low temperature. Therefore, the preferred operating window is between 60 and 100 °C. Fujiki et al.332 from RITE have overcome the diffusion limitation associated with low temperature operation of amine-based sorbents. This allowed them to use low temperature steam purge (which in prior studies degraded the sorbent and prevented high temperature operation) to assist a vacuum swing cycle. Through this means they were able to obtain high purity (>98% CO₂) and high recovery (>93%) – difficult to achieve with VSA alone. The reported energy consumption of 1.47 GJ per tCO₂ accounts only for the steam usage and apparently does not include vacuum power. A relatively modest vacuum level of 15 kPa was used. This is a promising approach and is worthy of continued effort. Avoiding TSA allowed these workers to retain the use of fixed beds.

Steam regeneration is at the heart of the VeloxoTherm™ Process of Invensys.333 This process is currently under testing to capture CO₂ from the slipstream flue gas exiting a 10 MW e coal-fired unit. This technology utilises the rotary adsorption process with a structured adsorbent (Section 4.2.4) and is based on the design of an existing regenerative air preheater.

Electrical swing adsorption (ESA) has been stated to present an attractive option for rapid thermal (Joule) heating of an adsorbent.334 In this sense, it is a derivative of temperature swing adsorption (TSA). The effectiveness of this option depends greatly on the details of the adsorbent/electrical system. Since the adsorbent must be electrically conductive, both the material and its configuration must offer a continuous electrical path. Packed beds of adsorbent therefore are eliminated from consideration and carbon monoliths are the most common configuration. Since zeolites offer more benefits for temperature swing adsorption given their strong adsorption of CO₂, they are more attractive for ESA applications. Efforts have therefore been made to integrate the zeolite into the carbon monolith walls or pack the zeolite within the carbon channels with some success.335 Grande et al.336 evaluated ESA for CO₂ capture from a Natural Gas Combined Cycle power station where the CO₂ concentration of the flue gas is 3.5%. Using an adsorbent comprising of 70% zeolite and 30% of a binder conducting material to treat this flue gas, it was possible to obtain a concentrated stream with 80% CO₂ with an energy consumption of 2.04 GJ per tCO₂ (electrical). This is equivalent to ~6 GJ per tCO₂ thermal and is significantly higher than conventional amine processes (Table 4). Importantly, the cooling step could be eliminated. It is likely that ESA is more suited to small scale operation where a small process footprint is important.

Moisture Swing Adsorption (MSA) is an intriguing concept evaluated by Wang et al.337 In this scheme (ideally suited for direct capture of CO₂ from air), an amine-based anion exchange resin dispersed in a flat sheet of polypropylene is prepared in alkaline form to enable CO₂ capture from air when dry and releases it when wet. This is a moisture induced cycle, and is a new approach to regenerating CO₂ sorbents – evaporation of water effectively provides the free energy that drives the cycle.

Hybrid systems – sorption enhanced capture and adsorbent/cryogenic systems. Adsorption processes have been integrated with reactors and membranes to exploit synergies between these technologies. Coupling adsorption with reaction is usually undertaken with the goal of shifting the equilibrium conversion by adsorption of CO₂ (one of the products from the reaction). Thus, blending adsorbents with steam reformers,338,339 or water-gas shift reactors is popular.340,341

The latter process (denoted sorption enhanced water gas shift or SEWGS) uses a high temperature adsorbent (e.g., promoted hydrotalcite or CaO) to remove CO₂, driving the reaction to the right hand side and maximising hydrogen production. The sorbent is then regenerated with steam.342 It is particularly suited to coal-based IGCC plants but is also applicable to natural gas plants. In the FP7 project, CAESAR, Air Products, BP, ECN, SINTEF and Politecnico di Milano worked together to develop the SEWGS process, improving the specific energy to between 0.8 to 1.0 GJ per tCO₂ (electric). A new adsorbent named ALKASORB+ was developed with a high capacity resulting in cost of CO₂ avoided for the IGCC application of approximately €23 per tonne of CO₂ avoided. This is almost 40% lower cost than the conventional Selexol process.

The purity of CO₂ produced from adsorbent processes is strongly dependent on operating parameters of the process. In contrast to chemical solvent systems in which 100% CO₂ is produced in the stripper, the CO₂ purity of the blow down gas is strongly dependent on blow down pressure, or, in the case of TSA, regeneration temperature. Therefore, there are considerable savings to be achieved by operating the adsorption system at lower CO₂ purity. This makes adsorption technology suitable for use as a front end “rough” separator, upstream of a “polishing” separator. Conveniently, cryogenic CO₂ capture systems become more cost effective as the CO₂ concentration increases (above ~70%). These systems are extremely attractive for producing liquid CO₂, which may be pumped to high pressure at much lower energy than compression of CO₂ gas. A hybrid process consisting of an adsorption process followed by a cryogenic process is therefore an ideal solution. Li Yuen Fong et al.343 explored this concept, using a vacuum swing adsorption (VSA) process as the initial CO₂ recovery stage. A multi-objective optimisation (MOO) technique in combination with heat integration was used to optimise the total shaft work and the overall CO₂ recovery rate of the capture process (including compression to 100 bar pressure). A minimum energy optimum was determined for the total specific shaft work required at an overall recovery rate of 88.9%, which consumes 1.40 GJ per tonne of CO₂ captured.343 This is considerably lower than conventional processes. A simple CO₂ liquefier was used in this study and there is considerable scope to employ a more sophisticated cryogenic process integrated with the adsorption process.
in the context of CO$_2$ capture, also discussing the development of advanced adsorbent structures.

Zeolites. Zeolites are microporous aluminosilicate minerals that exhibit a crystalline structure with pore sizes typically between 4 and 15 Å and surface areas around 200–500 m$^2$ g$^{-1}$. Both natural and synthetic zeolites exist for carbon capture. The main physico-chemical mechanism for CO$_2$ adsorption in non-modified zeolites derives from the large quadrupole moment of CO$_2$, which enables the molecules to interact with the electric field created by the cations in zeolites. Because cations are introduced into zeolites by charge compensation of substituents, CO$_2$ adsorption is governed by the zeolites framework structure and composition (i.e. Si/Al ratio), as well as the composition and location of extra-framework cations.$^{344,345}$ For instance, the zeolite channel diameter, hence the topology, directly influences the dispersion interactions between CO$_2$ and the zeolite walls. In addition, dual cation sites, i.e. sites where CO$_2$ can interact simultaneously with two cations, are known to favour adsorption.$^{344}$ An interesting phenomenon described recently is the so-called “selective trapdoor effect” or “cation gating effect”, whereby molecules able to interact with the cations located at the entrance of a channel, e.g. CO$_2$, can permeate through the material and be adsorbed while other molecules that do not interact as strongly cannot.$^{346}$ Adsorption can also be enhanced via modifications with large and electropositive, polyvalent cations.$^{344}$

There is considerable industrial knowledge of zeolite manufacturing and its applications in gas separations. From a more fundamental viewpoint, zeolites are crystalline materials and hence can be relatively easily modelled, which can eventually reduce the time needed to evaluate their performance as outlined in Section 4.2.2. The CO$_2$ uptake of zeolites is quite high and in fact, the synthetic zeolite 13 × is often taken as the benchmark of CO$_2$ (low T) adsorbents (capacity of about 3 mmol g$^{-1}$ at 0.15 bar of CO$_2$ and 313 K).$^{347}$ Large scale screening of all known and over 100,000 predicted zeolite structures has been achieved and has identified the best materials for CO$_2$ separations.$^{148}$ The key weakness of zeolites remains their sensitivity to moisture as water adsorbs strongly on zeolites, thereby reducing the CO$_2$ uptake.

Metal–organic frameworks. Another family of porous crystalline adsorbents are metal–organic-frameworks (MOFs). MOFs are obtained via the self-assembly of metal ions and organic ligands (Fig. 9). They exhibit extraordinary surface areas and pore volumes. Typical ligands used to synthesise MOFs include carboxylate and imidazolate compounds, and the metal “nodes” span a considerable range of the periodic table. The size and shape of pores in MOFs can influence its adsorptive properties via a molecular sieving effect.$^{349}$ In addition, chemisorption occurs either via interactions between, (i) CO$_2$ molecules and open metal sites in the MOFs, i.e. uncoordinated metal sites, and/or (ii) interactions between CO$_2$ molecules and functional groups located on the MOF ligands.$^{382,385}$ For examples, studies have shown that one could vary the strength of CO$_2$ adsorption by changing the type of uncoordinated metal sites.$^{385}$ CO$_2$ uptake can also be enhanced by using amine-containing ligands.$^{385}$ In addition, CO$_2$ adsorption in MOFs can be driven by the so-called breathing and gate-opening effects, though at present this behaviour is only observed at high pressures.$^{350}$ In these materials, the pore of the flexible MOFs contracts or opens upon adsorption. The addition of extra framework cations is another factor enhancing CO$_2$ capture in MOFs.$^{362}$

The inherent tunability of the MOFs chemistry and structure represent one of the key strengths of these materials, potentially allowing one to tune the CO$_2$ uptake, selectivity and heat of adsorption. Like zeolites, their crystalline structure makes them ideal candidates for simulation studies. In 2013, MOFs held the record for CO$_2$ adsorption capacity with MOF-74(Mg) exhibiting the highest reported uptake (5.5 mmol g$^{-1}$ at 0.15 bar, 313 K) (Fig. 9).$^{347}$ MOFs are often criticised for their chemical instability as they can react with flue gas components like water, NO$x$ and SO$x$. In recent years though, a number of robust MOF structures have emerged, such as UiO-66 and SIFSIX-6 Zn.$^{349,351,352}$ Unlike zeolites, most MOFs are not yet manufactured at a large scale and for those which are, they are most often supplied as powder rather than a structured adsorbent.

Carbonaceous materials. Carbon-based materials have also been investigated thoroughly for CO$_2$ capture.$^{386}$ This generic term represents a number of distinct materials whose structure is mostly composed of C atoms. For instance, we distinguish between low-cost pyrogenic carbon materials (e.g. charcoal, biochar), activated carbons, carbon molecular sieves, aerogels and carbon nanomaterials (e.g. graphene and carbon nanotubes). CO$_2$ adsorption in these materials relies mostly on physisorption and hence porosity is the predominant characteristic, with a high volume of pores, and particularly micropores, increasing the uptake. It is worth noting that heteroatoms (i.e. O-containing groups) may possibly be present in the materials as a result of the synthesis approach and these groups naturally influence the adsorption mechanisms by introducing desirable chemisorption interactions.

As with zeolites, many carbon-based materials (e.g. activated carbon) benefit from industrial maturity. With the exception of

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**Fig. 9** Example of a MOF. Here the structure of Mg-MOF-74 is shown. This MOF exhibits the highest reported CO$_2$ uptake for unfunctionalised adsorbents.
carbon nanomaterials such as nanotubes and graphene, carbonaceous materials are typically cheap and can be manufactured in large-scale. Owing to their hydrophobic nature, carbon-based materials are not strongly affected by moisture, though a decrease in capacity is often observed compared to the performance under dry conditions. The uptake and selectivity of non-functionalised carbon-based materials, however, are typically lower than those of zeolites. In fact, these performance metrics are limited at low pressure and non-functionalised carbon-based materials are thus preferred for high-pressure separations. Carbon-based materials are good candidates in ESA process protocols.

We note that carbonaceous sorbents could include polymeric compounds, which have also been tested for CO₂ capture. An example of such a polymeric adsorbent would be the so-called “polymers of intrinsic microporosity” (PIMs).354,355 However, these materials are most often investigated in the context of membrane separation rather than adsorption.

Functionalised adsorbents. Chemisorption can be tailored to dominate carbon capture at low pressure, and thus a number of researchers have looked at ways to add functional groups and/or reactive species to the adsorbents described above. This is particularly true in the case of carbon-based adsorbents. N-Containing functionalities have been incorporated either into the carbonaceous structure or into the adsorbent pore space via immobilisation of amine-containing compounds. Amine functionalisation has also been reported for mesoporous silica.353,357 The modification of silica typically follows one of two routes: (i) porous silica is physically impregnated with amine-containing molecules,357 or (ii) amine-containing compounds are covalently grafted on the surface of porous silica.353,357 In the former case, polyethylenimine (PEI) is often selected to modify porous silica owing to its high density of amine groups. In the latter case, the surface of silica is pre-functionalised with a derivatised silane, which can be reacted with amines to form covalent bonds. MOFs have also been impregnated with amine-containing compounds.358–362 A famous example is the functionalisation of a triazolate-based MOF with ethylenediamine molecules.

The mechanisms of CO₂ adsorption on amine-functionalised adsorbents are not as straightforward as one might expect and strongly depend on the type of amines as well as the type of support/adsorbent. These mechanisms include: (i) nucleophilic reaction with formation of a zwitterion or carbamate, (ii) base-catalysed hydration of CO₂ with formation of bicarbonate and (iii) cooperative adsorption process between adjacent amine molecules.353,362 Functionalisation typically enhances CO₂ uptake and selectivity but can limit gas diffusion when large organic molecules are used to modify the adsorbents. Chemical leaching is another typical issue that occurs when N-containing compounds are only physically impregnated on the adsorbent. In many cases amine-modified adsorbents have either not been tested under process cycling schemes or have limited lifetimes under such testing conditions.

While the four classes of adsorbents described above typically form the core of materials used for CO₂ capture, researchers have also tried to combine them and form composites to create synergistic effects and address one or more of the weaknesses of a given compound. Several of these composites are made of a carbon-based nanomaterial (i.e. graphene-based materials or CNTs) and a MOF.363,364

Developments in adsorbent structures. Conventional adsorbents are beaded or extruded of size 0.5 to 2 mm. While convenient for fixed beds, these are poor conductors of heat and prone to gas fluidisation or high pressure drop at high throughputs. For this reason, adsorbent structures have been investigated for CO₂ capture applications.365,366 These structures include monoliths,367 laminated structures or hollow fibres.368–371 The latter have been employed effectively for very rapid temperature swing cycles using either hot water or steam as regeneration agent. The VeloxoTherm™ Process (discussed above) uses a rotary structured honeycomb adsorbent for adsorption and desorption of large volumes of process gas. The temperature swing adsorption cycle is established by the rotation of the structured adsorbent, which completes a full revolution in about 60 seconds.

Thakkar et al.372 recently demonstrated how 3D printing techniques could be used to produce zeolitic adsorbent structures. 3D-printed monoliths with zeolite loadings as high as 90 wt% exhibited adsorption uptakes that are comparable to that of powder sorbents. These are modest early steps but there is great promise for advanced manufacturing to allow creation of cheap, integrated adsorbent/flow devices to achieve unprecedented advances in system performance.

4.2.5 Outlook for adsorption technologies. Since the first work on capturing CO₂ with adsorbents was conducted in the 1990’s, there has been a rapid development in adsorption processes. Adsorption has evolved from technology readiness level (TRL) of 2 (bench scale work) in the 1990s to TRL 5 (pilot scale) today. Some processes have even reached demonstration scale (TRL 7), for example, the dry regenerable sorbents being trialled by KEPCO Research Institute.321 For small scale CO₂ capture applications, pressure or vacuum swing cycles have already been employed in the industry sector to remove CO₂. As adsorbents continue to develop, it is likely that we will see further entry of adsorption processes into areas not suited for solvent processes. For example, the food and beverage industry cannot tolerate chemical based solvents on site and the very low environmental footprint of adsorption processes is a strong advantage.

One key area that needs addressing is that of materials testing and screening. As the research community understands better the performance of adsorbents under equilibrium conditions using a ‘simple’ CO₂/N₂ mixture, there is now a need to ‘challenge’ the materials by running dynamic tests and use simulated flue gas streams. The former aspect will enable to derive the kinetic properties of the various adsorbents and hence provide a more realistic picture of their performance. It is recognised that some kinetic studies have already been reported but they are not yet performed systematically.353 A number of impurities contained in the flue gas could potentially impair the performance of adsorbents and therefore testing involving multicomponent streams are particularly informative. We highlight here recent work on the
The development of a high-throughput analyser enabling multicomponent equilibrium experiments.\textsuperscript{373} Using this set-up, it was found that of the adsorbents studied, those containing allylamines performed well for CO\textsubscript{2} capture in the presence of N\textsubscript{2} and H\textsubscript{2}O. Further work around adsorber design is also crucial to allow faster cycles since it will directly influence the overall process. While the commonly proposed bed contactors include fixed bed, fluidised bed and moving bed,\textsuperscript{287} we note here the recent development of a rotary wheel adsorber to allow fast TSA cycles.\textsuperscript{374} Such rotary systems are incorporated in the Inventys\textsuperscript{35} CO\textsubscript{2} capture technology.

Industrial scale formulation of some of the novel advanced adsorbents (discussed in Section 4.2.4) will become increasingly important. To be integrated in a process, the materials must be manufactured as structured adsorbents, e.g., pellets, beads, monoliths, fibres. This is particularly true in the case of MOFs, which are still largely synthesised in a powder form. There are indications this is changing, as demonstrated by, for example, BASF and small companies such as the MOF company, NuMat, and Mosaic Materials. In the near future, we can expect the emergence of a number of spin-outs and start-ups producing MOF in different formats, e.g., Immaterial. Research studies have also started investigating the incorporation of MOFs into structured supports such as fibres and monoliths.\textsuperscript{375–381}

As we have amassed more knowledge concerning CO\textsubscript{2} adsorption, CO\textsubscript{2} adsorbents and their performance metrics from different experimental and computational viewpoints, there is now a need to consolidate that knowledge and propose a combined multi-scale approach to the development of CO\textsubscript{2} adsorbents and adsorption technologies. The examples of recent studies highlighted above are beginning to move towards that direction.

For mid-scale CO\textsubscript{2} capture applications, recent advances in adsorption technology are providing low cost and low energy options, thus potentially offering an attractive alternative to liquid scrubbing systems. Some promising developments include adsorbent structures, hybrid amine sorbents, low quality steam regeneration and rapid cycling. However, for large scale processes, it is unlikely that adsorbent technology will be competitive against established liquid scrubbing systems due to the complexity of large scale solids handling. Hybrid sorption enhanced reactive systems such as SEWGS have a strong role to play, particularly as hydrogen is promoted as an energy carrier in some economies. In a relatively short time, adsorption processes have developed rapidly and the future looks bright for further development and deployment in a range of CO\textsubscript{2} capture applications.

### 4.3 Calcium looping technology

Calcium looping (CaL) technology is a relatively new alternative for post-combustion CO\textsubscript{2} capture, and is based on the following reversible reaction:

\[
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2 \quad \Delta H = -178 \text{ kJ mol}^{-1} \quad (3)
\]

Although the use of lime as a means for removing CO\textsubscript{2} from hot gases is over 100 years old, the idea of using it in a reversible scheme to strip CO\textsubscript{2} from flue gases is relatively new\textsuperscript{382} and can be represented schematically by Fig. 10. Implicit in such a cycle is the requirement that the lime product be used in multiple cycles in order to minimise the costs, and increase the overall efficiency of the process and this demands the use of a carbonator and a regenerator, normally envisaged as being a small oxy-fuel power plant to regenerate the spent sorbent and produce a pure stream of CO\textsubscript{2} for storage, or possibly use (see Fig. 11).

Three key factors distinguish CaL from the other CCS technologies. First, because the carbonator/calciner can serve as a heat source for a steam cycle to produce additional power, the energy penalty associated with the technology can be several percentage points lower than that of conventional amine scrubbing.\textsuperscript{383,384} Second, the sorbent used, namely limestone, is available in industrial quantities, and is also a non-hazardous chemical whose price is of the order of £10–20 per tonne (~US$13–26 per tonne). In contrast, the cost of amine solvent MEA is much greater at US$1.8–2.9 kg\textsuperscript{-1}.\textsuperscript{385,386}

The third benefit of CaL is that there is a possibility of using the spent sorbent in industrial processes such as cement making, which, since lime manufacture represents 50% or more of the CO\textsubscript{2} output in cement production, offers an approach to partially decarbonise the cement industry\textsuperscript{153} or even to achieve near-zero emissions by incorporating the technology into the cement manufacturing process.\textsuperscript{145,387–389} Finally, there exists substantial capacity worldwide to take most of the spent sorbent from CaL should it become a dominant technology.\textsuperscript{390} For instance, spent CaL sorbent can be used in the production of cement clinker,\textsuperscript{153,154} ocean liming, steel manufacturing (to make slag or capture CO\textsubscript{2}), or for flue gas desulphurisation.\textsuperscript{390}

CaL technology has also been progressed to pilot scale. There are two major demonstration projects, one at the University of Darmstadt, in Germany\textsuperscript{191,192} and one in La Pereda, Spain,\textsuperscript{193} which have been used to extensively test circulating fluidised bed-based technology, and a 1.9 MW\textsubscript{th} pilot plant, which combines a bubbling fluidised bed carbonator and a rotary kiln calciner, in Taiwan that has been reported to have run for over 1 year.\textsuperscript{164} Based on its work, Industrial Technology Research Institute (ITRI) estimated that the integrated CaL process would offer a carbon capture cost of less than $30 per tCO\textsubscript{2}.\textsuperscript{394} These demonstration projects mean that the technology has achieved a technical readiness level of 6.\textsuperscript{395} Moreover, there is now an extensive number of small pilot plant facilities worldwide\textsuperscript{396} being used to address various aspects of the technology, from looking at aspects of CaL, such as sorbent attrition, and the behaviour of modified and synthetic sorbents to improve their overall performance, to the development of novel configurations for CaL applications.
experienced in real fluidised beds, as opposed to the more benign testing environment which is normally provided in a thermogravimetric analyser (TGA), which is still the most common tool used to investigate sorbent performance.

It was gradually recognised that the typical TGA environment used to assess sorbent performance was associated with major flaws. In particular, the chemical environment was unrealistic as it missed both the positive effects of water addition on capture and the negative effects of SO₂. More importantly, calcination in N₂ or environments with low levels of CO₂ at temperatures of 850 °C or below is unrealistic and tends to overestimate sorbent performance. In real systems, it appears that

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**Fig. 10** Schematic of the calcium looping (CaL) cycle.

**Fig. 11** Calcium looping within a post-combustion capture process. Note that some units of operation may generate power (e.g., the carbonator), whereas the GPU and ASU requires a power supply.
the water content typical of a combustion environment (10–20\%) partially compensated for the presence of SO₂,\textsuperscript{401} but higher temperatures necessary to drive calcination in the presence of nearly 100\% CO₂ always led to a significant deterioration in sorbent performance regardless of the modification process involved.\textsuperscript{402,403} It is also interesting to note that He et al.\textsuperscript{404} have reported a beneficial effect of steam on the ability of carbide slag to capture CO₂. Finally, it is worth noting that steam has been shown to produce clear beneficial effects on the carbonation process; it also appears that it can produce significant benefits in improving sorbent performance when it is added to the calciner of a 100 kWth pilot plant.\textsuperscript{405} These benefits do not appear to be related to a lowering of the calcination temperature due to the reduction in partial pressure of CO₂\textsuperscript{406} but instead it has been suggested that they are associated with reduction in sintering produced by the lower CO₂ levels in the calciner.

Despite ample evidence to the contrary, numerous studies on sorbent performance are compromised by the use of low calcination temperatures and unrealistic chemical environments. This has been pointed out again recently by Clough et al.,\textsuperscript{407} who have suggested a novel TGA protocol to ensure more realistic results are obtained on modified sorbent performance.

Sorbent attrition is another area which has received attention over an extended period. Although there are limestones that perform extremely poorly,\textsuperscript{408} the fact that there are both fully operational demonstration units and a large number of pilot plants\textsuperscript{396} is a clear indication that natural sorbents can perform adequately in CaL processes. Nonetheless, numerous attempts have been made to improve sorbent performance by various kinds of treatment, most notably pelletisation with a support material, often with mixed results (and a critical issue in such evaluations is again that tests be performed under realistic fluidised bed conditions).\textsuperscript{409} Another critical question for all such attempts is that the cost of such approaches may easily outweigh any benefit in terms of potentially superior performance and/or mechanical resistance.\textsuperscript{410} An interesting result from the work of Erans et al.\textsuperscript{411,412} is that some additives may actually weaken the resulting sorbent, and this is only apparent when tests are performed under fluidised bed conditions and that this phenomenon counters any reactivity benefit associated with the additive, in this case flour incorporated into the pelletised matrix, to serve as a representative form of biomass addition.

\subsection*{4.3.2 Sorbent enhancement and sorbent reactivation.} Erans et al.\textsuperscript{411} have recently provided an overview of the various approaches used to improve the performance of sorbents in Ca looping. These range from hydration, re-carbonation, doping with various reagents, pre-treatments by materials such as organic acids, and re-pelletisation of spent sorbents, as well as the use of methods such as thermal pre-treatment or preparation of extremely active sorbents by techniques like sol–gel or precipitation of calcium carbonate or the preparation of nano-materials. A number of interesting insights have been obtained from this work. Thus, for instance, treatment with organic acids to produce reactive sorbents now appears to be due more to the production of a reactive physical matrix in the sorbent rather than to the chemical changes produced by creating a Ca salt of the organic material.\textsuperscript{413} Earlier work also demonstrated that pore-size distributions of the sorbent and the changes thereof with cycling/doping are responsible for the differences in reactivity of different limestones.\textsuperscript{414,415}

The importance of the final physical matrix in terms of ultimate performance of a Ca sorbent has been further demonstrated by mixing low levels of biomass into a pelleted matrix, and observing a significant improvement in sorbent performance,\textsuperscript{416} which as noted above does not necessarily lead to superior performance in a real fluidised bed system as the resulting material becomes more susceptible to fragmentation and attrition. It should also be noted that while this discussion is focused on limestone, there are many natural Ca-based materials, some of which may well have superior performance, and there is a significant body of literature on the potential of various such materials, some of which appear to have superior capture performance (e.g., waste marble powders\textsuperscript{417}); however, the key issue here will be the overall amounts of such material available for significant removal of CO₂ from industrial processes and power production, which is the primary reason for restricting this discussion to limestone and sorbents derived from it, rather than looking at other materials potentially available.

Hydration to form Ca(OH)₂ at temperatures below 500 °C is beneficial due to the formation of cracks in the CaO particles creating paths to the interior of the particles and, therefore, improving CO₂ capture.\textsuperscript{418–421} Another positive effect of hydration is the formation of larger pores; unfortunately, this is also associated with weakening the sorbent matrix, and so any potential benefit can easily be outweighed by sorbent loss due to attrition and elutriation. The hydration reaction:

\begin{equation}
\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca(OH)}_2 \quad \Delta H = -109 \text{ kJ mol}^{-1}
\end{equation}

can be carried out at high pressure to avoid cooling the sorbent and thus reducing the parasitic energy consumption, but this would involve the use of a high-pressure vessel and, at least at this time, it seems likely than any benefits associated with this approach will be outweighed by the potential complexity and cost of such a sub-system.

An alternative to steam reactivation is to recarbonate the spent sorbent. This was first suggested by Salvador et al.,\textsuperscript{422} who proposed that recarbonation in high concentrations of CO₂ might be a reactivation strategy. Sun et al.\textsuperscript{423} subsequently showed that marginally increasing the carbonation times had a positive outcome on the capture capacity over several cycles. Chen et al.\textsuperscript{424} stated that extending the carbonation time substantially helped to recover some capture ability of the sorbents and although this recovery decreases with increasing number of cycles, the samples that experienced extended carbonation time showed better reactivity than those that did not. Further work demonstrated that carbonation time has a robust effect on carrying capacity. If the carbonation time increased, then the residual conversion also increased.\textsuperscript{425} More recently, the benefits of a recarbonation
strategy were explored with the 1.7 MWth, La Pereda plant in Spain, and it was reported that an improvement in sorbent performance of 10% in CO₂ carrying capacity of the sorbent was achievable, if the solids were allowed sufficient residence time in the loop seal, which acted as a recarbonator in this work.⁴²⁶

4.3.3 Hybrid systems. Although this review focuses primarily on the direct use of Ca looping for post-combustion capture, it should be noted that the technology lends itself to many other applications. Thus, for instance, CaL can be used for CO₂ capture in gasification processes⁴²⁷ or enhanced reforming processes for hydrogen production.⁴²⁸,⁴²⁹ There has also been some attempts to explore the possibility of combining the technology in various cycles with Chemical Looping Combustion (CLC), possibly with the reduction of CuO providing the heat for calcination, thus eliminating the need for an oxy-fired calciner. Initial work in this area focused on making core-in shell pellets of combined CaO/CuO and testing them in a TGA environment,⁴³⁰ and more recently there has been an effort to model the performance of such particles.⁴³¹

In experiments with combined CaO/CuO/calcium aluminate cements, Rahman et al.⁴³² have obtained results which suggest this is possible, albeit that they reported a decline in the oxidation potential of such pellets in a gasification environment. Duhoux et al.⁴³³ have carried out simulations for a process combining CaL and CLC for CO₂ capture and report that a combined CaL–CLC process could show a 10% process efficiency gain, and interestingly increased power output.

Another interesting possibility is combining CaL with thermal storage. At the simplest level, producing CaO from CaCO₃ offers the possibility of thermal storage by itself.⁴³⁴ In principle, this can be combined with other thermal energy storage options and Hanak et al.⁴³⁵ suggest that this option with cryogenic O₂ storage has the potential to increase the profitability of an integrated system over that of a reference coal-fired power plant without CO₂ capture.

There has also been increasing interest in combining CaL technology with solar power.³⁸⁹,⁴³⁶–⁴³⁷ In this case the goal would be operate the calciner using solar energy, and if this is successfully achieved the calciner could serve as part of a conventional CaL cycle and/or a source of thermal energy storage.

4.3.4 Novel configurations. Currently, most suggested embodiments of CaL involved dual fluidised beds, although other designs have been suggested or used for the calciner (e.g., rotary kilns, or fixed beds). In terms of improving the operation of such systems the calciner seems to be the most promising sub-system for substantial modification. Thus, Lara et al.⁴³⁸ have suggested that better heat integration and the development of a cyclonic preheater to increase the temperature of solids entering the calciner might be one such option. Other options might be to operate with very high oxygen levels to the calciner and depend on the calcination reaction to control temperatures, and this is the subject of a current Research Fund for Coal and Steel EU project.⁴³⁹

4.3.5 Outlook for calcium looping technologies. CaL is a rapidly evolving technology, which has considerable potential for post-combustion CO₂ capture. At the current stage of development its overall technical readiness level can be assessed as TRL 6, based on the existence of a number of pilot plant units at the several MWth stage. However, developments are progressing to allow it to be combined with CLC, or used in thermal storage applications or for the production of hydrogen. Significant developments are also being made to combine it with various industrial processes, most notably that of cement production.¹⁴³,¹⁵³ However, at the current time there are no larger demonstration units, and these are urgently needed before the technology can become fully commercialised.

5 Next generation CO₂ capture processes

This section considers next generation CO₂ capture technologies. These have been studied extensively, however, compared to conventional capture technologies (liquid-phase or solid-phase sorbents), they are in the earlier stages of development. These “new generation” technologies show particular promise in high temperature applications, with potential opportunities for use in process intensification.

5.1 Chemical-looping, progress and prospective

5.1.1 Background and history. The idea of chemical looping is not new, and has pedigree dating back to the early 20th century or earlier, and there is now an extensive body of literature on it (see for example the reviews of Adanez et al.⁴⁴⁰ and Fan et al.⁴⁴¹). In its most basic form, chemical looping involves the use of a solid metal oxide (an oxygen carrier) to transfer oxygen to a process stream, in effect allowing air separation to be carried out by the reversible reaction:

$$\text{MeO} \leftrightarrow \text{Me} + \frac{1}{2}\text{O}_2$$  (5)

where Me is some reduced phase, typically a metal or a metal oxide. Common examples include transition metals e.g. oxides of Fe, Mn, Cu, Co. The “simple” transition metal oxides undergo a reconstructive phase change to give up oxygen, and this is often seen as detrimental to longevity. Other more complex mixed oxides, such as those based on the perovskite structure, release oxygen without undergoing a phase change but are more costly and frequently have low uptake of O₂. The transfer of oxygen using reaction (5) can be used for a number of processes relevant to carbon capture depending on the equilibrium partial pressure [pO₂] that the reaction produces; in order of increasing pO₂: air separation chemical looping with oxygen uncoupling (CLOU) chemical looping combustion (CLC) chemical looping hydrogen production or fuel reforming. Fig. 12 illustrates a typical chemical looping combustion process configuration.

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³³ Perovskites have a cubic structure and formula ABO₃, where A and B are the ions at the vertices and centres respectively (e.g., in the mineral perovskite A = Ca²⁺, B = Ti⁴⁺). Their usefulness in chemical looping arises from the fact that they can show variable non-stoichiometry δ allowing a limited amount of oxygen to be transferred without reconstructive phase change. The variable stoichiometry also allows conduction of oxygen ions through the lattice.
One of the first uses of chemical looping was the Brin process used to manufacture gas phase oxygen (reaction (6)). The reaction has a sufficiently high oxygen partial pressure at \( \sim 700 \, ^\circ C \) that gas phase oxygen can be produced in the forward reaction (at 0.05 atm). The reaction is reversed by lowering the temperature and increasing the partial pressure of oxygen.443 The Brin process fell out of favour with the introduction of the Linde process based on cryogenic air separation. More recently this approach has been investigated under various names, including ceramic auto-thermal reforming,444 and chemical looping air separation (CLAS).445 The former using perovskite material, and the latter using materials such as copper oxide.

\[
\text{BaO}_2 \leftrightarrow \text{BaO} + \frac{1}{2} \text{O}_2 \quad (6)
\]

5.1.2 Motivation and current research. Why the interest after 100 years given the advantages of other commercially available processes currently used for air separation in e.g., oxy-fuel combustion? The large heat of reaction typically involved in the metal oxide redox reaction would initially seem to rule out using reaction (5) for air separation. Indeed, membrane processes in which oxygen is transferred through a metal oxide structure have many similarities to chemical looping and do not require the addition or removal of heat.446 The answer lies in the temperature at which these processes run. Traditional carbon capture processes are based on low temperature absorption or oxygen production via an air separation unit. Thermodynamics requires work to be expended to separate gases, either the CO₂ from the flue gases or O₂ from air. This work can be provided as heat with a certain capacity to do work (i.e., exergy) or directly as compression work. In low temperature processes, the work is taken directly from the power station, for example, steam bled from the turbine is used for amine scrubbing, steam whose exergy would otherwise have been used to generate electricity. Running a high temperature cyclic process overcomes this limitation in number of ways. Firstly, the heat rejected from the cyclic chemical looping process is at a temperature above the turbine inlet temperature (for a steam plant), meaning that all the heat released can be recovered back into the power cycle. Secondly, heat release from combustion would normally be transferred from a hot flame, to a relatively cold steam cycle, destroying a large amount of the heat's potential to do work. The combustion reaction itself also destroys exergy. Using this heat instead to separate gases, before it is transferred to the power cycle, uses work potential that would otherwise have been lost.

A similar argument can be made for chemical looping combustion, in which the fuel is brought into direct contact with the metal oxide. Here, the exergy loss associated with the combustion reaction itself is partially avoided. Chemical looping combustion was originally proposed as a way to increase the efficiency of fossil fuel power station because it avoided the exergy loss associated with combustion.447 Materials for chemical looping combustion need to operate with an equilibrium \( p_{O_2} > O \left( 10^{-5} \right) \); this ensures that the partial pressure of CO (or other un-combusted fuel) is low at the exit of a well-mixed reactor. Iron oxide for example has several oxidation states which can be used to transfer oxygen, the Fe₂O₃ to Fe₃O₄ transition has a \( p_{O_2} \) of \( \sim 3.6 \times 10^{-7} \) bar at 900 °C which means that, at equilibrium, the ratio of CO to CO₂ would be \( \sim 1 \times 10^{-5} \), i.e. near complete combustion.

5.1.3 Chemical looping for power production and scale-up. For power production, chemical looping combustion has gone from small scale tests in the laboratory, through to pilot scale at the tens of kilowatts through to a scale of around 1 MW (e.g., the 1 MWth unit at Damstadt448). Most work has focussed on interlinked fluidised beds, in which the oxygen carrier is circulated between two fluidised reactors. In the reducer, the MeO gives up oxygen to the fuel to produce CO₂ and water. The reduced oxygen carrier (Me) is then carried over into a cyclone where the solid is separated from the gas phase and sent to an oxidiser where Me is regenerated, taking in oxygen from the air. The regenerated oxide MeO is then returned to the reducer for another cycle.

![Typical chemical looping combustion (CLC) process. The metal oxide oxygen carrier (MeO) is circulated between two fluidised reactors. In the reducer, the MeO gives up oxygen to the fuel to produce CO2 and water. The reduced oxygen carrier (Me) is then carried over into a cyclone where the solid is separated from the gas phase and sent to an oxidiser where Me is regenerated, taking in oxygen from the air. The regenerated oxide MeO is then returned to the reducer for another cycle.](Image)

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad (7)
\]

\[
\text{CO} + \text{H}_2 + 2\text{MeO} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{Me} \quad (8)
\]
This can mean that the rate of solid fuel conversion is actually limited by the rate of gasification of the solid fuel.\textsuperscript{453,456} Research into the kinetics of the gasification reaction has a long history, beyond the scope of this discussion, however, two important features of relevance to chemical looping are: (i) the big differences in reactivity between different kinds of chars, and (ii) the effect of product inhibition. CO and \( \text{H}_2 \) retard the rate of gasification, so when gasification is carried out in the presence of a solid oxygen carrier, the gasification rate is accelerated.\textsuperscript{456–458} This acceleration rate, although significant, does not lead to an order of magnitude change in the rate of gasification. This means that for coals which produce un-reactive chars, the build-up of char in the system is problematic. The problem is compounded by the use of interlinked reactors if the char is recirculated to the air reactor, where it can burn releasing \( \text{CO}_2 \) back into the environment.

Two strategies for dealing with the low reactivity char are to: (i) physically separate the char from the oxygen carrier using carbon strippers\textsuperscript{459} or (ii) increase the rate of char conversion using CLOU combustion.\textsuperscript{460} In the former, the difference in density is used to separate the char from the oxygen carrier and return it to the fuel reactor, allowing a larger inventory and increased carbon conversion rate. In the latter, oxygen carriers which release gas phase oxygen can be used to increase the carbon conversion rate. Copper\textsuperscript{II} oxide\textsuperscript{461,462} and manganese based materials (e.g., mixed oxides of iron and manganese\textsuperscript{463} or perovskites based on calcium manganate) all have an equilibrium \( \text{PO}_2 \) which is significant at fuel reactor temperatures and also allow the material to be re-oxidised by air containing 21% oxygen at air reactor temperatures.

5.1.4 Economics and the future of chemical looping. In terms of economics, chemical looping will usually appear favourable compared with coal-fired power stations fitted with first generation capture technologies. The thermodynamic arguments put forward previously means higher efficiencies and lower costs. However, this argument only holds if capital and running costs, largely the cost of the replacing degraded oxygen carrier, are competitive. In addition, for natural gas powered systems, the chemical looping combustor must be pressurised in order to be integrated with the CCGT, otherwise the unabated chemical looping system would struggle to reach the efficiency of a standard CCGT with first generation capture. A gas-fired system would therefore be comparable to a chemical plant in complexity, but a power station in scale. Ekström \textit{et al.}\textsuperscript{464} assessed the economics of various capture technologies, including CLC as part of the European ENCAP project. For coal, CLC was found to be \( \sim \) 119\% as costly as an unabated reference plant, \textit{versus} oxy-fuel combustion with \( \sim \) 137\% the cost of the reference plant. For gas systems, they found CLC gave the lowest penalty of all technologies examined.

Economic assessments must consider the cost and lifetime of the oxygen carrier material, and also the availability of the plant. Paper studies will make sensible assumptions about the availability of the plant, but will not consider the case where the technology fails (i.e., a very low plant availability). This latter point is perhaps what holds back chemical looping technology, in that a chemical looping combustion power plant will be much more complicated than a standard power station, and will require a massive upfront investment. For an investor the risk \textit{versus} benefit argument becomes one of confidence in the technology at scale. Research effort has therefore been directed at precisely these issues, both in the (i) development of materials and understanding the costs, and in (ii) developing confidence at scale.

The contribution of the cost of the oxygen carrier to the overall operating cost is proportional to the supply cost and inversely proportional to the material lifetime; cheap easily degraded materials or expensive long lasting materials could perform equally as well. The conceptual design of a 1000 MW coal-fired system is given by\textsuperscript{465} assuming a low cost ore (ilmenite or manganese ore) as the oxygen carrier. They assumed a lifetime of only 200 hours and concluded that the contribution to the cost of carbon capture of the oxygen carrier would be \( \text{€1.3}–\text{€4 per t}_\text{CO}_2\text{ captured} \), less than cost of the final polisher step. For coal-based systems it is hard to see how a very expensive material could be used, since it will quickly become contaminated with the components of the coal ash. Natural gas systems are cleaner and therefore perhaps easier in this regard. Porrazzo \textit{et al.}\textsuperscript{466} modelled the performance of a natural gas-fired CLC system, operating at 10 bar with an oxygen carrier consisting of \( \text{NiO} \) on alumina ($\text{\$15.3 per kg}$). Given the difficulties of presenting consistent economic data, they explored the sensitivity to material lifetime. The levelised cost of electricity (LCOE) fell to a plateau (at around 500–1000 h of lifetime), at which point material cost was no longer significant. To break even with a NGCC system fitted with an amine scrubber, the particles would have to last around 300 to 700 hours. These lifetimes do not seem unreasonably difficult targets to achieve, and it is likely that materials for chemical looping can be made cost effective.

On building confidence, progress has been made on moving from laboratory tests, through to pilot scale, in order to answer the questions of (i) reliability, and (ii) durability of materials over long-term trials. Recent demonstrations have focussed on larger scale (e.g., 1 MW\textsubscript{th} CLC using ilmenite,\textsuperscript{449} 3 MW\textsubscript{th} Alstom calcium sulphate process\textsuperscript{467} or longer trials (e.g., 99 hours of operation in a 10 kW CLC system using calcium manganate,\textsuperscript{468} 200 hours in 25 kW\textsubscript{th} CDCL system\textsuperscript{469}). All the indications from these trials suggest that chemical looping combustion and chemical looping hydrogen production have promise.

5.1.5 Outlook for chemical looping processes. The use of a redox reaction to transfer oxygen between from the air to process stream is a well-established idea, and processes making use of these solid oxide carriers were proposed in the early 20th Century or earlier. They fell out of favour with the development of modern air separation technologies for the production of oxygen, but are now of interest because of the ability of a chemical looping cycle (operating at a high temperature) to be heat integrated into a power plant flow sheet. Cycles based on chemical looping, theoretically at least, allow power production with carbon capture with very low energy penalties. Moving from theory to practice, particularly at power generation scale,
has been the subject of a large research effort in recent years. With the current demonstrations at the megawatt scale, chemical looping has already demonstrated itself to be a promising second generation carbon capture technology.

5.2 Membrane-based technology for CCS

Membrane processes for CO₂ capture can, in a manner similar to other technologies, be classified as pre-combustion, oxy-combustion and post-combustion processes. Here, we focus our discussion on the opportunities for process intensification through the use of membranes in CO₂ capture. Inorganic membranes are capable of high temperature operation. Intensification is achieved through the integration of these membrane processes with reforming, shift and oxidation reactions. Organic membranes are unsuitable for high temperature applications, and most are also unsuitable for low temperature shift (LTS) processes (around 180–250 °C). We confine ourselves to the consideration of dense inorganic membranes, as porous inorganic membranes do not currently have sufficient selectivity for application to the processes of interest here. For details on other membranes that may be applied to CO₂ capture processes (e.g., organic membranes and porous inorganic membranes), the reader is referred to a number of reviews published previously. In the case of application to CCS processes we thus seek to exploit high temperature membranes that are selective for hydrogen, oxygen and CO₂ permeation.

Membrane permeability is considered an important property of membrane material and not associated with geometry. If the permeability of the membrane is known, along with its dimensions and the driving force across the membrane, then flux can be determined and process design calculations performed. However, this is assuming that transport within the membrane is the rate-determining step. This in general need not be the case; the rate may be determined by surface exchange processes or indeed mass transfer processes.

In Section 5.2.1 we describe the properties of a membrane that are important in conferring such CCS-relevant selectivity. Furthermore, we summarise the kinetic behaviour of such membranes through the use of permeabilities. Section 5.2.1 also discusses the classes of membrane that have the potential for use in process intensification of CCS. Section 5.2.2 describes how such membranes may fit into CCS processes, and the work that has been conducted to date. We conclude with the future outlook for membrane-based CCS processes.

5.2.1 Dense inorganic membranes for CCS

Metallic membranes for hydrogen permeation. Hydrogen-selective membranes have potential applications in pre-combustion CO₂ capture. Hydrogen selectivity is a result of the greater propensity for hydrogen, over other permanent gases, to dissolve and diffuse in metals. In addition to Pd, hydrogen will also diffuse through other transition metals such as Ti, V, Nb, Zr, Mn, Fe, Co and Ni. However, Pd and its alloys are most commonly used in membranes due to the ability of Pd to rapidly dissociate hydrogen while possessing the ability to incorporate a large amount of hydrogen and maintaining structural integrity. Pd–Ag is the most common alloy to use.

The permeability of the membrane simply depends upon the product of the solubility of hydrogen in the membrane, S₄H, and an appropriate diffusion coefficient, D₄H:

\[ \text{Permeability} = S_4D_4 \] (9)

where the solubility of hydrogen in the membrane relates hydrogen partial pressure to hydrogen concentration in the metal through a power-law relationship. In the case of hydrogen in a metal, concentration depends upon partial pressure raised to the value of one-half; and the solubility relationship is known as Sievert’s law.

Pd and Pd-alloy membranes usually have permeabilities of around 10⁻⁸ mol m⁻¹ s⁻¹ Pa⁻¹.5, at 350 °C. Clearly, such membranes can be expensive. The cost of the materials is dependent upon the thickness of the active membrane layer, subsequently, most of the research tends to focus on fabricating membranes that are as thin as practical. For more information on hydrogen permeation in metals, the reader is referred to the review by Al-Mufachi et al. Also, the prospects for commercialisation of Pd membranes has been reviewed by Gallucci et al.

Ion-transport membranes for oxygen and CO₂ permeation. Materials exploiting solid-state ion conduction can also be used to fabricate highly selective membranes for use at high temperature. Selectivity is conferred by the fact that, e.g., an oxygen ion vacancy within an ionic oxide is unlikely to be occupied by any species other than an oxygen ion due to the very specific chemical environment of that vacancy. However, it may be possible for similarly sized ions such as hydroxyl ions, or fluorine ions, to occupy the vacancy. Oxygen-ion transport may then occur by oxygen ions “hopping” from one vacancy to another. Appropriate oxides to consider for use as membranes include fluorites, pyrochlores, brownmillerites and perovskites. In many cases, such materials can be doped to create intrinsic oxygen defects (i.e., oxygen-ion vacancies in the case of our discussion), or employed under conditions where oxygen defects will be created as the result of gas-solid reactions with the prevailing atmosphere.

A membrane that shows pure oxygen vacancy diffusion cannot be employed as a gas separation membrane. A steady flux of ions across such a membrane cannot be achieved due to the development of a potential difference across the membrane. To achieve a steady flux, an equal and opposite flux of another charge carrying species must be permitted, either: (i) through the use of an external circuit (thus becoming a solid state electrochemical cell and not covered here), or (ii) by the introduction of a charge transfer pathway internal to the membrane. In the case that this additional charge carrier is an electron, the material is known as a mixed ion and electron...
conductor (MIEC). A second example of an ion-transport membrane includes the dual-phase ion-conducting gas separation membranes. These membranes will be discussed in more detail below.

Mixed ionic and electronic conducting (MIEC) membranes thus have both ionic charge carriers and electronic charge carriers. In the case of an oxygen-ion and electron conductor, if there is equilibrium on both sides of the membrane between gas-phase oxygen, oxygen ionic charge carriers and electrons, it can be shown that the flux of oxygen, $j_0$, is:

$$j_0 = \frac{RT}{4F^2\sigma_O + \sigma_e} \frac{d\ln P_{O_2}}{dx}$$

where $\sigma_O$ is the oxygen-ion conductivity, $\sigma_e$ is the electronic conductivity, $R$ is the general gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $F$ is the Faraday's constant (96 500 C mol$^{-1}$), $T$ is temperature, and $P_{O_2}$ is the partial pressure of O$_2$. Application of the Nernst-Einstein equation relating conductivity to diffusion coefficient allows one to show that, once more, permeability depends upon a diffusion coefficient and a solubility. During permeation experiments, the permeate side of the membrane is often fed with an inert sweep gas, which leaves the logarithm of $P_{O_2}$ poorly controlled (and dependent upon an oxygen material balance on the permeate side). This is not an ideal way to perform a permeation experiment. Oxygen partial pressures should be controlled on both sides of the membrane (ideally, with the oxygen partial pressure difference being small). The flux is then determined by measuring what would be small changes in oxygen partial pressures over the membrane module. Such a technique has not been adopted by the research community possibly due to the difficulties of gas analysis but it would be a significant improvement in current experimental design.

MIEC oxide membranes tend to have oxygen fluxes of about 1 ml (STP) cm$^{-2}$ min$^{-1}$ or about $10^{-6}$ mol cm$^{-2}$ s$^{-1}$ at temperatures of around 800 °C. For a typical driving force of 104 Pa, the permeance can be estimated to be about $10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. Assuming a membrane thickness of 1 mm would yield a permeability of $10^{-9}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$. MIEC oxide membranes can be unstable in the presence of CO$_2$ if the cations employed within the membrane have a propensity for carbonate formation. Thus materials selection must be considered carefully, e.g., in the case of perovskites, ABO$_3$, La on the ‘A’ site is preferred over Ba in the presence of CO$_2$.

There are a number of reviews covering the use of MIEC membranes for oxygen permeation alone and for chemical production. MIEC membranes have been employed for oxygen permeation with good results over times scales of 1000 hours.

Another application of MIEC oxide membranes is in hydrogen permeation. An oxygen vacancy in an oxide membrane has the possibility to react with water, forming a hydroxyl-like species and releasing a proton, which combines with a lattice oxygen species to produce a second hydroxyl species. Protons may then hop from one lattice oxygen site to another lattice oxygen site, leading to hydrogen permeation. The level of proton-conduction versus oxygen-ion conduction in such a material is a strong function of its degree of hydration. Hydration of the oxide lattice itself is exothermic, and thus, if high proton to oxygen-ion conductivity ratios are to be achieved, lower operating temperatures are necessary. However, lower temperature operation will limit flux. Hydrogen permeation using this class of membranes has not been exploited seriously in CCS applications to date. Interested readers are referred to a review by Phair and Badwal for further information.

The dual-phase ion-conducting class of membranes uses two phases to conduct charge carriers instead of one, i.e., one ion conducting phase and an electronic conducting phase. If both phases are solid, the membrane can suffer from thermal expansivity mismatch problems, leading to failure. There is a body of work investigating dual-phase systems with a solid oxygen-ion conductor and a solid electronic conducting membrane for oxygen permeation.

One promising approach recently adopted uses a molten salt as one of the phases. This avoids problems with thermal expansivity mismatch and allows for the opportunity of tailoring membrane properties. Perhaps most interesting for the field of CO$_2$ capture is the use of molten carbonate systems, where the carbonate is housed within a porous solid, providing a route for carbonate ion transport. The carbonate can be: (i) supported in an oxygen-ion conducting oxide, leading to pure CO$_2$ permeation, or (ii) supported in an oxygen-conducting host, resulting in the co-permeation of CO$_2$ and oxygen.

Carbonate ions supported in oxygen-ion-conducting oxide are incorporated into the carbonate melt via the reaction of CO$_2$ with oxygen ions within the ion conducting support:

$$CO_2 + O^{2-} \text{ (oxygen-ion conducting support)} \rightarrow CO_3^{2-} \text{ (carbonate melt)}$$

This results in CO$_2$ permeation across the membrane due to the equal and opposite counter diffusion of oxide ions and carbonate ions. The membrane functions as the result of the transport of two different ions, a dual ion conductivity mechanism, rather than an ion and electrons.

In contrast, carbonate ions in an electron-conducting support are incorporated via a reaction between CO$_2$ and oxygen, with electrons from the electron-conducting support:

$$CO_2 + \frac{1}{2}O_2 + 2e^- \text{ (electron-conducting support)} \rightarrow CO_3^{2-} \text{ (carbonate melt)}$$

This leads to the co-permeation of CO$_2$ and oxygen across the membrane, which is facilitated by the equal and opposite counter diffusion (in terms of charge) of carbonate ions and electrons. By definition, this membrane is also an example of a mixed ion and electron conducting (MIEC) membrane. A fixed CO$_2$ to oxygen permeation ratio of 2:1 should be observed when employing this class of membrane, if this counter diffusion was the dominant mechanism. However, this is often not
the case, \textsuperscript{499} indicated that the mechanism in such membranes is likely to be more complex.

Supported molten carbonate membranes have CO\textsubscript{2} fluxes of about 10\textsuperscript{-8} mol cm\textsuperscript{-2} s\textsuperscript{-1} at temperatures of \sim 650 °C. For a typical driving force of 5 \times 10\textsuperscript{4} Pa, the estimated permeance is approximately 2 \times 10\textsuperscript{-9} mol m\textsuperscript{-2} s\textsuperscript{-1} Pa\textsuperscript{-1}. For a membrane thickness of 1 mm, the permeability is around 2 \times 10\textsuperscript{-12} mol m\textsuperscript{-1} s\textsuperscript{-1} Pa\textsuperscript{-1}. However, Zhang \textit{et al.}\textsuperscript{500} have achieved much higher permeances of approximately 10\textsuperscript{-10} mol m\textsuperscript{-1} s\textsuperscript{-1} Pa\textsuperscript{-1} at 650 °C through the application of highly interconnected three-dimensional channels, demonstrating that there is room for improvement.

There has been too little research on this class of membrane to clearly identify the major problems and modes of degradation under operating conditions. However, we might anticipate that possible problems with this class of membrane may include carbonate conversion to oxide in low CO\textsubscript{2} partial pressure atmospheres. Although the oxide will initially remain dissolved in the carbonate, it will eventually solidify at common operating temperatures once the mole fraction reaches saturation. This will impact membrane function and will also eventually lead to gas leakage across the membrane. Furthermore, other gases are known to dissolve in molten carbonates and may also undergo reaction with the carbonate or dissolved oxide in the carbonate. The effects of any such processes will need to be studied and accounted for in the design of the membrane and process. It must be emphasised that this is a relatively new research area, and as a consequence, further work on the mechanism is required to develop good understanding of membrane behaviour.

5.2.2 Process intensification using membranes. Table 6 identifies a number of processes that are likely to be amenable to process intensification and take advantage of dense inorganic membranes for hydrogen, oxygen and CO\textsubscript{2} permeation. Some examples consider primary fuel inputs of natural gas (i.e., methane) and synthesis gas produced from a reforming process.

\textit{Membrane integration into the shift process.} Membrane integration into the shift process requires CO\textsubscript{2} or hydrogen permeable membranes, which would be used to remove these products whilst the reaction is occurring.\textsuperscript{475,501} This approach using membranes can overcome the equilibrium limitations associated with the water-gas shift (WGS) reaction, which enables higher equilibrium conversion at higher temperatures.\textsuperscript{1} It is desirable to operate at higher temperatures in order to access favourable kinetics and reduce equipment footprint. Therefore, WGS processes would require CO\textsubscript{2} or hydrogen permeable membranes that are stable within different temperature ranges. A trans-membrane pressure difference is required if high mole fractions on the permeate side are to be achieved\textsuperscript{502} or if the system is to be operated in the absence of a permeate-side carrier gas (i.e., sweep gas). The sweep gas can be chosen to facilitate separation of the permeating gas from the sweep gas itself; water vapour is a common choice as it is condensable. Another possibility is to perform a reaction on the permeate side to consume the permeating gas, which would provide a chemical driving force for permeation, avoiding the need for a pressure difference across the membrane. Regardless of such considerations, there is a significant opportunity for intensification through removing the WGS equilibrium constraint. Ultimately, it is important to evaluate all process modifications \textit{via} a whole-systems analysis with an aim to understand the impact of that modification on the cost per unit of decarbonised product, etc.\textsuperscript{503}

Early work on hydrogen permeation for WGS process intensification demonstrated the effectiveness of using a Pd membrane to overcome the WGS equilibrium. Since then, a large number of studies have investigated the importance of Pd membrane thickness, temperature of operation, nature of the WGS catalyst etc. From this large body of work, we present a small representative sample of the relevant work that has been performed. Uemiya \textit{et al.}\textsuperscript{504} investigated a 20 micron thick Pd membrane supported on a porous glass cylinder operating at 400 °C with an argon sweep gas. A commercial iron-chromia catalyst was used in this system, which achieved carbon monoxide (CO) conversions in excess of those predicted from equilibrium calculations. More active catalysts (such as Pt-based systems) and thinner Pd–Ag membranes have been employed, \textit{e.g.}, Bi \textit{et al.}\textsuperscript{505}

Work has also been performed at the more-demanding lower temperatures of 200 to 300 °C,\textsuperscript{506} where higher hydrogen removal rates are required as the WGS equilibrium favours hydrogen production at lower temperature. Considered test conditions included both inert sweep gas and vacuum with no sweep gas at the permeate side of a Pd–Ag membrane. Lower temperatures and higher CO mole fraction can result in more significant co-adsorption of CO on the membrane surface, which can inhibit hydrogen adsorption and transport.\textsuperscript{507,508} However, under certain operating conditions, very high overall hydrogen recovery can be achieved, which is also associated with high CO\textsubscript{2} mole fractions on the feed side of the membrane.\textsuperscript{506,508} Hydrogen production has also been demonstrated at larger scales in the laboratory,\textsuperscript{509} with membrane areas of 0.02 m\textsuperscript{2}, thickness of 10 microns, and hydrogen production rates in the order of 0.25 N m\textsuperscript{3} h\textsuperscript{-1} at >99% purity. Operation temperature was in the range of 420 to 440 °C, at pressures up to 20 bar, and a ferrochrome catalyst was employed.

An alternative integration strategy is to use a combined reformer and membrane unit. Reforming occurs within the membrane unit to produce CO and H\textsubscript{2}, which is then followed by the shift step and hydrogen removal through the membrane. Tokyo Gas have successfully demonstrated an integrated reformer-shift-membrane unit rated for 40 Nm\textsuperscript{3} h\textsuperscript{-1} of hydrogen production and incorporating a Pd with rare-earth metal alloy film of less than 20 micron thickness supported on a stainless steel support.\textsuperscript{510} The unit has operated over 3000 hours with

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\textsuperscript{1} The WGS reaction is mildly exothermic and has lower equilibrium conversions at higher temperature.

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Table 6 Summary of membrane processes for application in carbon dioxide capture. The (M) in the reactions denotes membrane.

<table>
<thead>
<tr>
<th>CCS process</th>
<th>Potential membrane processes</th>
<th>Application and conditions</th>
<th>Reducing or fuel side membrane</th>
<th>Oxidising or permeate side reaction</th>
<th>Nature of membrane</th>
<th>Overall membrane Process</th>
<th>Suitability for process intensification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-combustion</td>
<td>Post-shift CO₂ or hydrogen separation</td>
<td>Low temperatures, may require pressure difference driving force</td>
<td>Within a post shift mix: CO₂ → CO₂(M)</td>
<td>CO₂(M) → CO₂</td>
<td>CO₂ or hydrogen permeable membrane. Possibly organic membrane as post shift temperatures are low.</td>
<td>Simple separation</td>
<td>Limited. To date, work has not been performed on coupling these processes to, e.g., another chemical reaction such as hydrogenation.</td>
</tr>
<tr>
<td>Membrane integration into the shift process with or without reforming in the membrane unit prior to shift</td>
<td></td>
<td>Remove products as the shift reaction occurs, range of temperatures possible, may require trans-membrane pressure difference</td>
<td>During shift reaction: CO₂ → CO₂(M)</td>
<td>With or without sweep gas: CO₂(M) → CO₂</td>
<td>Direct integration of a supported molten carbonate CO₂ permeable membrane not demonstrated. Significant work on Pd hydrogen permeable membranes to higher TRL.</td>
<td>Simple separation but can be used to overcome equilibrium limitations of secondary reaction.</td>
<td>Yes. Separation is performed while the shift reaction is occurring, which removes equilibrium limitations to conversion of the shift reaction.</td>
</tr>
<tr>
<td>Unmixed reforming</td>
<td></td>
<td>High temperatures, water may be required with feed to limit carbon deposition.</td>
<td>Oxygen supply to a reforming reaction: CH₄ + O(M) → CO + 2H₂</td>
<td>Oxygen consumption from water feed: H₂O → H₂ + O(M)</td>
<td>Oxygen permeable MIEC membrane</td>
<td></td>
<td>Yes. Separate syngas and hydrogen streams are produced.</td>
</tr>
<tr>
<td>Unmixed shift with hydrogen separation</td>
<td></td>
<td>High temperature shift with no equilibrium limitation</td>
<td>Reformate is oxidised: CO + O(M) → CO₂</td>
<td>H₂O → H₂ + O(M)</td>
<td>Oxygen permeable MIEC membrane</td>
<td></td>
<td>Yes. Separate CO₂ and hydrogen streams are produced.</td>
</tr>
<tr>
<td>Air separation only</td>
<td></td>
<td>High temperature oxygen permeation</td>
<td>O(M) → 1/2O₂</td>
<td>1/2O₂ → O(M)</td>
<td>Oxygen permeable MIEC membrane</td>
<td>Simple separation</td>
<td>Limited</td>
</tr>
<tr>
<td>Air separation integrated with membrane oxygen-combustion</td>
<td></td>
<td>Increased driving force for oxygen permeation, high temperature.</td>
<td>CH₄ + 4O(M) → CO₂ + 2H₂O</td>
<td>2O₂ → 4O(M)</td>
<td>Oxygen permeable MIEC membrane</td>
<td></td>
<td>Yes. Nitrogen is not mixed in with combustion exhaust while chemical driving force of combustion drives permeation.</td>
</tr>
<tr>
<td>Post-combustion</td>
<td>Capture of CO₂ alone or co-permeation of CO₂ and oxygen</td>
<td>Separation may occur at either high or low temperature, requires trans-membrane pressure difference.</td>
<td>CO₂ → CO₂(M)</td>
<td>CO₂(M) → CO₂</td>
<td>Supported molten carbonate CO₂ permeable membrane and molten carbonate CO₂ co-permeation membrane.</td>
<td>Separation only but co-permeation of CO₂ and oxygen could be exploited for thermo-dynamic benefit.</td>
<td>May be possibilities but not explored yet in any detail.</td>
</tr>
</tbody>
</table>
better than 99.99% hydrogen purity. The operating temperatures were in the range of 495 to 540 °C with a natural gas feed at 9.5 bar. A nickel–alumina catalyst in pellet form was used in the primary reformed catalyst bed and a further nickel–alumina catalyst in monolithic form was used in the vicinity of the membrane itself. Even at the highest natural gas supply rates, the CO₂ mole fraction in the off-gas was above 60%.\(^{510}\)

At the time of writing, there does not appear to have been any significant experimental work performed with organic membranes for hydrogen permeation coupled with the WGS reaction. Organic membranes are more suited for low-temperature operation, \(e.g.,\) have the potential to be used for low temperature shift (around 180–250 °C).\(^{470}\) Scholes \textit{et al.} \(^{475}\) reviewed the opportunities for membrane integration with WGS processes, noting that there is the need for a WGS catalyst to be integrated with the membrane module. Furthermore, if the catalyst and membrane are fully integrated, then much of the membrane at the reactant inlet is relatively inactive due to the low hydrogen and CO₂ mole fractions in this zone. As the work by Tokyo Gas demonstrates, this is easily avoided by the use of a primary reforming or shift process.\(^{510}\)

The removal of CO₂ from the WGS reaction mixture is possible with the use of CO₂-permeable membranes. Supported molten carbonate membranes could be operated at temperatures in excess of those associated with high-temperature shift (HTS) processes, \(i.e.,\) 350–450 °C.\(^{476}\) Molten carbonate membrane permeabilities are currently quite low, which is due to the necessity of solid state oxygen-ion diffusion to occur and temperatures in excess of 700 °C. Low-temperature shift could be integrated with a polymeric membrane, given that an appropriate catalyst is used, such opportunities have demonstrated through modelling work.\(^{511}\) The two approaches to combine CO₂ permeation with WGS, \(i.e.,\) organic and dual phase molten carbonate membranes, or low- and high-temperature shift, remain in the early stages of development and have not been demonstrated at scale.

\textbf{Unmixed reforming and unmixed shift.} As an alternative to catalytic steam reforming, the unmixed reforming process involves separate air and fuel/steam feeds to create a cyclic process (\(i.e.,\) the air and fuel/steam feeds do not mix).\(^{512}\) Membranes can be used to facilitate unmixed reforming. The oxygen permeable membrane would operate at high temperature with feeds of methane and water to opposite sides of the membrane.\(^{\dagger\dagger\dagger\dagger\dagger}\) Synthesis gas would be produced on the methane side, and hydrogen on the water side; it is this hydrogen stream that can be used for a CO₂ free combustion process. As this membrane process is endothermic, combustion of the synthesis gas may be required to provide energy. The combustion would only produce CO₂ and water, provided oxy-combustion conditions are used, which would make CO₂ separation relatively straightforward. High conversions can be achieved for steam-methane reforming (SMR) by using high temperatures, thereby avoiding the need for a trans-membrane pressure difference to increase hydrogen mole fraction. This process does have the potential for intensification through significant process simplification, \(e.g.,\) combine reforming processes, HTS and LTS into one membrane reactor.

One approach for unmixed reforming is to direct the reformate or synthesis gas product to a membrane reactor that houses an oxygen permeable membrane with water being fed to the other side of the membrane. Alternatively, the two processes of unmixed reforming and subsequent unmixed shift could occur in series and operated in one membrane unit. The synthesis gas would provide the reducing gas to further drive water splitting on the water side of the membrane (overall this is a combined unmixed WGS and hydrogen purification). The WGS reaction is slightly exothermic, therefore no heat input is required. However, if the syngas produced from the unmixed reforming is not combusted, the overall process becomes endothermic. It is important to consider the energy requirement for such a process and avoid unacceptable CO₂ emissions (\(e.g.,\) due to syngas combustion). Similar to the previous unmixed reforming scenario, no trans-membrane pressure difference would be required to get high mole fractions of CO₂ and water (on the reformate side) and hydrogen (on the water side). Also, process intensification is possible by combining the HTS and LTS in one membrane reactor.

The membrane-based processes for unmixed reforming and unmixed shift both result in hydrogen production using a reducing gas to provide, \(via\) an oxygen permeable membrane, the driving force to split water on the other side of the membrane. Some studies have begun to investigate membrane-based reforming and shift processes,\(^{513–515}\) however, further research is necessary. Jiang \textit{et al.}\(^{513}\) tested a BCFZ (BaCe₀.9Fe₀.1O₃₋ₓ) oxygen-permeable MIEC membrane at temperatures between 800 and 950 °C. There was a methane feed to the reducing side of the membrane, and a water feed to the oxidising side. A nickel-based catalyst was packed around the hollow fibre membrane in the reducing side chamber. The process produced syngas on the methane-feed side and hydrogen on the water-feed side.\(^{511}\) Using a BCF (Ba₀.9Ce₀.05Fe₀.95O₃) oxygen-permeable MIEC membrane, Li \textit{et al.}\(^{515}\) tested slightly different conditions. Similarly, there was a methane feed to the reducing side, but in this case, a mixture of water and air was fed to the oxidising side. The membrane was operated between 800 and 925 °C with ruthenium-based catalysts present on both sides of the membrane. The oxygen flux was sufficient to remove all of the oxygen from the oxidising side as well as split the water to form hydrogen. Thus, the oxidising side produced a stream containing hydrogen and nitrogen suitable for ammonia synthesis. On the methane side, syngas was formed with an appropriate composition for methanol synthesis.\(^{515}\)

\textbf{Air separation integrated with membrane oxy-combustion.} An oxygen-permeable membrane can be directly integrated into a fuel combustion chamber for oxy-combustion. Air is fed to one side of
the membrane and fuel to the other. Oxygen permeation leads to combustion with a nitrogen-free exhaust gas, facilitating CO2 capture, produced on the fuel side of the membrane. Such a process is often referred to as the advanced zero emission power plant, AZEP.516,517 A number of papers have dealt with the optimisation of the AZEP concept using modelling approaches,518–521 and a number of review papers consider the nature and operation of such processes.518,522,523 Although there are many papers on oxygen permeation in MIEC and dual-phase membranes, the literature covering the application of such membranes in a membrane-based oxy-combustion is much more limited.

Any membrane that is to be operated in AZEP must be stable in CO2-containing atmospheres. Subsequently, there is a body of work that evaluates the stability of oxygen permeation membranes in such atmospheres. However, these papers usually fall short of actually investigating membrane-based combustion. Carbon dioxide-tolerant single-phase MIEC membranes that have been investigated include (Nd0.9La0.1)2Ni0.74Cu0.21Ga0.05O4 and (Pr0.9La0.1)2(Ni0.74Cu0.21Ga0.05)O4.525–527 A number of studies have focussed on the use of CO2-tolerant dual phase membranes.528–530 Studies in which oxygen permeable membranes are actually subjected to combustion conditions are much more limited, these include experimental work of direct relevance,527,531 as well as investigations into how combustion chemistry couples with the permeation process.532,533

Post-combustion capture of CO2 alone or co-permeation of CO2 and oxygen. Although post-combustion capture can be considered to be a simple separation process with little opportunity for intensification, there may be some interesting unforeseen possibilities for improved processes. In the case of a membrane that exhibits co-permeation of CO2 and oxygen, we can reverse the direction of CO2 permeation such that it may proceed against its own chemical potential difference. This would require using an oxygen chemical potential difference of opposite sign that is more than double (based on the reaction stoichiometry of carbonate formation) the CO2 chemical potential difference. Although permeation results in an increase in CO2 chemical potential, it leads to a greater decrease in oxygen chemical potential. Papaioannou et al.498 have demonstrated such ‘uphill’ CO2 permeation. However, the use of oxygen co-permeation to ‘drive’ a post-combustion capture process has not been the subject of any other studies.

5.2.3 Membranes: future perspective & key research needs. Here we have investigated the possibilities for intensification of CO2 capture processes through the use of membranes. The advantages of such membrane processes are clear from a thermodynamic perspective, primarily when reaction and separation are combined. This enables chemical reaction equilibrium limitations to be overcome (here, we primarily discuss the water-gas shift reaction), leading to simpler plant designs with fewer units, and as such, the future prospects of such processes should be bright. Very significant progress has been made towards commercialisation of such technologies. Tokyo Gas have demonstrated a reformer and shift unit that incorporates a Pd hydrogen-permeable membrane, advancing the technology to a TRL of 5 or 6. In the case of MIEC oxygen permeable and supported molten carbonate CO2 permeable membranes, there are currently no examples of intensified membrane processes for CO2 capture in near-commercial use, and is considered in the early stages of development at TRL 3 or 4. Such application requires a number of issues to be addressed. Membranes must be demonstrated at scale and over long periods of operation under realistic conditions. To advance the development of supported molten carbonate membranes, work should be performed to confirm they maintain their selectivity in different gas environments over relevant timescales. Problems associated with membrane sealing and failure must also be addressed. Finally, the cost associated with CO2 emissions must be sufficient to make investment in such membrane processes sufficiently attractive.

5.3 Ionic liquids for CO2 capture

Ionic liquids (ILs) are substances completely composed of ions and are arbitrarily liquid below 100 °C.534 Those ILs with melting points below room temperature are referred to as room temperature ionic liquids (RTILs).534 ILs are now widely used in various areas of chemistry (and are emerging in areas of chemical engineering) including as solvents for organic synthesis,534–538 as solvents for or as agents of catalysis,539–543 in separations,544–547 for the synthesis of nanomaterials,548–552 in energy applications,553–557 and for biofuel production.558–561 The reason that ILs have garnered such interest is that they possess unusual (and often extreme) physical properties which provide some advantages in handling and storage.544 The most often cited property is a vanishingly low vapour pressure,562 which is important for CO2 capture applications, but other common IL properties include high thermal and chemical stability (also of import for CCS),563,564 non-flammability,565 and high viscosity.566 Their main strength lies in their designation as “designer solvents” because it is possible to synthetically alter the cation and anion independently, allowing for customisation of many solvent properties, including polarity, acid/base character, density, viscosity and thermal stability.534 The high thermal stability and low volatility allow for use of ILs for CO2 capture in either a pressure-swing configuration567 where CO2 desorption is not accompanied by evaporative solvent losses, or temperature-swing desorption where the high thermal stability of ILs (typically over 300 °C)538 also negates degradative solvent losses. Combined, these properties provide an opportunity to regenerate the solvent at a very wide range of temperatures and pressures, providing an excellent opportunity for process optimisation that is not available using traditional aqueous liquid capture media.1 However, the viscosities of ionic liquids are high compared to conventional solvents (66 to 1110 cP at 293 to 298 K),568 which may cause processing issues as discussed later.

ILs have been proposed for use in carbon capture for many years.569 This is mainly due to a perceived high capacity for CO2 dissolution, though as Carvalho et al.570 recently observed, this is only strictly true for certain subclasses of ILs.570 Most of the CO2 solubility work in ILs has been carried out at high pressures and with pure CO2 gas streams (in order to overcome low CO2 solubility during physisorption), conditions useful for scientific study, but unlikely to merit consideration for
There has also been a marked emphasis on physical absorption of CO₂ though many chemisorbing ILs have come to prominence recently. For the physisorption studies, the major driver of IL selection has been high capacity, with this parameter influenced mainly by the anion selection (and fluorine content) and the length of the cation alkyl chain, though the majority of studies have focussed on dialkylimidazolium cations. 2 Despite several generation of ILs for CCS, the CO₂ capacity at post-combustion CO₂ partial pressures remains limited, unless referenced on a molar (mol L⁻¹) rather than molal (mol kg⁻¹) basis, suggesting a practical limitation that will not be easily overcome.

Due to the reduced capacity at flue gas type pressures and CO₂ concentrations (<0.05 mole fraction at 0.15 bar CO₂ partial pressure), it is no longer expected that conventional, physisorbant ILs will be feasible for large scale CCS applications. In order to increase capacity, a range of “task-specific” ILs have been designed with functionalities (such as amine groups or azolates) capable of chemisorption of CO₂, thereby significantly driving up capacity at ambient pressure (0.5–2 mol CO₂ per mole of IL). This has led to a diversity of structures and numerous publications on the design of anions or cations for CO₂ chemisorption with ILs. The ability to tune the physical and chemical properties of ILs through ion design is well established. However, the difficulty facing chemisorbing ILs is very slow mass transport due to the extremely high viscosity of most “task-specific” ILs. This led to a partial divergence of academic research efforts away from solving issues with IL CCS, and toward the design and synthesis of more novel (and inevitably ever more complex) anions and especially cations for CO₂ sorption. More recently, several studies have looked at physicochemical properties of IL–CO₂ systems, including thermodynamic modelling, transport, kinetics of CO₂ uptake, and the mechanisms of CO₂ capture. However, in order to take full advantage of the tunable synthesis of these IL structures, chemical functionalisation remains the preferred route to increased capacity.

### 5.3.1 Functionalised ILs for chemisorption of CO₂

A comprehensive review on the topic of active-site functionalised ILs in CO₂ uptake was recently published by Cui et al. Here we provide a summary of CO₂ chemisorption, discussed in the context of CCS applications at large scale. Functionalisation of ILs, particularly the cation of ILs, is a classic means of IL solvent design. There are several different functional group classes that have been explored for increasing the affinity of ILs for CO₂, each of which is rooted in traditional CO₂ binding chemistry. The starting point of this field in normally seen as the amino-functionalised ILs, as a means of introducing the most common liquid-based reactive site for the efficient and reversible capture of CO₂. While this continues to dominate the literature since its inception in 2002, many other functionalities have since been developed.

**Amine-functionalised cations.** Bates et al. reported the first synthesis of an IL specifically designed to chemically bind CO₂ with the IL 1-propylamido-3-butylimidazolium tetrafluoroborate, which is essentially a cation-bound amino group. They reported up to 0.5 moles of CO₂ could be captured per ion pair at atmospheric CO₂ pressure. The mechanism they reported was similar to aqueous amines, though only one carbamate salt can form per two ion pairs. This highlights one of the drawbacks listed above for IL-based CCS: amine functionalised cations cannot bind as much CO₂ per amine on a molar basis, much less compete on a mass or volume basis where the molecular weight of the IL outdistances that of a traditional amine several fold at similar densities.

Further, as discussed below, the functionalisation of the cation inherently lowers electron density at the amine site, leading to reduced interactions with CO₂. A similar IL, 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate, demonstrated relatively slow kinetics for CO₂ uptake compared to aqueous amines, due to the high viscosity of amine-functionalised ILs. However, although the viscosity increases dramatically upon complexation with CO₂, the absorption of CO₂ was significantly higher than for the analogous physisorbing IL 1-butyl-3-methylimidazolium tetrafluoroborate. Further studies confirmed the 1:2 carbamate formation motif, suggesting a potential upper limit for CO₂ capacity in amine-functionalised ILs. Indeed, given the much higher molar mass of the IL cation and anion (essentially “dead weight” for this application), the CO₂ uptake on a mole per unit mass basis is obviously poor for any IL functionalised in this manner. Much cheaper and simpler anions (sulfonate) and cation units (ammonium) can be used to mitigate this effect, though only to a small extent. A final limitation on this approach lies in the chemical similarity to traditional amines: tertiary amine-based ILs can only perform physisorption, while primary amines can engage in chemisorption. While not surprising, this does confirm the chemical limitations of amino-functionalised ILs are analogous to those of the corresponding amines.

In order to overcome the stoichiometric limitations associated with amine-functionalised ILs, Wang et al. synthesised a series of tunable alkanolamine-functionalised ILs coordinated to alkali metal ions in a quasi-aza-crown ether. This afforded an extra degree of freedom depending on the nature of the inorganic ions utilised. These led to molar ratios slightly above 1:2, but with much improved kinetics, indicating the carbamate mechanism still prevailed. Later, Yang and He used PEG-functionalised ILs chelated to Li ions to achieve molar ratios well above 1:2 (nearly up to 1:1). However, the molar mass of these ILs is very high, suggesting less improvement on a mole per unit mass basis. There are also general concerns surrounding IL cost – in order to mitigate cost concerns, Vijayaraghavan et al. created a series of less expensive protic ionic liquids based on diamines to achieve CO₂ loadings of 13% w/v, thus using lower molar mass to improve performance at the same carbamate limit. This aspect of IL design (cost) has only recently gained attention for potential large-scale application of ILs.

**Amine-functionalised anions.** Since the anion of the IL is the more electron rich centre, it is a natural source for CO₂ interactions. This has commonly involved the use of
(deprotonated) amino acids with tethered amine groups (such as lysine) as the anionic component of the IL. While amino acids are naturally abundant, there are several misconceptions about their nature. For example, they are relatively high in cost (owing to difficult synthesis or isolation), and fairly toxic.\textsuperscript{610} However, they are unquestionably biodegradable, and their use is not regulated. Their incorporation into ILs is fairly difficult, however, due to the need to use a hydroxide intermediate,\textsuperscript{611} which is normally obtained through ion exchange chromatography. Also, amino acid ILs are highly viscous, highly basic and (as with amino acids themselves) have low thermal stability. In order to overcome the relatively poor mass transport in these ILs, Zhang et al.\textsuperscript{612} synthesised silica-supported amino acid ILs with an extra amine group and created 1:2 complexes with CO$_2$. The viscosity of these ILs was later reduced by using small tetralkylammonium cations in place of Zhang’s tetralkylphosphonium centres.\textsuperscript{613,614} with similar CO$_2$ capacities. While a range of amino acids can be used, the necessity of a free amine group to increase capacity is obvious. This necessitates the use of the deprotonated, highly basic free amine form of the amino acid, with negative consequences for potential thermal or chemical stability of the IL. As the most common mechanism of IL degradation is nucleophilic attack of the cation by the anion (followed by dealkylation of the cation),\textsuperscript{615} the basic (and nucleophilic) nature of these amino anions is detrimental. More stable cations, such as tetralkylphosphonium salts, can alleviate this effect to some extent.\textsuperscript{576,616} creating ILs which compete with aqueous amines on a (molar) capacity basis. Glycine and sarcosine ILs with phosphonium cations\textsuperscript{617,618} and tetralkylammonium methionine\textsuperscript{619} have each shown essentially equimolar CO$_2$ uptake, though not all amino acid ILs showed this level. Additionally, according to Luo et al.,\textsuperscript{620} functionalised methylbenzolate-based ILs and nicotinate-based ILs with an amino group at the para or ortho position exhibit both higher capacity and lower enthalpy than related structures. It was later pointed out that the absorption was significantly affected by the nature of anions, due to different entropic driving forces for the reaction with CO$_2$.\textsuperscript{585}

While the ILs mentioned thus far relied on long chain (triethyltetradecyl phosphonium or ammonium) cations, traditional amino acid based ILs pair a much smaller cation. This can have disadvantages for transport properties, but more importantly bring the molal (mol kg$^{-1}$) absorption values up due to smaller molecular mass. Tetrabutylphosphonium cations paired with a variety of amino acid anions have shown equimolar CO$_2$ uptake (often at several bar of pressure),\textsuperscript{621} though alkylation of the amino acid removes chemisorption possibilities.\textsuperscript{622} While transport and stability are issues with the shorter cation systems, supporting the IL on silica can help.\textsuperscript{623}

**Aprotic heterocyclic anions (AHAs).** Since amine-functionalised ILs chemisorb CO$_2$ similarly to liquid amines (by making the carbamate half of a liquid amine complex), the resultant solutions always suffer from extremely high viscosities post-capture, limiting their potential as usable solvent systems.\textsuperscript{579,584,585,612} There are many alternative structures that can bind CO$_2$ without forming carbamates – and after all, the synthetic flexibility of ILs is what attracts researchers to the field. Therefore other anions have been employed to bind CO$_2$ without forming high-viscosity carbamate disalt structures.

Azolate ILs (aprotic heterocyclic anion ILs)\textsuperscript{624,625} capture CO$_2$ in equimolar quantities, and the anions are fairly straightforward to obtain through neutralisation of an azole superbase. Examples such as tetralkylphosphonium pyrazolate can capture equimolar CO$_2$ at atmospheric pressure, while tetrazole, triazole, and even pyrrolidonate anions have been shown to be moderately effective, and the use of imidazolate as an anion provided a nice symmetry to the field of ILs by incorporating the most common cation structure as an anion.\textsuperscript{580} These very basic anions even sometimes show a slight decrease in viscosity upon CO$_2$ absorption,\textsuperscript{580,626} though viscosities still typically range close to 1000 cP. Refining the structure of these salts led to the development of the aprotic heterocyclic anion (AHA) based ILs or azolide ILs.\textsuperscript{584,594,598,627–633} These anions absorb nearly equimolar amounts of CO$_2$ at much lower viscosities than azolate ILs. Molecular dynamics simulations have shown that the CO$_2$ uptake is enhanced through chemical interaction with the anion.\textsuperscript{624} Both kinetics\textsuperscript{625} and thermodynamics\textsuperscript{584,632} for CO$_2$ uptake by tetralkylphosphonium AHAS have been investigated. It is clear that substituted imidazolate anions can be used to vary reactivity, enthalpy of binding and CO$_2$ capacity. This can clearly be attributed to the relative electron density (and therefore reactivity) of the active site on the anion. By varying the alkyl chain lengths on the cation (from 38 total carbons down to 14), the viscosity could be reduced to under 100 cP without impacting molar uptake.\textsuperscript{634} This was later attributed to differences in reaction entropy and ionicity,\textsuperscript{635} though it is additionally important to note that the uptake in moles per unit mass would now be significantly higher, resulting in an intensified process.\textsuperscript{570}

What is clear from the AHAs is that the anion basicity has a controlling influence on the CO$_2$ uptake. This is similar to the amine-functionalised cation dominance, and is unsurprising – the more electron-rich the reactive site of the ion, the more CO$_2$ will be chemisorbed. However, traditional ILs with very basic anions become both highly viscous and unstable, and the AHAs appear to at least be able to avoid the viscosity issues. While tuning anion basicity does enable greater control over CO$_2$ uptake, the highly complex nature of these ion structures does not lend much promise to industrial application for cost reasons. Additionally, higher capacity through electron density increase is normally associated with higher enthalpies of binding and therefore more energy on regeneration. One proposed method to break this co-dependence is to use alkali metal salts in conjunction with IL–PEG mixtures.\textsuperscript{529,636} This enables the use of less basic azolate anions, though PEG is also a highly viscous solvent. However, equimolar absorption can be achieved with lower desorption energies.\textsuperscript{636} This can be exploited to ensure easier reversibility,\textsuperscript{637} as the balance between physisorption and chemisorption can be manipulated, changing the Gibbs free energies of the capture between somewhat negative and slightly positive.\textsuperscript{585}

### 5.3.2 CO$_2$ capture through IL-based proton transfer.

It is well established that there are acidic protons on most IL cations,
most famously the C2 position of dialkylimidazolium salts.\textsuperscript{534} This can create opportunities for interactions with CO\textsubscript{2} through the quasi-carbene structure of these moieties.\textsuperscript{538} Taken to an extreme, CO\textsubscript{2} can be induced to react into the IL system through the construction of chemical elements designed for this to happen. The C2 proton itself can of course be removed to form an N-heterocyclic carbene (NHC) and this was demonstrated by Mathews \textit{et al.}\textsuperscript{639} to occur during Suzuki couplings in ILs.\textsuperscript{639} Cabaco \textit{et al.}\textsuperscript{648} used this to great effect to react the dialkylimidazolium cation with CO\textsubscript{2} in a carboxylation reaction, and identified the product through IR spectroscopy. This creates a 1:1 CO\textsubscript{2} complex with the cation, rather than the anion, and is a reversible adduct. However, neither the NHC intermediate, nor the ILs themselves are especially stable,\textsuperscript{581} and the presence of impurities such as water has been noted as likely to prevent this mechanism from occurring.\textsuperscript{2} The absorption was shown to proceed through an NHC-CO\textsubscript{2} complex based on NMR results,\textsuperscript{640} and it was later demonstrated that the C2 could be deprotonated by very basic anions alone.\textsuperscript{541} Unfortunately, the theoretical mol fraction of maximum capture relative to IL is only 1:3 for this mechanism,\textsuperscript{585} thus leading to only moderate sorption, but these salts are more readily available for other applications,\textsuperscript{642} and the complex itself is reversible.\textsuperscript{643,644} Interestingly, tetraalkylphosphonium acetates\textsuperscript{645} also demonstrate high CO\textsubscript{2} sorption, despite the lack of any possible NHC adduct. This can be attributed to CO\textsubscript{2}-anion interactions, though the mechanism of this remains unclear.\textsuperscript{546} As this effect is restricted to highly basic anions, and these have already been mentioned as having low stability, it is not clear how this limitation can be effectively prevented. Wang \textit{et al.}\textsuperscript{647} attempted this by mixing imidazolium ILs with superbases, forming a dicationic–dianionic complex (zwitterionic imidazolium carboxylate) wherein the imidazolium cation was deprotonated by the superbase during CO\textsubscript{2} sorption. Alkylation of the C2 position was confirmed to prevent this effect entirely, thus establishing the mechanism of equimolar capture, though the stability of the salts was not analysed.

An interesting combination of the imidazolium-anion proton transfer concept involves the use of imidazolium azolates.\textsuperscript{648,649} Here the azolate anion is used to effect deprotonation of the imidazolium cation, resulting in CO\textsubscript{2} carboxylation. Seeo \textit{et al.}\textsuperscript{649} proposed that the carbene intermediate was responsible through two distinct pathways (anion–CO\textsubscript{2} binding and NHC–CO\textsubscript{2} complexation). However, the complex resulted in 1:2 complexation of CO\textsubscript{2} and was only reversible if the resulting carbamate salt was broken. The ability to mediate CO\textsubscript{2} chemisorption through transfer of CO\textsubscript{2} from the anion to the cation is an interesting concept, though it is again unlikely that these carboxylated cationic complexes will form in the presence of water from flue gas; the presence of water vapour is likely to prevent the NHC intermediate from forming or from being re-protonated, resulting in diminished sorption capacity. While the AHAs can also be used to create ILs where CO\textsubscript{2} can react directly with a protonated cation,\textsuperscript{650,651} this provides a system that has a very high regeneration energy.\textsuperscript{585}

A prior (similar) example of this approach was the series of “switchable” ILs demonstrated by Jessop \textit{et al.}\textsuperscript{652} where a superbase (1,8-diazabicyclo[5.4.0]undec-7-ene or tetramethylguanidine) can deprotonate the alkylation reaction from an alcohol reacting with CO\textsubscript{2}, forming a transiently stable salt. These CO\textsubscript{2}-binding organic liquids (CO\textsubscript{2}BOLs) have near equimolar capacity\textsuperscript{652–655} though regeneration is not trivial. Similar effects have been demonstrated for amino acid (OH) deprotonation by Wang \textit{et al.}\textsuperscript{656} where a hydroxyl-functionalised IL cation and superbase combine to react with CO\textsubscript{2}. While equimolar capture is again possible, release is difficult under CO\textsubscript{2} atmospheres, and heating can cause decomposition or volatilisation of the components. Some of the normal limitations, such as transport issues, can be obviated by using the alcohol as a diluent and reactant, as with β-amino acid anion-based ILs diluted in simple alcohols.\textsuperscript{657} This is a similar approach to MEA in water, and the methyl-carbonate salt (formed in methanol) is key to the equimolar capture process (relative to the IL). A variety of cationic species were demonstrated as effective, including some relatively simple cations such as tetramethylammonium – here the small molecular weight of the cation could be advantageous for process intensification. However, there is a generic issue with superbase-IL CO\textsubscript{2} capture – the need for releasing the CO\textsubscript{2} under CO\textsubscript{2}-free atmospheres limits application.

An alternative approach is to directly capture the CO\textsubscript{2}-based protons through protonation of a sufficiently active amine base.\textsuperscript{658} In the presence of water, this becomes similar to aqueous amine capture processes, where a carbamate or carbonate-based equilibrium protonation will dominate, as the carbamate salt is hydrolysed into a bicarbonate salt, even with tertiary amines.\textsuperscript{659} This yields somewhat higher capacities for tertiary amines (1:1) vs. primary or secondary amines (1:2 to 1:1) though the absorption is very slow.\textsuperscript{4}

5.3.3 Hydroxylate ILs. While the reaction of CO\textsubscript{2} with hydroxides is well known, it can also be applied to ionic liquids (or at least organic salts), as for tetrabutylammonium hydroxide aqueous solutions.\textsuperscript{560} While this is efficient sorption, the bicarbonate salt formed would not be regenerable without decomposing the cation.\textsuperscript{585} The same principle was applied to other ILs based on deprotonated alcohols, such as trifluoroethanol or other fluorinated alcohols, with equimolar sorption achieved.\textsuperscript{580} However, it should be noted that these salts are unlikely to be stable, and regeneration will be difficult to achieve without decomposition. These “superbase” ILs can be regenerated with N\textsubscript{2} bubbling at elevated temperatures\textsuperscript{661} but this is not representative of a CO\textsubscript{2} capture process, where the CO\textsubscript{2} would not be released through N\textsubscript{2} displacement.

Other alcohol-based cations include phenolate anions, which Wang reviewed recently.\textsuperscript{585} These can be prepared from the corresponding hydroxide salt by neutralisation with any substituted phenol.\textsuperscript{662} This is a general limitation of strongly basic ILs – the weakly acidic conjugate species must be deprotonated by a strong base such as hydroxide, and hydroxide salts are difficult to prepare at scale. However, this did demonstrate the utility of a series of substituted phenolate ILs for CO\textsubscript{2} uptake and the surprising variation in CO\textsubscript{2} sorption that could be achieved by varying the electron density in the anion, as was
discussed above for azolate salts. The recurring theme of tuning CO₂ capture through anion electronegativity or reactivity is a core part of the appeal of ILs for use in this field, though the synthetic complexity required to achieve this may render scale-up of these salts difficult.

5.3.4 ILs with multiple functional groups for capture. The ability to introduce multiple functional groups (onto the cation, anion or both) and retain a liquid state is one of the more attractive aspects of IL research. Attempts to use this for CCS purposes have met with mixed results, normally as higher capacity fights with increased viscosity due to functionalisation. For example, two amine groups on the cation have been shown to increase CO₂ capacity to 1.05 equivalents,663 while three amines increase capacity to 1.49 equivalents at 1 bar.664

Even more success has been found with anion functionalisation, where (deprotonated) lysine and histidine based anions captured up to 2 equivalents of CO₂ at 1 bar618,619 though the rate of absorption was very slow. This is an unfortunate consequence of increased functionality – higher capacity is a trade-off with slower kinetic uptake due to higher viscosity. It should be noted, however, that the anion functionalisation are relatively simple (amine acids) compared to functionalisation of the cation (to create azo-crown ethers, for example). Amines can also be placed on both the cation and the anion579 to increase capacity, but uptake remains slow even when immobilised on silica. Alternatively, amine-functionalised cations combined with AHA s can be used for simultaneous captures through carbamate and carbonate mechanisms,548 though once again the increase in capacity comes at a cost of rate and water stability.2

Since anion functionalisation is easier (and the anions come with built-in CO₂-phlicity due to the negative charge), multi-functional anions have been proposed where multiple capture sites are designed to be co-operative. This is analogous to the stabilising effects present in alkanolamines, though the methods differ. For example, high CO₂ capacity and reversibility can be achieved by using a second interacting site on the AHA anions (phenolate, imidazolate) to stabilise the CO₂ adduct.565,666 This includes hydroxypyrridine (capacities up to 1.65 equivalents) where simultaneous carbamate/carbionate formation introduces added capacity, as demonstrated spectroscopically.566 This multi-functional cooperation could provide a blueprint for future anion design.

5.3.5 Methods for overcoming mass transport limits. The high viscosity of ILs is a widely acknowledged limitation in CCS-based applications. As such, several approaches have been used to get over these limitations, most notably blending ILs with water (usually), and supporting ILs on solids,585 including very high viscosity ILs, such as amino acid salts, which have been blended with water, or absorbed on silica surfaces with water.612 The mechanisms employed do change, with a transient carbamate species giving way to more stable (bi)carbonate salts,647–670 similar to aqueous alkanolamine capture. While the equimolar (to IL) CO₂ sorption capacity remains, the dilution does remove some of the advantages of ILs over aqueous amines (including volumetric capacity and energy of regeneration).585,671,672 Similarly for acetate IL–water blends, the carboxylation capture mechanism gives way to carbonate formation,673 which is irreversible,644 and acetic acid,673 though the stability is concentration dependent and water content may be manipulated to form a reversible system.674

5.3.6 IL blends with amines. Blends of ILs with amines have been demonstrated as a means of providing hybrid media for CCS with lower volatility and higher thermal stability than aqueous amines, at a lower regeneration energy.675,676 Blends of amino acid ILs with aqueous MDEA show high capture ability dependent on composition677 and the ability to regenerate through either pressure- or temperature-swing desorption678,679 with superior performance at relatively low (5–10 wt%) IL concentration in 30 wt% aqueous amine.677 Other amino acid IL blends with AMP680 and MEA681,682 show similar promise, although the advantage over amino acid blends with amines remains unclear.

5.3.7 Challenges and opportunities with IL-based CCS. By far the largest technical challenge associated with using ILs for CCS lies in the high viscosity of most ILs.2,575,585,683,684 Highly functionalised ILs, including those designed with CO₂ reactive sites, show higher viscosities than unfunctionalised ILs and this increases post-capture.579,586 Several approaches have been used to overcome this viscosity issue, including mixing of ILs with other solvents, and supporting ILs on solids to increase mass transfer rates. Although some improvements in performance are noted when bulkier cations are used,617 it should be noted that this is largely an effect on a purely molar (mol L⁻¹) rather than molal (mol kg⁻¹) basis. Supported ILs show drastically increased rate of gas uptake,579,612 suggesting that supporting the ILs in a thin film on a substrate (such as porous silica) is a viable means of accelerating CO₂ absorption. However, it is unclear how the increase in raw mass of the packing will impact column performance in a real CCS scenario. Likewise, while higher CO₂ pressures can be used to increase capacity toward that of aqueous amines,594,666 this suggests an unrealistic scenario for post-combustion capture.

The use of IL solutions, where amines or water reduce the solution viscosity, are viable alternatives, though the loss of advantages in regeneration energy are noteworthy. The use of other blending agents (such as low molecular weight polymers) has shown less promise.624,665,666 It is clear that water remains the preferred dilution medium for reducing IL viscosity in CCS applications585 as the viscosity of both the pre- and post-capture solutions decreases with increasing water content,585,618,670 with minimal impact on absorption capacity,584 likely due to complex stabilisation through increased hydrogen bonding.624 An alternative to this approach is to directly tether an amine (such as MEA) onto the IL, with an (unsurprising) improved performance when tethering to the anion rather than the cation.663 Possibly the most forward-looking approach recently proposed is to attempt to tune the basicity (and therefore CO₂ interaction strength) of functionalised ILs.585 This takes advantage of the inherent synthetic flexibility of ILs, one of their greatest strengths. The interaction strength can be tuned by weakening the cation–anion ion pairing (as has been done in chemical systems),534 and this has also been employed in gas sweetening.588,589 This idea shows great potential if cost considerations can be balanced successfully.
6 SAFT-based approaches for solvent design for CO2 capture; from molecules to processes

6.1 Chemical approaches to modelling the thermodynamics of aqueous amine solutions

The capability of the amine solvent to absorb CO2 is quantified by assessing both the specific chemistry of the complexation and the overall phase equilibria. The overall stoichiometry of the various reactions involved in CO2 absorption in aqueous MEA (forms a monoethanolammonium carbamate pair) can therefore be summarised as:

\[ \text{CO}_2 + 2(\text{HO–CH}_2\text{CH}_2\text{–NH}_2) \rightleftharpoons [\text{HO–CH}_2\text{CH}_2\text{–NH–CO}_2^- \]
\[ + \text{NH}_4^+\text{–CH}_2\text{CH}_2\text{–OH}] \]

(13)

The overall reaction of the process with a 1:1 amine to CO2 stoichiometry forms a monoethanolammonium bicarbonate pair (shown between square brackets) and is characterised by the following:

\[ \text{CO}_2 + \text{HO–CH}_2\text{CH}_2\text{–NH}_2 + \text{H}_2\text{O} \rightleftharpoons [\text{HCO}_3^- + \text{NH}_3^–\text{–CH}_2\text{CH}_2\text{–OH}] \]

(14)

As a consequence of the complexity of the chemical processes involved and their influence on the chemical and phase equilibria, the description of the thermodynamics of the relevant multicomponent mixtures necessary for the accurate modelling of post-combustion carbon capture poses a particular challenge.

Traditionally, the thermodynamics and phase equilibrium of reactive systems of this type are described with a so-called “chemical” approach first introduced by Dolezalek690 in the early twentieth century. In this case one has to identify the number of species that are present after assuming particular equilibrium schemes and then specify the state dependence of each of the equilibrium constants; the interactions between the various species are often treated at the level of an ideal mixture to simplify the description. As alluded to by van Laar691,692, the arbitrary manner in which the various species are assigned a priori and the number of thermodynamic variables required to describe the chemical and phase equilibria imply that chemical theories have limited predictive value. For example, in order to fully describe the thermodynamics and fluid-phase behaviour of the reactive mixture of CO2 in aqueous ammonia one would require 72 temperature-dependent interaction parameters;693 it is clearly challenging to estimate the necessary parameters reliably without extensive experimental data for the specific system under consideration, limiting the predictive capability of the method. This having been said, very successful methodologies have been developed to couple a description of the chemical equilibria with an activity coefficient model for the solution phase and an equation of state for the gas phase to incorporate “physical” effects arising from the non-ideality of the intermolecular interactions.694–696

In the particular case of the reactive equilibria of CO2 in aqueous amine solvents, the system is often treated at the level of a weak electrolyte solution, essentially involving the empirical determination of the chemical equilibrium constants for the various reactions (or equivalently the activity coefficients of all of the species). One of the most popular approaches employed in process modelling of carbon capture in alkanolamine solvents was presented by Austgen et al.,697,698 who combined the electrolyte non-random two liquid (eNRTL)699,700 description of the activity coefficients for the equilibrium ionic species in solution with the Soave–Redlich–Kwong (SRK)701 cubic equation of state for the fugacities of the species in the vapour phase; the vapour–liquid is not obtained by solving for phase equilibria but is described instead by using Henry’s law constants. It is worth noting that the original eNRTL approach has been shown to lead to an inconsistent description of mixtures of mixed ions702 and improved versions have now been developed and used703–705 to describe the complex speciation of CO2 in alkanolamine solvents. Another excellent example of this type of approach is the work of Faramarzi et al.,706 who instead couple the extended universal quasi-chemical (UNIQUAC) approach for electrolyte solutions707 with the SRK equation of state for the vapour phase; a good description of the fluid-phase behaviour is obtained for the ternary mixture of CO2 in aqueous monoethanolamine (MEA) and other alkanolamines using a consistent determination of the vapour–liquid coexistence by imposing the conditions of phase equilibrium. Within chemical approaches, the first attempt to use a single equation of state to describe the properties of the vapour and the liquid phase is due to Kuranov et al.,708 who proposed a new method to treat the vapour–liquid equilibria of alkanolamine solutions with CO2 and H2S based on a hole quasichemical hole model (partially filled lattice model to deal with compressible fluid phases) modified to incorporate chemical reactions and electrostatic interactions in the liquid phase.

Methodologies which are based on a unified statistical mechanical treatment of both the liquid and vapour phases offer more promise as a predictive platform for the prediction of molecular thermodynamics and fluid-phase equilibria of complex fluid systems. The reversible reactions involved in carbon-capture in amine solvents can be represented as strong association equilibrium processes, where the properties of the mixture are attributed to large differences in the associative intermolecular interactions between the species which lead to aggregation. This type of “physical” perspective originally promoted by van Laar691,692 and his followers may at first seem diametrically opposed to the “chemical” view of the reacting system, leading to “harsh polemic” between the opposing camps from the very beginning.709 The two standpoints are but extreme representations of the real system and an unambiguous distinction between the role played by the chemical and physical interactions is often arbitrary and in many cases only a matter of taste or convenience.710

In the case of the readily reversible reactions involved in acid–gas scrubbing, it is reasonable to assume that the interactions characterising the associated species are not too dissimilar from those of the parent compounds and that a physical treatment is appropriate; when the products are significantly different from the reactants, a chemical perspective becomes
essential. The statistical mechanics description of lattice models within the quasi-chemical approximation of Guggenheim is well suited to represent the properties of mixtures of strongly associating molecules (as exemplified by the early work of Barker and Fock), gaining much popularity in engineering applications following the pioneering work of Abrams and Prausnitz, most notably with versatile group-contribution methods such as UNIFAC (universal quasi-chemical functional group activity coefficients) and its variants. As mentioned earlier, the related UNIQUAC approach has been used successfully to describe the thermodynamic properties and phase equilibria of CO₂ absorption in amine solvents. It is, however, more appropriate to use equations of state which are firmly grounded in the fluid state rather than approaches based on lattice models because the latter are generally incompressible and as a consequence require a separate treatment of the vapour and liquid phases.

The statistical associating fluid theory (SAFT) is cast from the physical perspective of the interactions between the particles characterised by strong intermolecular forces responsible for hydrogen bonding or complexation. The description of the reactive phase equilibria of CO₂ in aqueous alkanolamines with equations of state of the SAFT family is the central theme of our current review.

6.2 SAFT physical approach of chemisorption of CO₂ in aqueous amine solvents

The SAFT equation of state is based on the Wertheim first-order perturbation theory (TPT1), which provides a compact platform to describe the thermodynamic properties of mixtures of associating species. The association interactions are mediated by off-centre bonding sites placed on the molecules, the number and nature of which control rich equilibrium association schemes including the formation of complex chain-like and network aggregates as well as simple dimerisation equilibria. The multiplicative associative equilibria are treated implicitly within the theory without having to specify the detailed equilibrium reactions, in contrast to a chemical treatment. The equivalence of a SAFT description of the associative equilibria and a chemical or quasi-chemical description has been demonstrated by Economou and Donohue, though care has to be taken with the stoichiometry of the reactions in the detailed comparison. The SAFT equation of state is finding ever increasing use in the accurate description of the thermodynamic properties of fluid mixtures for industrial applications. Examples of the more-popular versions of SAFT in current use include SAFT-VR for variable-range potentials, soft-SAFT, based on the Lennard-Jones potential, and the perturbed-chain PC-SAFT, the cubic plus association (CPA) equation of state, which couples the Wertheim TPT1 treatment of associating fluids with the SRK equation of state, is also worth a particular mention.

An important advantage of employing a physically-based SAFT treatment is the significant reduction in number of parameters required to describe the associating or reacting system. Group-contribution approaches based on the chemical functionality of the molecules in the mixture (the interactions for which are estimated from the thermodynamic properties of systems comprising simpler target components) offer additional predictive capabilities; the SAFT-γ approach represents a recent reformulation of SAFT-VR equation of state within a group-contribution framework.

In order to exemplify the application of the physical approach inherent in the SAFT (and Wertheim) treatment, the molecular models employed to represent the reactions associated with the chemisorption of CO₂ in aqueous monoethanolamine (MEA) are depicted in Fig. 13. Four association sites (two H to represent the hydrogens, and two e for the oxygen lone pair of electrons) are employed to mediate the hydrogen-bonding interactions between the electron lone pairs on the oxygen atom with the hydrogen atoms on different water molecules. Six association sites (one e and two H on the amine NH₂ group, and two e and one H on the hydroxyl OH group) mediate the multiple hydrogen-bonding interactions between the MEA molecules.

Details of the development of the SAFT models used to represent the asymmetric interactions between the MEA and CO₂ (and H₂O) molecules are provided in ref. Just two physical “reaction” sites x₁ and x₂ on the CO₂ molecules are employed to describe the formation of the monoethanolammonium carbamate complex (reaction (13)) by association with the hydrogen sites on the NH₂ of MEA allowing for a 2:1 stoichiometry between MEA and CO₂; association to the single x₁ site can be used to quantify the formation of the monoethanolammonium bicarbonate pair (reaction (14)). A testament of the adequacy of this type of SAFT description of the complex chemical reactions between CO₂ and MEA in aqueous solution can be seen in Fig. 14, where the experimental data, for the separate concentrations of the carbamate and bicarbonate products as a function of CO₂ loading are compared with the theoretical predictions (note that in this example the calculations are carried out within the SAFT-γ SW group-contribution formalism).

The SAFT physical treatment has been used extensively to describe the thermodynamic properties and fluid-phase equilibria of the reactive systems associated with CO₂ chemisorption in amine-based solvents including MEA, ammonia, 2-amino-2-methyl-1-propanol (AMP), linear alkylamines, diethanolamine (DEA), and methyl diethanolamine (MDEA). We should also point out that that the eNRTL description of the activity coefficients of the ionic species in solution has been coupled with the PC-SAFT equation of state for the fugacities of the vapour phase to model the chemisorption of CO₂ in aqueous MEA and MDEA. A group-contribution version of the theory (SAFT-γ SW) has now been deployed to assess the suitability of a broad family of multifunctional alkanolamine solvents including representative examples such as MEA, AMP, DEA, MDEA, methylmethanolamine (MMEA), ethylmethanolamine (EMEA), 3-amino-1-propanol (monopropanolamine, MPA), 5-amino-1-pentanol, and 6-amino-1-hexanol. An example of the quality of the SAFT-γ description of the degree of absorption...
of CO₂ in aqueous MEA as a function of pressure and temperature can be seen in Fig. 15 in comparison with experimental data⁷⁴¹,⁷⁴²,⁷⁴⁹,⁷⁵⁰ and with the correlation of Gabrielsen et al.⁷⁵¹

It may now be apparent that a key advantage of the SAFT-γ group-contribution methodology provides a high degree of predictive capability allowing one to describe the thermodynamic properties of a large number of compounds and mixtures with a relatively small number of parameters (see, for example, Fig. 14 of ref. 743).

6.3 Explicit SAFT treatment of the electrolyte species

In the models described in the previous section, a SAFT treatment of the reactions associated with CO₂ capture in amine solvents does not explicitly take into account the speciation products nor the electrolytic nature of the system. Though it is apparent that a good representation of the thermodynamics and fluid-phase equilibria can be obtained for the chemisorption of CO₂ in a variety of amine solvents using SAFT without an explicit treatment of the polar and electrostatic interactions, a physical approach is expected to be increasingly inadequate when the reaction products are highly charged and chemically distinct from the parent reactants.

As was mentioned in the introductory section, the eNRTL approach is often employed to represent the thermodynamic properties (activity) of the species formed in solutions of CO₂ in aqueous amines⁶⁹⁷,⁶⁹⁸,⁷⁰³,⁷⁰⁴ and a different model (an equation of state) is used to treat the gas phase. Kuranov et al.⁷⁰⁸ treated these systems by extending the quasichemical hole model with electrostatics following the Pitzer⁷⁵² modification of the Debye–Huckel approximation in a framework where, for the first time, the same equation of state was used for the liquid and gas phases. They obtain good correlative results in comparison to experiments with the use of a number of adjustable parameters. It is clearly advantageous to treat the liquid and gas phases within the same thermodynamic framework and Fürst and co-workers⁷⁵³,⁷⁵⁴ followed in this vein, using a different equation of state for electrolytes⁷⁵⁵ (which extends the capability of the SRK equation using the mean-spherical approximation, MSA,⁷⁵⁶ for the contribution to the free energy of the charged species) to represent the fluid-phase equilibria of in aqueous alkanolamine solutions. Unfortunately, the use of the SRK equation of state as the reference for the uncharged aqueous systems comes at the cost of a poor description of the properties of water which are dominated by the strong hydrogen-bonding association interactions. A natural step is the use of extensions of the SAFT approach to electrolytes to describe the chemical and phase equilibria of CO₂ in aqueous alkanolamines.

The SAFT framework was first extended to treat electrolyte solutions by incorporation of free energy contributions to take into account the presence of charged species assuming fully dissociated charged species. A Coulombic term, usually written following the expressions of the primitive models of Debye and Hückel⁷⁵⁷ (DH) or the mean spherical approximation (MSA),⁷⁵⁶ is typically added to the classic SAFT Helmholtz free energy expression. The original SAFT equation was first combined with
they treat the liquid phase as an ideal solution with respect to the activity coefficients of the charged species (i.e., making them equal to 1). Only recently, Uyan et al.\cite{778} have presented a model in which the activity coefficients of the ionic species are calculated, although in their approach the dielectric constant of the solution is not treated as dependent on the concentration of CO$_2$.

In future, it will be of interest to continue developing approaches that combine the physical framework of Wertheim from which SAFT approaches stem and the speciation frameworks to deliver models better suited to study the reaction kinetics of amine solvent solutions with CO$_2$ with increasing accuracy and predictive capability as these attributes are key for their use in process and solvent design and optimisation.

6.4 The role of thermodynamic models in the design of novel solvents for CO$_2$ capture

Most thermodynamic models of CO$_2$ absorption in aqueous amine solutions have been developed with the aim to enable the design and operation of chemical absorption and desorption processes, whether in the context of gas sweetening or in that of flue gas treatment. Detailed models based on chemical theory, such as those briefly discussed in Section 6.1 (e.g., Zhang et al.\cite{704}), are very well-suited for this purpose: they take into account every chemical species in the postulated reaction mechanism and therefore allow the calculation of quantities that can have an impact on process performance when operating away from chemical and phase equilibrium.

This is the case for instance of the ionic strength, which affects mass transfer, and of the concentrations of all species, which have an effect on reaction kinetics as well as mass transfer. Indeed, such detailed models have been used extensively and quite successfully in modelling pilot plant data without the need for fitting any model parameters to plant data;\cite{779,780} they have an important role to play in developing better processes.

With the imperative to develop processes that can capture vast quantities of CO$_2$ from post-combustion flue gas at low cost and with minimal environmental impact, however, there has been an increasing focus on effecting step-change improvements in the performance of absorption processes,\cite{781} through novel equipment (rotating packed beds)\cite{782} but also through novel solvents.\cite{783} In the latter case, extensive research has taken place to gain a better understanding of solvent mixtures or additives that have been found to provide some advantage, such as reduced degradation or increased reaction kinetics, as afforded for instance by the combination of methyl diethanolamine (MDEA) and PZ.\cite{784}

The search for novel solvents has mainly been based on extensive experimental programs. For instance, within the CESAR project funded under the FP7 programme of the European Commission,\cite{785} experiments from laboratory to pilot plant scale were undertaken for monoethanolamine and several alternative mixtures. This painstaking work allowed the identification of PZ/AMP as a promising candidate. As discussed in Papadopoulos et al.,\cite{783} the thorough experimental investigation of a single solvent requires the deployment of
significant resources over a number of years, hindering the search for improved amine-based carbon capture processes.

To support the search for novel solvents, there is thus a pressing need for predictive thermodynamic models of CO$_2$ absorption that can be applied to solvents that have never been used for CO$_2$ capture previously, or even to molecules that have never been synthesised. The prediction of the thermodynamic behaviour of novel solvents is an important enabling capability in overcoming the challenges to the implementation of solvent-based post-combustion capture. Even where new process topologies are sought, the benefits that can potentially be derived from flowsheet innovation are intimately connected to the nature of the solvent. This is the case for instance with phase-change solvents, which have been gaining increasing attention as a means to reduce the energetic cost of solvent regeneration, as discussed in Section 4.1.3. The performance of a process based on such a solvent depends greatly on the thermodynamic phase behaviour of solvent + CO$_2$ mixtures as a function of composition, temperature and pressure. As seen in Section 6.2, the development of such models is a challenging task, but given that they are to be used to guide the search for novel solvents at an early stage, they need not be subject to the same stringent conditions on accuracy and fidelity as those models that are used for detailed process design.

In order to accelerate further the search for novel solvents and process configurations, systematic approaches to identifying candidate solvents have been proposed. These include rule-based approaches$^{786,787}$ that can be used to identify promising classes of solvents. To enable a search among a wider set of compounds, computer-aided molecular design (CAMD) approaches have recently been proposed, based on the prediction of a range of properties.$^{783,789,785}$ In all but two cases,$^{783,789}$ the extent of CO$_2$ absorption in the designed solvent and, by extension, the energetic requirements of desorption, were either not considered explicitly as a design target or were predicted on the basis of detailed thermodynamic models that were parameterised for other solvents, and thus likely to be of limited accuracy for novel solvents. The usefulness of CAMD approaches as a tool to identify the most promising solvents for experimentation is limited when such key solvent performance metrics are neglected during the generation of candidate molecules and mixtures.

The emergence of the SAFT-$\gamma$ SW group-contribution models of CO$_2$ absorption mixtures described in Section 6.2 has the potential to make the in silico identification of better solvents for CO$_2$ chemisorption much more effective. To date, such models have been deployed as a final computational step in the solvent design methodology of Papadopoulos et al.$^{783}$ A ranked list of solvents is first generated by considering a wide range of pure component properties, as well as reactivity and sustainability. The extent of CO$_2$ absorption in the resulting solvents is then predicted with the SAFT-$\gamma$ SW equation of state in order to refine the priority list of solvents to be investigated further. The explicit use of predicted CO$_2$ absorption as a means of selecting solvents paves the way for a much more effective computational exploration of the molecular design space and more realistic design criterion.

Looking ahead, one can envisage the development of much more holistic approaches to the identification of promising solvents and solvent mixtures among the extremely large space of possibilities. Approaches for computer-aided molecular and process design (CAMPD),$^{793,794}$ where molecular structure and process design are optimised simultaneously, have already been deployed successfully in the context of physical absorption processes for CO$_2$ capture using the perturbed-chain polar-statistical-associating-fluid theory (PCP-SAFT) equation,$^{795-798}$ the SAFT-VR SW equation$^{799,800}$ and the SAFT-$\gamma$ Mie equation.$^{801,802}$

The various SAFT equations of state that have been used in these CAMPD approaches provide a reliable description of the phase equilibria of the mixtures involved and, in the case of the SAFT-$\gamma$ Mie equation,$^{737}$ of the caloric properties. Chemical absorption processes are, however, significantly more challenging than the physical absorption processes investigated so far with CAMPD due to the presence of chemical reactions that had until recently prevented the development of predictive models linking molecular structure to phase and chemical equilibria. Even with the advent of predictive SAFT-$\gamma$ SW models, one must note that the use of a physical representation of the chemical reactions (see the scheme in Fig. 13) implies that the product concentrations are not explicit in the model calculations, that the ionic nature of the products is not explicitly taken into account and that the reactions are necessarily at equilibrium. In contrast, in many chemisorption processes, chemical equilibrium may not be reached in the liquid phase and, even if it is reached, the concentrations of product species and their charge impact on mass transfer rate and hence on overall process performance.

Nevertheless, it has been shown that it is possible to use such an implicit representation of product species within a process model of a CO$_2$ absorption and to achieve good agreement with pilot plant data using monoethanol-amine.$^{745,746,803-807}$ These encouraging results suggest that SAFT-based physical models of aqueous amine and CO$_2$ mixtures can be integrated within an iterative discovery and design process, as illustrated in Fig. 16. Design targets ranging from physical properties to economic performance and sustainability, as well as a design space consisting of atom groups (e.g., -NH$_2$, >NH, -OH) are defined in step 1. One can then use SAFT-$\gamma$ physical models of phase and chemical equilibria, in combination with other models, to link molecular structure and solvent composition to the design targets and apply CAMD or CAMPD. The outcome of this step (step 2 in Fig. 16) is a prioritised list of solvent candidates. Top candidates are then experimentally tested iteratively in step 3 in terms of their key physicochemical properties. For those that are confirmed to be most promising, additional data are gathered to build detailed thermodynamic and kinetic models that include speciation explicitly (step 4). Such models are detailed enough to help plan pilot plant studies and proceed with process design (step 5). If issues are identified at that stage, one can return to step 3 to test additional candidates. Otherwise, one can proceed with implementation (step 6). In this overall scheme to develop CO$_2$ capture processes, the physical
models of Fig. 13 and the chemical models are used in tandem to evolve from early stage molecular design to detailed process design.

7 CO₂ transportation

Whilst at small scale other options are available, the significant volumes of CO₂ requiring transport as a result of large scale carbon capture means that only two methods are practical, networks of pressurised pipelines and ship transport. The efficacy of either of these two depends to a great extent on the quantity of CO₂ and the distance from its point of storage or utilisation; except over large distances (>1500 km)⁸⁰⁹,⁸¹⁰ where it's expected that ship transport would be preferable, it is generally expected that the vast majority of transportation will occur via pipeline.²

In both cases consideration must begin with the compression and/or liquefaction of the fluid, effectively the interface between capture and transport.⁸¹¹,⁸¹² During this process stage, the stream is transformed into a supercritical or dense-phase, i.e. above the critical pressure but below the critical temperature, to take advantage of the greater density in these phases.⁸¹³ Of these, for CO₂ transported by pipeline, dense-phase is likely to be preferred as keeping the temperature above critical temperature can in practice be problematic due to cooling through heat transfer effects.⁸¹⁴,⁸¹⁵ The actual amount of compression is chosen in concert with the expected flow rate and the pressure drop along the pipeline, which itself is dependent on the hydrodynamic and thermophysical properties of the fluid fed into the pipe. These properties are a function of the stream's composition, which therefore plays an important role in the analysis and design of transportation systems. Hence, for the cost-optimal design of a pipeline system, and to a lesser extent shipping, an understanding of the interaction between all of these factors is essential.

7.1 Composition of the CO₂ stream

The particular components in the mixture as well as the amount of impurities remaining in the stream can significantly affect the thermophysical properties and phase equilibria of the fluid.⁸¹⁶–⁸¹⁸ The recent study of Porter et al.⁸¹⁹ sought to define ranges of impurities expected from a number of carbon capture technologies. For the purposes of pipeline transport, particular impurities of concern include: water, which is important with regards to potential corrosion of the pipe steels, and non-condensable gases (i.e. N₂, O₂ or Ar) which can significantly alter the mixture's vapour–liquid equilibrium.

Of practical importance for both shipping and pipeline transport is the impact that the composition has on the phase envelope. As Fig. 17 shows, as the amount of non-condensable

Fig. 16  An overview of an approach to the design of solvents and processes for CO₂ capture, highlighting the role of different modelling and experimental activities.
gases in the mixture increases an appreciable expansion of the phase envelope is observed. This has both a considerable impact on the energy requirements for compression or liquefaction of the fluid as well as, for pipeline transport, the higher cricondenbar\textsuperscript{†††††} necessitating higher pipeline operating pressures. While this is sufficient for steady state operation, the additional uncertainty in the behaviour of the fluid during transient operations has led to a great deal of focus on assessing the impact of the variations in the composition of the CO\textsubscript{2} mixture on the dynamic flow behaviour.\textsuperscript{818,820}

7.2 Compression

As the first stage in the transportation, the compression or liquefaction stage represents a significant use of energy, suggested to be as high as 12%\textsuperscript{821,822} of the loss of efficiency of a power plant; as such, the selection of the most efficient compression strategy\textsuperscript{823,824} is of significant importance to the overall performance of the CCS system. A number of studies have therefore sought to optimise this process, for example Witkowski \textit{et al.}\textsuperscript{825} investigated 13 compression strategies ranging from various multistage compression with intercooling, compression coupled with liquefaction and pumping as well as more novel technologies such as supersonic shockwave compression. It was found, for example, that using integrally geared compressors could result in energy savings of more than 20% compared to conventional strategies. Other work has focussed on improving the efficiency by reusing the heat recovered as part of the intercooling system.\textsuperscript{822,826}

Recent work has sought to quantify the impact of composition on the energy and process requirements for the compression. The analysis of Martynov \textit{et al.}\textsuperscript{808} found, using the compositions from various processes suggested by Porter \textit{et al.}\textsuperscript{819} that little difference is observed when dealing with relatively clean CO\textsubscript{2} streams (>95% v/v purity), but large penalties (increases in power requirements of between 12–30%) are incurred for less concentrated streams. Similar findings were reported by Skauen \textit{et al.}\textsuperscript{815} where conditioning costs as a whole for an impure stream were increased by 13% or 2.3 € per t\textsubscript{CO2}. Given the substantial energy demand represented by the compression stage of transportation further work is required to continue to find efficiencies; additionally, given the likelihood of the dynamic operation of CCS plants the impact of this on the design of the compression train should be evaluated.

7.3 Pipeline transportation

Whilst CO\textsubscript{2} pipelines must be designed and constructed as to ensure that they are reliable and safe to operate they must also be designed in as cost efficient fashion as possible. For the purposes of normal operation, the design requirements for a pipeline are primarily a function of the flowrates and of the hydrodynamic properties of the CO\textsubscript{2} stream which it must transport,\textsuperscript{2} for example the density, compressibility and viscosity. One important constraint is that the phase transition should be avoided as, should it occur, it can result in operational problems such as liquid slugs. To avoid this, feed pressures and temperatures must be chosen so that the fluid remains in the single-phase region along the length of the pipe under normal operating conditions.

Given that the stream fed into the network is also unlikely to be pure CO\textsubscript{2}, the composition of the CO\textsubscript{2} mixture will impact the design by altering not only the fluids thermophysical properties but the vapour/liquid equilibrium, potentially altering the permissible operating envelope. Furthermore, the level and type of impurities can influence the material requirements of the steel used for the pipeline’s construction; this includes both the steel strength needed to prevent fracture and the possibility of corrosion.

7.3.1 Pipeline network design. The cost of the construction of a pipeline infrastructure sufficient to transport CO\textsubscript{2} over large distances represents a significant capital cost.\textsuperscript{827} As such a range of studies have sought to develop cost-optimal pipeline networks for various regions around the globe.\textsuperscript{814,828–831} The design of such networks in the literature depends to a certain extent on the cost estimates used, for which there is a large literature [see for example Mccoy and Rubin,\textsuperscript{813} Roussanaly \textit{et al.}\textsuperscript{835}], and operating conditions, \textit{i.e.} the feed flowrates and pressure and temperature of the fluid.\textsuperscript{814,833}

Network designs have generally assumed the use of a trunk pipeline to which various emitters can link.\textsuperscript{833–835} This has the benefit of providing a shared infrastructure that future sources can join as CCS is rolled out. It has been suggested that the trunk pipeline itself should be oversized to account for the growth of CCS, and therefore volume of CO\textsubscript{2} requiring transportation.\textsuperscript{836}

The ability of the networks designed to deal with intermittency of feed flowrate, such as predicted by Mac Dowell and Staffell,\textsuperscript{837} has received relatively little attention. Of the few available studies Liljemark \textit{et al.}\textsuperscript{820} investigated the fluid transients during various load changes and found that for some cases phase transfer may occur, which, as in the case of steady state flow, is considered to be operationally problematic. Chaczekowski and Osia'dacz\textsuperscript{838} showed that the composition of

\textsuperscript{†††††} The highest pressure at which liquid–vapour mixtures can exist.

![Fig. 17 Boundaries of VLE region in pressure–temperature phase diagram for pure CO\textsubscript{2}, pre-combustion, post-combustion and oxy-fuel streams (85 and 96.7% v/v CO\textsubscript{2}) calculated using PR EoS.\textsuperscript{908}](image-url)
the CO₂ stream may have a considerable effect on the dynamic behaviour of the fluid under such scenarios. However, these studies consider only single point to point pipelines, more work is required to understand these dynamics in networks containing multiple sources and evaluate operational risks. Finally, Mechler et al. show that considering the evolution of the electricity system in the design of CO₂ transport infrastructure can lead to non-negligible cost reductions without compromising safety or operability.

Furthermore, there are >6500 km of CO₂ pipelines worldwide, most of which are associated with EOR operation in the United States. Whilst experience of CO₂ pipelines exists, these tend to be away from densely populated regions. The deployment of CO₂ pipelines closer to population centres has led to a body of work seeking to develop high fidelity tools in order to perform detailed quantitative risk assessments. Such analysis has the additional benefit of reducing unnecessary conservativeness in design by removing unwarranted safety concerns.

7.3.2 Material considerations. Selection of the correct grade of pipeline steel can impact both the structure’s ability to resist failure and corrosion as well as the cost of construction. The selection of an appropriate steel for construction of the pipeline must be informed by its ability to resist fracture propagation, which can be initiated as a result of accidental failure due to corrosion or third party interference. Additional measures are often employed to prevent corrosion of CO₂ pipelines, these include cathodic protection, external protective coatings, gas dehydration systems (offshore in Europe requires moisture to be <50 ppmv). Furthermore, pipelines are equipped with leakage mitigation devices such as emergency shutdown valves, which rapidly isolate leakages, and crack arrestors (i.e., strengthened joints/sections).

Fracture can occur in two modes: ductile and brittle, the majority of work has focused on the risk posed by the first of these. The process of ductile fracture involves significant deformation of the pipeline material and is driven primarily by the residual pressure of the fluid within the pipe, which is known to be a strong function of the mixture composition, exceeding the toughness of the steel. These are normally assessed using semi-empirical methods such as the Battelle Two Curve method, and an adequate toughness selected. However, the application of such a method has been shown to be insufficient for the purposes of obtaining conservative designs for linepipe by full scale fracture experiments performed in the UK. In order to avoid the burden of the costs associated with over-specification of the pipes structure, a number of works have sought to directly simulate the crack propagation/fluid decompression itself by coupling both fluid and structural models. While such an approach is computationally demanding, it offers the most convenient route of analysis given the lack of a simpler assessment method and the expense of full scale testing.

7.4 Transportation by ship

As compared to transportation by pipeline the use of shipping has received far less attention in the literature, summaries can be found in the recent reviews by Brownson and Munkejord et al. While as described previously, shipping is considered to be the lower cost option over very large distance, this is also the case for small distributed sources, for example in a recent study, Kjærgård et al. have shown that for small sources around the Baltic, ships may provide the cost optimal solution. Discussion of relative costs is typically performed in terms of the point at which shipping becomes cheaper than pipeline for a given capacity, in both offshore and onshore storage scenarios. Interestingly, Roussanov et al. found that this distance was a function of, amongst other things, the project duration; this results from the larger proportion of the total economic cost of shipping being operational expenditure.

Contrary to the case of pipeline transport, where the capital cost is the main driver, the operating costs make up the bulk of total cost for shipping: the majority of which results from the liquefaction process. The reduction of this cost therefore represents a key technical challenge, along with the design and operation of the injection system. Only a limited comparative Life Cycle Assessment (LCA) for pipeline and shipping is available in the literature, the results of which are seemingly dependent on the precise design of pipeline system used as a reference. Given the importance of the greenhouse gas footprint of CCS systems, thorough analysis of this aspect is required.

A further issue raised in the literature is that, along with any technical difficulties, there are potential legislative difficulties in the use of ships for CCS in Europe, given that under the EU emissions trading system (ETS) this CO₂ would be accounted for as released rather than stored.

7.5 Outlook for CO₂ transportation

The transportation system acts as the gateway between the CO₂ emitters and the storage sites and imposes requirements on the design and operation of both. There remain uncertainties around material selection and operation which necessarily introduce conservativeness in design. The key challenge, however, is to understand the constraints for each transport technology to reduce the over-design and associated costs, as well as where restrictions placed on the feed streams, for example purity can be relaxed to allow a reduced-cost whole-system design, as observed by Kolster et al. Further, this must account for the evolution of the CCS network in order to avoid over-capacity that will not be utilised, as well as the dynamic use of the infrastructure to reduce risk.

8 CO₂ storage

8.1 Research challenges in subsurface CO₂ storage

The state of knowledge around CO₂ storage has seen a remarkable increase over the past 10 years. The injection and sequestration of CO₂ at rates over 1 MtCO₂ per year at individual sites is technically viable, demonstrated by 14 currently operating industrial scale projects, including three injecting into
saline aquifer systems.\textsuperscript{862} The leading edge of research has thus moved beyond the viability of the technology which is now clearly demonstrated. Throughout all aspects of the injection of CO\textsubscript{2} underground – thermophysics, geoscience, reservoir engineering, monitoring, and evaluation of large scale capacities and technology potential – research is addressing challenging questions where answers would lead to better characterisation, prediction of plume migration, lowering of uncertainty, managing the risks of leakage, and evaluation of the global role of CO\textsubscript{2} storage in energy systems.

8.2 Fluid properties and geoscience

Thermophysical properties of CO\textsubscript{2} and its mixtures with reservoir fluids play an important role in storage-site selection, the design of injection strategies, and in predicting the long-term fate of injected CO\textsubscript{2}. Phase behaviour and diffusivity control the extent and rate of CO\textsubscript{2} dissolution into the connate fluids. Interfacial tension (IFT) and fluid–fluid–mineral contact angles are key parameters influencing CO\textsubscript{2} mobility at the pore scale. Finally, properties of the solutions formed when CO\textsubscript{2} dissolves in the reservoir fluids play are role in determining field-scale convective flows. A great deal of effort has been expended on understanding the thermophysical properties of CO\textsubscript{2}–brine systems. The miscibility behaviour has been extensively studied at reservoir conditions and beyond, and reliable correlations are available.\textsuperscript{863,864} Diffusion coefficients have also been reported for CO\textsubscript{2} in both water and brines\textsuperscript{865,866} and the effects of CO\textsubscript{2} dissolution on both the density and viscosity are reasonably-well understood.\textsuperscript{867–870} The IFT of the baseline CO\textsubscript{2}–water system has been the subject of numerous studies. While there is a lack of agreement between some sources, recent high-quality measurements appear to be consistent.\textsuperscript{871–875} The addition of salts is found to result in a small increase of the IFT as demonstrated by Li et al.\textsuperscript{876,877} In summary, it can be said that the thermophysical properties of CO\textsubscript{2}–brine systems are well understood over relevant ranges of temperature and pressure and that these properties can be confidently predicted from knowledge of the temperature, pressure and brine chemistry. Current research is focused mainly on the effects on these properties of the impurities that are inevitably present in the CO\textsubscript{2} stream.

Dissolution of CO\textsubscript{2} in the reservoir brines of course creates an acidic solution that can dissolve minerals (e.g. carbonates) at significant rates and transport them to regions of higher pH where they may then precipitate again. The dissolution rates of calcite and several other carbonate minerals have been measured experimentally at reservoir conditions by Peng et al.\textsuperscript{876,879} and used to help interpret pore-scale imaging of dynamic dissolution of limestones during injection of CO\textsubscript{2}-saturated brine.\textsuperscript{880}

The presence of hydrocarbons, especially oil, complicates the problem substantially, mainly due to their diverse chemical compositions. Given the typically low miscibility of hydrocarbon and aqueous phases under reservoir conditions, the phases formed when CO\textsubscript{2} dissolves in the reservoir fluids are primarily CO\textsubscript{2}–brine and CO\textsubscript{2}–hydrocarbon mixtures. To predict the thermophysical properties of the latter, bottom-hole oil samples are required; traditional techniques of reservoir fluid analysis and property modelling can then be applied.\textsuperscript{881}

One of the most challenging properties to predict is the contact angle formed between partially miscible fluid phases and the mineral surfaces. A recent review of contact angle measurements in CO\textsubscript{2}–brine–silica systems shows the data scattered over a range of almost 90\textdegree.\textsuperscript{882} This variation is attributed to the variations in surface morphology and impurities. A perhaps more promising approach is direct imaging, by means of X-ray computed tomography (CT), of the contact angles formed in the pore space of a representative reservoir rock during controlled fluid injection.\textsuperscript{883,884}

Much of the uncertainty around the petrophysics of CO\textsubscript{2} storage, and particularly the relative permeability, has been resolved over the past 5 years.\textsuperscript{885,886} It has been established that drainage and imbibition processes are typical of water-wet systems in sandstones\textsuperscript{887–891} and carbonate rocks.\textsuperscript{892} One of the key field scale implications of this has been the confirmation that capillary trapping will be a significant mechanism for immobilisation of the CO\textsubscript{2} plume in saline aquifer systems. This has been frequently estimated through modelling studies, e.g., Juanes et al.\textsuperscript{893} Another important implication is that the flow properties – relative permeability and residual trapping – are insensitive to reservoir conditions of pressure, temperature, and brine salinity.

Less well understood are the flow properties in systems altered by the presence of hydrocarbons. Research focused on petroleum systems has demonstrated that hydrocarbon-altered rock units trap less of the non-aqueous fluid phase.\textsuperscript{894,895} For carbon dioxide systems, Al-Menhali and Krevor\textsuperscript{896} and Al-Menhali et al.\textsuperscript{897} have shown that indeed residual trapping is significantly reduced in carbonate rocks with the “mixed-wet” state characteristic of many oil fields. There are no observations reported in the literature of the impact on relative permeability and capillary pressure functions, or dependencies on reservoir conditions. Injection of CO\textsubscript{2} into oil reservoirs dominates the current suite of industrial scale projects, making up over 90% of the approximately 30 Mt per year of anthropogenic CO\textsubscript{2} captured and sequestered and 11 of the 14 currently operating projects.\textsuperscript{862} It has been estimated that there is sufficient capacity for oil reservoirs to take up to 350 Gt of CO\textsubscript{2}, sufficient for the majority of the first generation of industrial scale CO\textsubscript{2} storage.\textsuperscript{897} It is thus important that the petrophysics of these systems be more thoroughly investigated.

Incorporating the impact of natural reservoir rock heterogeneity on flow is a rapidly developing area of both laboratory petrophysics and larger scale flow modelling. Much of the uncertainty around the understanding of relative permeability in CO\textsubscript{2}–brine systems was due to the impact of rock heterogeneity on laboratory scale core flood experiments.\textsuperscript{890,898,899} It is increasingly understood that these small scale features can manifest in the reservoir at larger scales with significant impacts on flow\textsuperscript{900,901} and trapping.\textsuperscript{902–904} This may be an important source of discrepancies between predicted flow dynamics and observations of plume migration in field and
8.3 Site development and reservoir engineering

Site characterisation involves the evaluation of a field with the aim of assessing its suitability for the injection of CO₂. Most of the techniques were established in the petroleum industry. They include sampling and geophysical observational activities that allow for the construction of a geological model of the injection zone and overburden. This model is then used for dynamic reservoir simulations that assess possible outcomes of injection into the field, and to construct site development plans.

The development practices for gas injection enhanced oil recovery projects are well established, whereas there is little experience with the development of dedicated CO₂ storage projects injecting into saline aquifers. Industry field development plans for injection into a saline aquifer at the Gorgon storage injection project in Australia have been reported in Flett et al. and for the now cancelled Peterhead project in the UK. Detailed development plans, including simulations, have also been proposed in a screening study of prospective early storage development sites in the UK by Pale Blue Dot and Axis Well Technology.

The presence of wells and previous hydrocarbon production activity is viewed as a significant factor in speeding up the development. Of the proposed development plans for five UK reservoirs in the report by Pale Blue Dot and Axis Well Technology, only two were deemed to require appraisal wells for initial site characterisation. A typical timeline inclusive of the use of appraisal wells, the final investment decision, and preparation for industrial scale injection will be 7–10 years.

Reservoir engineering for CO₂ storage also largely follows practices established in petroleum engineering. The guiding principles are to meet injection targets while minimising the risk of leakage through overpressure and fracturing of the cap rock, or plume migration to zones with potential leakage pathways. Plume migration has in practice not been a concern due to the size of the geologic units relative to the injection volumes of the first-mover projects. Pressure increases that limited injection have occurred at the Snøhvit site in the Norwegian Barents Sea as well as at the In Salah site in Algeria. Both of these involve injection into saline aquifer systems, without the pressure alleviation provided by past or ongoing hydrocarbon production. In the case of the In Salah project, the overpressure resulted in a fracturing of the lower part of the sealing cap rock unit and a cessation of injection activity. At Snøhvit, the pressure buildup was not entirely unexpected given the uncertainty about compartmentalisation of the initial target reservoir unit. Contingency plans were in place and injection was successfully switched to an overlying formation from the original target. Other important industry scale projects injecting into saline formations, i.e. without hydrocarbon production, include the Sleipner project and the Quest project in Alberta, Canada. These have operated without incident or the need for brine production.

Pressure management through brine production is a key area of ongoing research. In many locations injection targets can be met without any pressure relief from the reservoir system. This is particularly the case for injection coupled with enhanced oil recovery – where pressure relief is provided by hydrocarbon production – and in depleted gas fields where prior production has lowered the pressure below hydrostatic. Brine production has not yet been implemented in an operating storage project but it is included in the development plans for the Gorgon project in Australia. It is also widely considered to be necessary to take full advantage of regional storage systems over decadal timescales. Engineering strategies for brine production focus on maximising pressure relief while minimising the risk to leakage through CO₂ plume migration to the brine production wells, the analogue to gas or water breakthrough in oil production projects. Costs due to well construction and brine handling must also be minimised. A number of brine handling strategies have also been proposed, including those that enhance the rate of residual or dissolution trapping of CO₂ through brine re-injection into the reservoir or dissolution of CO₂ into brine at the surface prior to injection. These strategies remain at the research stage.

8.4 Monitoring, leak detection, and remediation

Monitoring of CO₂ storage relies on a suite of technologies developed for petroleum production applications. Instrumentation in the well bores – down hole data includes pressure, temperature logging, fluid geochemical sampling, the use of tracers, near well geophysical saturation monitoring, and potentially crosswell seismic reservoir characterisation. Over large spatial scales, the use of seismic surveys has been demonstrated to be useful in monitoring the growth and migration of CO₂ plumes. A major development was the successful demonstration of the use of InSAR technology at the In Salah field site to monitor movements in surface elevation over the injection site. This provided detailed constraints on the pressurisation of the subsurface. Jenkins et al. provides a comprehensive review of the state of the art.

The main challenge in the further development of these technologies concern their use in ways that allow for quantitative estimation the amount of CO₂ stored and the extent of the plume at the outer reaches of migration. This quantification is needed to verify the efficacy of storage. With seismic imaging, for example, there are significant limitations on quantifying fluid plume thickness and fluid saturation in the pore space. Additionally, CO₂ plumes will frequently have long thin tongues migrating as a gravity current in response to buoyancy, difficult to detect with seismic monitoring. Current research efforts are focused on extending the interpretation of seismic surveys so that thin layer features may be identified and saturation quantified, e.g. Ghaderi and Landrø, Trani et al. Similarly, saturation quantitation is also being extended to down well geophysical measurements such as crosswell seismic and near well observations, e.g., pulsed-neutron logging.
Another significant challenge for monitoring and verification lies in the development of techniques for quantifying the extent to which CO₂ has partitioned into the aqueous phase or has become residually trapped. Geochemical techniques show the most promise, with the use of both artificial and naturally occurring partitioning tracers allowing for estimates of residual trapping and the extent of CO₂ dissolution.933–936

Leak detection and remediation is a significant challenge for CO₂ storage with little analogue in the petroleum industry. Pressure monitoring in injection and observation wells is a key tool due to its precision and responsiveness. At the In Salah site, pressure monitoring combined with InSar data was effective in diagnosing leakage of CO₂ into the cap rock, with fractures in the cap rock induced by overpressuring of the system during injection.914 Pressure monitoring in overburden layers has been proposed and may also provide sensitive indicators of CO₂ leakage away from the target formation.937 Environmental monitoring for CO₂ flux at the surface over storage sites, either on land, or at the sea floor, has also been deployed.918,939 Techniques can be used to monitor CO₂ concentrations or isotopic signatures in soil gas or the atmosphere over the site, or changes in other chemical signatures like pH. The challenges here reside in detection. The signature of CO₂ leakage at the surface over a site is not well understood. It may be diffuse or focused through faults or abandoned wells.940 Similarly the isotopic composition of the fluid may have evolved as it percolated through the leakage pathways over the storage site. Once CO₂ is released into the atmosphere, it is quickly diluted. Natural background variation in CO₂ is also usually substantial, with daily and seasonal variations even in areas with little interference from industrial activities.

The mitigation of leakage risk and the remediation of leaks or their effects has recently emerged as an area of research interest.941 Applicable techniques developed in the hydrocarbon industry focus on the management of problematic wells and are directly applicable to CO₂ storage. For leakage away from wells, management of the local hydrogeology through the injection of brine has been proposed.937,942 adapted from techniques used in groundwater protection. The use of chemical seals emplaced in the reservoir have also been proposed by Vialle et al.943 The major challenges in developing in-reservoir leak mitigation technology comes from the major uncertainties of the subsurface rock heterogeneity that will control the effectiveness of these strategies. Due to the significant costs of, e.g., drilling a single well, and time required to evaluate the response, the uncertainty around the success of these strategy must be significantly reduced before these can be implemented in an industry setting.

8.5 Storage capacity and the role of CO₂ storage in energy systems

Storage capacity refers to the potential for a specific location or region to permanently store CO₂ in the subsurface. Evaluating capacity for specific storage sites is seen as a routine aspect of the characterisation and reservoir management stages, e.g., Pale Blue Dot and Axis Well Technology.913 As injection progresses at a given location, models may be updated for more accurate pictures of the local storage capacity.

The support for the importance of CO₂ storage, however, is predicated on the large scale potential for managing CO₂ emissions that would arise from the combined impact of sequestration across thousands of individual storage projects.6,944 This in turn is based on the assumption that there is far more pore space available to inject CO₂ into the subsurface than would be required for substantial CO₂ mitigation.945 Global scale assessments of CO₂ storage capacity support that view. Recent compilations of the global distribution of storage capacity include those of Benson et al.,945 Dooley,946 and Cook and Zakkour.947 Most of the modelling underpinning the IPCC assessment reports are based on earlier estimates from Hendriks et al.34 or do not consider capacity limiting at all.947 The estimated capacities, however, are such that updates to more recent compilations would not substantially impact the models used for the IPCC.

These capacity estimates, however, are known as “static” capacity estimates. They are estimated assuming that some fraction of the total pore space of a geologic unit, usually between 1–10% and known as the storage efficiency, can ultimately be made available for CO₂ storage.948 A more rigorous analysis of storage capacity would incorporate dynamic modeling of the pressure and plume migration during injection. A number of studies have shown that these are more likely to be limiting factors over decades to a century than the pore volume available in a geologic unit.949 Moreover, there is little correlation between static estimates of storage capacity and those making use of dynamic pressure and plume evolution (Fig. 18).

Estimating the time-varying capacity of storage resources by modelling the dynamics of injection is known as a dynamic approach to capacity estimation. The most comprehensive regional evaluation of dynamic capacity has been performed for the Nordic region under the NORDICCS project.955 Capacity estimation was largely based on the use of reservoir simulation tools developed for the petroleum industry, e.g., ECLIPSE. Simplified analytic or semi-analytic models have also been proposed which capture the dynamics of plume migration, pressure evolution, average regional pressure buildup, and impacts on injectivity around a well.956–959 There is significant potential for the use of these simplified models for dynamic regional evaluations of CO₂ storage, e.g., Szulczewski et al.,960 but there are also significant complications in the use of these models to represent regions with multiple injection sites.961 Assessments that evaluate the impact of regional development characteristics (e.g., number of injection sites, distance between injection sites, CO₂ injection rate, frequency of rate variation) on CO₂ storage962,963 provide valuable insight into improving models of CO₂ storage. If these models could be successfully incorporated into systems level analysis of energy systems, e.g., IPCC,6 it would significantly deepen our understanding of the potential role for CCS in future scenarios of low carbon energy production.

8.6 Outlook for CO₂ storage

CO₂ storage research has progressed significantly over the last decade. The technical feasibility of CO₂ storage has been
demonstrated through a number of industrial scale projects, with most being EOR projects. Subsequently, much of the existing CO2 storage experience is based in the oil industry and knowledge about CO2 storage in saline aquifers is limited. Similarly, the technology for CO2 storage monitoring was originally developed for the petroleum industry. Further development of monitoring instruments is required to enable quantitative predictions of the amount of CO2 stored, the extent of plume migration, geophysical saturation, and the extent of CO2 trapping and dissolution. Although leak detection has not been a focus for the petroleum sector, advances in leak detection technology is required to ensure that the storage of CO2 is permanent. Sensitive CO2 leakage indicators include pressure monitoring and measuring CO2 flux at the surface over storage sites (either as CO2 concentration in the soil/atmosphere or pH at the sea floor). To prevent CO2 leakage, safety measures that have been developed are chemical seals and pressure management of the site (e.g., brine production to prevent overpressure).

The thermophysical and flow properties of CO2 are generally well understood. Furthermore, there are well established procedures for site characterisation and determining the suitability of an injection site (e.g., cap rock or rock heterogeneity that control/prevent leakage). However, to further de-risk CO2 storage, research is required on studying the effect of: (i) impurities introduced via the CO2 stream on the thermophysical properties of the CO2–brine system, (ii) hydrocarbons already present in the geological system, and (iii) heterogeneity of reservoir rock on flow properties. Ultimately, the capacity of permanent CO2 storage needs to be quantified on a global scale to ensure that all of the CO2 captured can be adequately stored. However, this has typically been evaluated using “static” capacity models, which does not account for the dynamics of injection. Recent advances in models now provide time-varying capacity estimates, which consider the influence of system dynamics, e.g., plume migration, injectivity, pressure build-up. Future work on integrating these dynamic storage capacity models into energy systems models could provide valuable insight into the impact of storage capacity on meeting demand for low carbon energy.

9 CO2 enhanced oil recovery (CO2-EOR)

Carbon dioxide enhanced oil recovery, CO2-EOR, has been practised for many decades as a means to enhance the recovery of oil from depleted reservoirs.965 The process (illustrated in Fig. 19) is most effective by operating in ‘miscible’ mode, whereby the injected CO2, usually in the liquid or supercritical state, is fully miscible with the oil phase in the reservoir, reduces the viscosity of the oil phase which is then displaced from the rock pores in a single-phase drainage process. This requires the temperature-pressure conditions in the reservoir to be above the minimum miscibility pressure (MMP) for the CO2–hydrocarbon mixture. This is typically about 75 bar for light crude at reservoir temperatures of about 70 °C and rises with temperature. Whilst immiscible displacement using CO2 can also lead to moderate enhancement of recovery, this miscibility condition does mean that there is a limited window of opportunity to exploit the much more efficient miscible CO2-EOR process in depleting reservoirs before the pressure has declined below the MMP. Because of the lower viscosity and density of the injected CO2 relative to the in situ oil, there is usually significant fingering into the oil and breakthrough of the CO2 leading to about 50% recycle. Alternating injection of water and gas (WAG) is a widely practised technique to improve the displacement and recovery of oil.966

Carbon capture and storage enhanced oil recovery, CCS-EOR, is a similar process but with the dual objective of recovering additional quantities of oil from reservoirs whose oil production has fallen below critical levels whilst at the same time storing some of the injected CO2 permanently in the depleted reservoir rather than pumping it back to surface. The driver here is to generate as much income as possible from incremental oil to offset the high costs of the CCS process – of order $70 per tonne of CO2 stored. Whereas in CO2-EOR, the objective is to produce as much incremental oil as possible using as little CO2 as possible, without any concern for CO2 retention in the reservoir (or in optimum scenarios to recover as much CO2 as possible so that it can be recycled), with CCS-EOR there clearly needs to be a balance between recovered hydrocarbon (to generate income) and the amount of CO2 stored, which for the process to be economically viable needs to be significantly greater than the optimal amount required for efficient miscible displacement. This balance turns out to be critical in determining the viability of CCS-EOR processes.

CCS-EOR is a form of CO2 utilisation967 and is currently the only way to add value to CO2 at the mega-tonne per annum scale. Typical incremental oil values for optimised CO2-EOR
processes are 5–15% of the original oil in place (OOIP), and the typical utilisation is about 3 tonnes of CO₂ purchased and injected leads to about 1 bbl of incremental oil.

9.1 Current CCS-EOR activity

Globally there are currently more than 140 CO₂-EOR projects, producing about 300,000 bbl of incremental oil per day, equivalent to about 0.35% of global oil production. Most of this production is in the United States Mid-West. The objective is mainly EOR, not CO₂ storage, aiming to minimise net CO₂ injection and maximise oil recovery. For the process to be a viable route for high volume CCS requires a paradigm shift where the business target is to maximise both oil recovery and CO₂ storage. Since 2000 about six projects have been commissioned which are truly CCS-EOR, of which the largest are both in Saskatchewan, Canada: at Weyburn-Midale and at Estevan (Boundary Dam).

The Weyburn-Midale project run by Cenovus and Apache, was fully monitored between 2000 to 2012 and verified as a CCS project. The incremental oil was approximately 220 Mbbl over the project lifetime, producing 3 bbl per t CO₂ purchased. More than 20 Mt CO₂ have been stored to date and the expectation is that 40 Mt CO₂ will be stored over the project lifetime, 30 Mt CO₂ in the Weyburn field and 10 Mt CO₂ in Midale. The daily injection of CO₂ consists of 6500 t CO₂ of fresh feed accompanied by 6500 t CO₂ of recycle; the CO₂ feed comes from the North Dakota Beulah synfuels gas plant via a 320 km pipeline. The project has extended the lifetime of the fields by over 25 years.

By contrast the SaskPower Boundary Dam Integrated CCS Project is very recent. Opened in October 2014 as the world’s first fully commercial CCS plant, it cost about $1.3bn, of which $300m was provided by government. It involves post-combustion capture (90% efficiency) of CO₂ from a 110 MW coal-fired power station. Its target is to store 1 Mt of CO₂ per year in steady state operation; it reached a total storage of 1 Mt CO₂ in August 2016 and is now operating close to the design storage rate. This is equivalent to removing 250,000 cars from the road. The CO₂ is pumped via a 66 km pipeline to the Weyburn depleted oil reservoirs where it is used for EOR before storage, hence adding significant value to the captured CO₂. The remainder is stored in the 3.4 km deep Deadwood saline aquifer, which is only 2 km away, within the Aquistore project administered by the Petroleum Technology Research Centre (PTRC).

Other significant CO₂-CCS-EOR (i.e., CO₂-EOR combined with CCS) projects are summarised in Table 7. In 2004, IEAGHG identified 420 CO₂-EOR ‘early opportunity’ candidates but relatively few of these have been exploited.

9.2 Combining CO₂-EOR with CCS

In order to add CCS capability to a CO₂-EOR project (CO₂-CCS-EOR), several further issues need to be considered. Additional site characterisation and risk assessment is needed to assure storage integrity, together with additional measurements of gas venting and fugitive emissions associated with inadvertent gas releases from surface equipment. Long term integrity needs to be assured through additional monitoring of the subsurface and enhanced field surveillance using surface monitoring.

Fig. 19 Schematic diagram of CO₂-EOR process. Source: Global CCS Institute.
Changes in abandonment processes to ensure long-term well seal integrity also need to be implemented. All this adds costs to conventional CO2-EOR.

One of the most detailed analyses of the viability of combining CO2-EOR with CCS was carried out recently by the IEA. In their 2015 report they call this process ‘CO2-EOR+’ and identify three possible scenarios:

- **CO2-EOR+ Conventional (or ‘Light’),** where conventional CO2-EOR is supplemented by a full CCS risk assessment, monitoring and verification but little attempt is made to increase the amount of CO2 injected. Representative values given for this scenario are a net utilisation of 0.3 tCO2 per bbl oil produced with an incremental oil recovery of 6.5% of OOIP.

- **CO2-EOR+ Advanced (or ‘Balanced’),** where the aim is to increase both the amount of CO2 stored and also the incremental oil recovered – a win-win scenario. Here, typical values could be a net utilisation of 0.6 tCO2 per bbl oil produced for an incremental oil recovery of 13% OOIP.

- **CO2-EOR+ Maximum Recovery (or ‘Heavy’)** where there is a strong focus on CO2 storage, with representative values of injecting 0.9 tCO2 per bbl oil produced for the same incremental oil recovery of 13% OOIP as in the Balanced scenario. Here, there would be no produced water reinjection or CO2 recycle.

### 9.3 Is there enough storage volume for CO2-EOR+?

The brief answer to this question is ‘Yes, but maybe not in the right places’. Current CO2 emissions are about 36 Gt pa, equivalent to about 100 Mbbbl CO2 per day, compared with oil production levels of about 90 Mbbbl per day. We need to capture 15–20% of total CO2 emissions to meet global carbon mitigation targets (the remaining being accounted for by energy efficiency/savings measures [up to 50%] or through increased deployment of renewables and nuclear [about 30%]). CCS targets to meet the COP21 target of limiting mean global temperature rise to 1.5–2°C through capping atmospheric CO2 levels at about 450 ppm require capacity to store 120–160 GtCO2 at a rate of about 10 GtCO2 pa by 2050, equivalent to ~3000 major facilities. The storage requirement by 2100 may be as high as 1200–3300 GtCO2.

The global storage potential for CO2-EOR+ Light has been estimated at 70–140 GtCO2, in principle, resulting in about 470bn bbl of incremental oil (see Table 8). However, this may be a highly optimistic estimate of the total deployable CO2-EOR capacity. As illustrated in Table 8 and Fig. 20, the majority of this capacity exists in the Middle East/North Africa and in the USA at 50% and 13% respectively, whereas the estimated CO2-EOR in South Asia is essentially zero with the Asia Pacific region accounting for only about 3%.

In other words, as illustrated in Fig. 20, there appears to be an unfortunate disconnect between regions of substantial CO2-EOR potential and those regions with the largest anticipated population growth, dependence on fossil fuels and requirement to sequester CO2 over the course of the next century. In fact, the only region where it appears certain that there is sufficient CO2-EOR capacity to meet the CO2 storage requirements to 2050 is the Middle East and Africa – although the requirements are close in North America and the Former Soviet Union. Given the size and rate of growth of the CO2-EOR industry in the USA, it is likely that this region will be a leader. If we recognise that in some cases CO2 injection will be restricted by availability rather than by CO2-EOR capacity, a more realistic estimate is likely to be on the order of 40 GtCO2 injected and stored via CO2-EOR. This is in line with the recent IEA estimate. If we adjust this for the net emissions from the additional incremental oil (see later), the total capacity for CO2-EOR+ Light is about 35 GtCO2, which is ~30% of the 2050 target and 4–5% of the total CO2 mitigation target.

The IEA analysis used the industry U-Cube capacity database on a field-by-field basis. It estimates that the global capacity for CO2-EOR+ ‘Balanced’ is ~240 Gt and for CO2-EOR ‘Heavy’ is about 360 Gt, two and three times respectively the IEA’s estimate of CO2 storage. Outside North America, the main capacity is focused on the Middle East (>100 Gt), Russia (>70 Gt), North Africa (~35 Gt) and Central Asia (~20 Gt). The potential for incremental oil for conventional CO2-EOR up to

### Table 7 Major current CO2-CCS-EOR projects968

<table>
<thead>
<tr>
<th>Project</th>
<th>Description</th>
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</thead>
</table>
| Weyburn-Midale; IEAGHG, Cenovus, Apache (2000) | - CO2 from North Dakota Beulah synfuels gas plant via 320 km pipeline  
- >20 MtCO2 injected to date; 40 MtCO2 target  
- Anticipated 220 Mbbbl incremental oil from Weyburn-Midale fields                                                                                                                                       |
| Boundary Dam Unit 3, SaskPower, October 2014  (Saskatchewan, Canada) | - Continuous mode 110 MW coal (lignite)-fired power station  
- Captures 95% of CO2 emissions (and 100% of the SO2)  
- 1 MtCO2 pa transported in 65 km pipeline to Weyburn field for EOR  
- Some CO2 stored in close (2 km) Deadwood saline aquifer (Aquistore Project)                                                                                                                             |
| NRG Petra Nova, Texas (2015)                  | - 240 MW coal plant with gas post-combustion capture (90%)  
- 1.4 MtCO2 pa injected into West Ranch oil field                                                                                                                                                        |
| Petrobras, BG Brasil, Petrogal Brasil (2013)  | - 0.7 MtCO2 pa from natural gas production  
- Injected for EOR 5–7 km sub-sea, 300 miles offshore Rio  
- Deepest CO2 injection in the world                                                                                                                                                                       |
| Saudi Aramco Uthmaniyah Project, Saudi Arabia (2015) | - 0.8 MtCO2 from gas processing used for EOR from Uthmaniyah field                                                                                                                                       |

- Boundary Dam Unit 3, SaskPower, October 2014 (Saskatchewan, Canada)  
- Petrobras, BG Brasil, Petrogal Brasil (2013)  
- Saudi Aramco Uthmaniyah Project, Saudi Arabia (2015)
2050 is 190bn bbl, whilst the ‘Balanced’ and ‘Heavy’ scenarios could deliver an additional 375bn bbls during that period, over ten times the current annual oil consumption. Therefore the technical global capacity of CO₂-EOR+ to both store CO₂ and to deliver significant incremental oil to deliver revenue through CCS is therefore considerable, capable of meeting current targets to meet the 2 °C scenario. The main issue is whether the economic drivers will be in place to make the process financially viable.

9.4 What about the economics?

Conventional CO₂-EOR is profitable at ~ $65 bbl oil with CO₂ costs at $30 per tCO₂. CO₂ prices are even lower than this for naturally occurring CO₂ sources which explains why several of the existing CO₂-EOR projects are located close to such sources. The major future drivers for CO₂-EOR+ will be:

- A regulatory requirement or fiscal incentive (carbon price through a tax or trading system) to store CO₂.
- High oil prices – a major factor as this controls the value of the incremental oil produced per tonne of CO₂ stored.
- Lower CO₂ supply prices, which will be strongly dependent on the level of a carbon price. Currently the EOR operator pays the CO₂ generator for acquisition of the CO₂, whereas under a 2 °C regime supported by a realistic carbon price, by 2050 the generator could be paying the EOR operator a large fraction of the carbon price to store the CO₂ generated in power production or industrial manufacture e.g. up to $125 per tonne CO₂.
- Reductions in core EOR process costs, especially the additional cost requirements of CCS mentioned earlier.

The recent IEA study calculated the NPV of typical CO₂-EOR+ projects for a range of ETP future scenarios where, as the mean global temperatures rise from 2 °C to 6 °C, both the oil price and the CO₂ supply cost increase. Fig. 21 shows the sensitivity of the project profitability to the oil and CO₂ prices.

The conventional CO₂-EOR+ ‘Light’ process remains the best option for low oil and high CO₂ prices (costs), down to the point where carbon pricing forces CO₂ prices to be negative. The ‘Balanced’ scenario is the favoured option once CO₂ prices become negative (CO₂ producer pays) or oil rises above about $90 per bbl, which is where oil prices were 2008 to 2014, driven by income from both incremental oil and CO₂ disposal payments. Once the latter rise further, with further rises in the carbon price, then the ‘Heavy’ CO₂-EOR+ option becomes increasingly viable with increased CO₂ disposal revenues. Hence the economic viability of CO₂-EOR is closely linked to both the global oil-gas economy and to regional and global geopolitics governing the existence and level of a carbon price.

In the absence of either high oil prices or high carbon prices, it is unlikely that CO₂-CCS-EOR will move from its current position of opportunistic localised projects with minimal impact on reaching the required global CCS levels.

9.5 Does CO₂-CCS-EOR really reduce emissions?

A final critical issue for CO₂-CCS-EOR, in the light of the production of incremental oil (and sometimes gas), which will be subsequently burned for fuel or power, is whether CO₂ emissions are actually reduced by storing CO₂ in the subsurface alongside increasing oil production to partially offset the costs of CCS. Here it is crucial to carry out a life cycle analysis from the production of the original hydrocarbon, through its use, then its capture, transport and storage via CO₂-EOR, including CO₂ recycle and separation of produced natural gas liquids, to the eventual use of the incremental oil.

<table>
<thead>
<tr>
<th>Region name</th>
<th>Recovery (MMBO)</th>
<th>Basin count</th>
<th>CO₂-oil ratio (tonnes per bbl)</th>
<th>CO₂ stored (GtCO₂)</th>
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</thead>
<tbody>
<tr>
<td>Asia Pacific</td>
<td>18 376</td>
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<td>2.7–5.0</td>
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</tbody>
</table>
Considering just the storage process itself, project level emissions are significantly carbon negative when disposing of anthropogenic CO₂, ranging from ~0.76 tonnes CO₂-equivalent per tonne of CO₂ delivered for CO₂-EOR+ ‘Light’ to ~0.86 tonne CO₂-equivalent for the ‘Heavy’ process.⁹⁶⁸ When emissions from the use of the incremental oil are included, the ‘Balanced’ CO₂-EOR+ process is essentially carbon neutral whereas the ‘Heavy’ scenario results in a net storage of ~33% of the injected CO₂. However, the additional oil produced by CO₂-EOR can displace oil which would otherwise have been produced elsewhere with additional cost and additional CO₂ footprint. Once these displaced emissions are taken into account, then the net CO₂ emissions vary from about 0.7 to 0.8 tonne CO₂-equivalent per tonne CO₂ stored.⁹⁶⁸ This clearly depends on the type of oil recovered by EOR and displaced. In an era where new oil may consist of an increasing proportion of heavier crudes or unconventional tar sands or oil shales, the net emissions benefit of using CO₂-EOR+ on conventional light oil reservoirs can rise to as much as 1.5 tonne CO₂-equivalent per tonne CO₂ stored.⁹⁶⁸

9.6 CO₂-EOR: future challenges and opportunities

Overall, the emissions reductions resulting from the use of CO₂-EOR+ will vary with the precise conditions, but they will always be negative and typically above 0.7 tonne CO₂-equivalent per tonne CO₂ stored. Yet the processes of CO₂-EOR and CCS are currently far from optimal so better understanding and optimisation of miscible CO₂ displacement processes in porous reservoirs for both enhanced recovery and storage⁹⁷⁹ should result in improved efficiencies and lower costs. There is an element of risk reduction and public reassurance that such processes are safe and secure, particularly on land. To enhance public reassurance and reduce risk, R&D and field trials focus on key assurance issues such as decommissioning, fugitive emissions monitoring and sub-surface monitoring of fluids migration and real-time process control. Although progress has been made, there is a need for further reconciliation of the legal frameworks for carbon storage and EOR, and ensuring CO₂-CCS with EOR can remain part of the Clean Development Mechanism.

There are significant CO₂-CCS-EOR opportunities in unconventional gas recovery: enhanced coal-bed methane production,⁹⁸⁰ shale gas,⁹⁸¹ even combined gas hydrate production and exchange/storage.⁹⁸² These should be explored as potential routes to lower net costs of CO₂ storage in coal seams, shale reservoirs and gas hydrate sediments, as well as accessing additional non-conventional gas reserves cost-effectively. In the absence of a strong carbon pricing driver, the linkage of CO₂-CCS-EOR to relatively pure, low cost sources of CO₂, such as that from the Leilac cement capture process,⁹⁸³ or co-produced CO₂ from gas wells, would be cost-effective routes to ramp up the approach.

10 CO₂ conversion and utilisation (CCU)

10.1 The role of CCU in climate change mitigation

Carbon capture does not only enable CO₂ storage but also utilisation and chemical conversion of the captured CO₂. The resulting concept of carbon dioxide re-use (CDR) or CO₂ conversion and utilisation (CCU) has been gaining significant attention in recent years.⁹⁸⁴–⁹⁸⁷ For a long time, CO₂ has been used industrially for a variety of applications ranging from carbonated drinks to urea production.⁹⁸⁸ The recent interest in CCU is motivated by climate change mitigation as a societal issue⁹⁸⁹ but also by recent breakthroughs in catalysis for CO₂ activation as technological driver.⁹⁹⁰,⁹⁹¹ Several plants demonstrating novel pathways for carbon dioxide re-use are already in operation.⁹⁹²

Carbon dioxide may be re-used directly as technological fluid, e.g., as solvent, by conversion to chemicals and fuels, and by mineralisation to solid inorganic carbonates⁹⁸⁴ (Fig. 22).

The simplified life-cycle for CCU (shown in Fig. 22) identifies potential roles of CCU in climate change mitigation from a carbon-accounting perspective:

- Carbon-negative products: CCU can be carbon-negative, if and only if (1) atmospheric CO₂ is used (either directly from direct air capture or via biomass)⁹⁹³ and (2) a solid inorganic
carbonate is produced which is thermodynamically more stable than CO\textsubscript{2} and thus provides long-term storage. If CO\textsubscript{2} is captured from fossil sources such as power-plants or industry, CCU cannot be carbon-negative over its life cycle.

- Carbon-neutral products: CCU allows carbon-neutral pathways, if and only if atmospheric CO\textsubscript{2} is used or CO\textsubscript{2} is captured during the end-of-life treatment of a CO\textsubscript{2}-based product. Alternatively, converting fossil-based CO\textsubscript{2} by mineralisation would also be conceptually carbon-neutral.

Beyond the simple carbon-accounting perspective, CCU could contribute to climate change mitigation via further mechanisms:

- Carbon-reducing products: even when a CCU pathway is not overall carbon-negative, it can be carbon-reducing by replacing an existing product with less greenhouse gas (GHG) emission intense alternative. A recent example is the production of polyethercarbonate polyols from CO\textsubscript{2} (which can be processed further to polyurethane (PU) foams). The novel polyols contain about 20 mass\% CO\textsubscript{2} and could reduce GHG emissions by 11–19\% compared to conventional polyether polyols. Often, the carbon reduction depends on the availability of hydrogen with low or even very low global warming impacts.

- Temporary carbon storage: chemicals or fuels produced from CO\textsubscript{2} offer temporary storage of CO\textsubscript{2}. While the storage duration is usually short for fuels, it would be longer for chemicals, e.g., polymers used for housing insulation. Still, permanent storage is usually only assumed for storage longer than 100 000 years. The impact of temporary CO\textsubscript{2} storage on climate change is not sufficiently understood yet. Life-cycle assessment (LCA) does usually not account for emissions timing. Several methods have been proposed for this purpose. In the absence of an accepted method, standards currently recommend to separately report the amount stored and the duration for temporary storage.

The life-cycle of CCU (Fig. 22) is also helpful to clarify the relation between carbon dioxide re-use and carbon capture and storage. Often, CCU has been contrasted to CCS and proposed as an alternative. This viewpoint may be tempting due the joint capture step and the similar acronyms CCS and CCU used for CO\textsubscript{2} re-use in the literature. However, it is also misleading. Even though both CCU and CCS aim at mitigating climate change, the approaches are rather complementary than in conflict. While CCS addresses the end-of-life problem, CCU addresses a beginning-of-pipe problem, i.e., a raw materials problem, by providing a sustainable carbon source. Thus, the CCU life-cycle integrates naturally into the CCS life-cycle. A storage step could be added to all CCU routes where CO\textsubscript{2} is released at the end-of-life. The debate about CCU should therefore be separated from CCS.

The preceding discussion of CCU focuses on its potential in climate change mitigation, which is also at the centre of the current debate in public and science. However, it has to be emphasised that one major environmental driver for CO\textsubscript{2} utilisation is the provision of a non-fossil carbon feedstock for the chemical industry which helps to reduce depletion of resources. Avoiding fossil-based feedstock then often induces savings of GHG emissions as a secondary effect. An example is the replacement of fossil-based epoxides by CO\textsubscript{2} in the production of polyols. In addition, CCU products may also lead to other environmental benefits. The direct synthesis of the potential fuel additive dimethoxymethane from CO\textsubscript{2} has been recently demonstrated. Dimethoxymethane is the first member of the homologous series of poly(oxyethylene) dimethyl ethers (OME) which have been shown to reduce soot formation during combustion and might thus lead to cleaner fuels.

An additional driver can be economics as CCU leads to a valuable product and may thus generate a revenue in contrast to carbon storage. It has therefore been argued that CCU
might incentivise CO₂ capture technologies. This argument, however, neglects the different scales of potential CCS installa-
tions and most CCU products. For most potential CCU pro-
ducts, even producing the global demand completely from CO₂
would not be able to take up the CO₂ generated by a single
state-of-the-art coal-fired power plant. The current total global
anthropogenic CO₂ emissions from fuel use is 32.3 GtCO₂ per
year. The eight most CO₂-emitting thermal power plants in the
European Union alone generate sufficient CO₂ to cover the
current global demand for CO₂ of about 200 Mt per year. The upper limit of current CO₂ demand for the manufacture of chemicals is estimated to be around 300 MtCO₂ per year, with the potential to increase up to 500 MtCO₂ per year. Although CO₂ demand is expected to increase, re-using CO₂ for chemicals will always be limited since the total mass output of the chemical industry is 14–20 times smaller than the current output from the energy industry. The production of fuels could increase the CO₂ demand by up to 2050 Mt per year. CO₂-based fuels, however, usually require hydrogen that (a) comes from low-carbon sources to achieve environmental benefits, and (b) is available at low cost to be economically viable. One important point, the end-of-life for CO₂-based fuels and chemicals will be the eventual release of CO₂. Thus, CO₂-based fuels/chemicals are carbon-neutral in the best case (as discussed earlier).

The discussion in the previous paragraph focused on the amount of CO₂ utilised which is often used as a proxy for the amount of CO₂ avoided. However, the amount of CO₂ avoided might differ significantly from the amount of CO₂ utilised as the discussion of climate-change mitigation mechanisms above has shown. In fact, CCU might even increase CO₂ emissions, e.g., if hydrogen from fossil sources is used to produce fuels. Carbon dioxide re-use can also reduce CO₂ emissions beyond the amount of CO₂ used. Aresta et al. estimate based on stoichiometric analysis that the production of ethane carbonate could avoid up to 17.9 tons of CO₂ emissions for every ton of CO₂ used; using data from an industrial pilot-plant, it was shown that using 1 ton CO₂ captured from a lignite-fired power plant to produce polyols reduces CO₂ emissions by up to 2.98 tons. Thus, the benefits have to be evaluated on a case-by-case basis for each CCU technology, along with the required setting to achieve them.

10.2 Future perspective and key research needs

Carbon dioxide re-use will have a role in climate-change mitigation – but the size of this role is still unclear. A number of key issues need to be addressed to make best use of the potential benefits from implementing CCU. These issues are discussed in the following.

The scale of CCU will mainly depend on the large-scale implementation of CO₂-based fuels since the potential for CO₂ re-use in fuels is about 12–14 times higher than for chemicals. CO₂-Based fuels have been shown to be able to reduce GHG emissions over the life cycle. Several pilot-plants are already in operation for CO₂-based methane and methanol. The George Olah Renewable Methanol Plant in Iceland is producing 4000 tonne per year. However, the large-scale implementation of CO₂-based fuels still requires to overcome several challenges.

The production of potential fuels such as methane, methanol by Fischer–Tropsch synthesis still requires major progress in catalysis and the design of efficient processes. CO₂-Based methanation is expected to increase the cost of natural gas by a factor of 2.4 based on the most optimistic estimate for the year 2050 while current worst estimates predict a cost increase as large as a factor of 30. For methanol, CO₂-based production are estimated to increase the selling price by a factor of 1.8. Thus, cost efficiency has to be addressed in all aspects; most importantly for the hydrogen source but also for the feedstock CO₂ and for investment cost. It has been argued that CO₂-based fuels could provide an important link to the energy sector by providing chemical energy storage as well as flexibility to the electrical grid. Thus, dynamic operation of CO₂-based fuel production may provide opportunities but will require the development of novel technologies. In this case, hydrogen storage might become a cost and design factor. For methanation, the strong exothermic reaction provides opportunities for heat integration. For methanol production, highly selective and long-term stable catalysts are required as well as more efficient separation technologies for the methanol–water mixture. Novel process concepts are tailored for CO₂-based fuels. Integrating CO₂ capture with conversion could provide efficiency gains. Developing suitable reaction systems is therefore important, which allow the conversion of CO₂ directly in aqueous amine solutions used for CO₂ capture. The integrated capture and conversion can increase efficiency. However, an increased efficiency is not guaranteed because the solvent needs to be separated from the final product instead of CO₂ which might be more difficult. At the research level, electrocatalytic processes are gaining more interest since they allow the targeted integration of renewable energy into the conversion steps. However, even with much improved future electrocatalytic processes, the cost of renewable energy is expected to remain the main obstacle for implementation.

The production of CO₂-based fuels usually requires the reduction of the oxidation state of carbon to 2+ or lower. For this purpose, high energy exchanges are needed by strong reducing agents such as hydrogen. Even assuming a conversion process that achieves ideal performance at the thermodynamic minimum, the availability of hydrogen at low-carbon impacts and low cost often remains the crucial element for CO₂-based fuels. Thus, efficient production of hydrogen with low environmental impacts will be the key enabler for large-scale CCU. Machhammer et al. compared the cost and carbon footprint related to the operation of hydrogen production technologies. The identified Pareto-efficient technologies for hydrogen production are: water electrolysis using wind power (zero carbon footprint for operation; high cost), methane pyrolysis (medium carbon footprint; medium cost) and conventional methane steam reforming (high carbon footprint; low cost). Taking a full life-cycle assessment into account suggests
that methane pyrolysis could even become more CO₂ efficient than water electrolysis driven by wind power if the produced carbon is stored.1029 In this case, however, the demand for fossil resources is more than doubled. Hydrogen production by water electrolysis has only low emissions if renewable surplus electricity is available. Renewable energy, however, will still be limited in most places for the foreseeable future. Thus, overall process efficiency remains a key performance indicator since power-to-fuel technologies would be competing with other pathways to utilise renewable energy. Most competing Power-to-X technologies currently offer a higher CO₂ abatement per kWh electricity used than CO₂-based fuels.1015 CO₂-Based fuels would thus have to generate additional value, e.g., from the functionality as fuel or by avoiding expansion of the electricity grid. Systems level analysis of whole value chains is required to identify promising scenarios for CCU.1030 Here, regionalised concepts could help to identify promising locations combining sources for CO₂ and H₂ with suitable sites for fuel production. Hereby, the amount of fuels needed in the future is itself an open question due to electrification of the transportation sector and of heating. In such an analysis, CO₂-based fuels need to be benchmarked to other low-carbon fuels such as biofuels,1031 or nitrogen-based fuels.1032 In this context, the integrated design of biorefineries with CO₂ utilisation could provide a promising avenue for efficient carbon use.1033

Carbon dioxide can also be re-used while keeping the 4+ oxidation state of carbon. These routes target the production of urea, polymers, and inorganic carbonates.988 The production of solid inorganic carbonates by CO₂ mineralisation seems a particularly promising target for market-entry of CO₂-based products. Mineral carbonation can generate construction materials by conversion of suitable silicates. These routes are favoured by thermodynamics and lead to stable products. Mineralisation even offers opportunities to convert wastes, e.g., steel slags, with CO₂ to valuable construction materials.1034 Thereby, the start-up company Carbon8 is able to charge its suppliers $190 per ton of waste, e.g., from fly ash, since the suppliers would pay more for landfill.992 The challenges for mineral carbonisation to be addressed are energy use, slow reaction rates and material handling.994 CO₂ storage in solid carbonates is expected to enhance public acceptance since “this method of storage is highly verifiable and unquestionably permanent.”809

CCU has the potential to play a role as renewable carbon feedstock for the chemical industry. While the chemical industry contributes only 4% to the global GHG emissions from fossil fuel combustion, the emissions are large compared to other industries.1035 Thus, after the energy sector, the chemical industry is certainly one of the next targets to reduce GHG emissions. For the chemical industry, CCU could avoid emissions of several million tons of CO₂ while at the same time decreasing the dependence on fossil fuels as carbon source for chemical production. The replacement of a fossil-based product with CO₂-based production has no impact on the overall GHG emissions unless global fossil fuel demand is actually reduced. System-wide consequential life-cycle assessment1036,1037 is required to capture these interdependencies and to identify future tipping points away from fossil-based production of chemicals. For this purpose, a large variety of potential chemical products are currently explored to be produced from CO₂.984–987

We expect the first implementations for processes where CCU improves the production of established products. The CO₂-based polyols are such an example: 5000 tonne per year are currently produced commercially in a first demonstration plant.992 A further opportunity results from the production of formic acid1038 which can be synthesised directly from CO₂ and H₂.991,1039 while several process steps are required in the conventional production. Several companies are therefore working on the production of CO₂-based formic acid.1040 Cost are currently still estimated to be 2.5 times higher than fossil-based production due to hydrogen production and current catalysts.1041 For the production of the antifungal agent butenafine, CCU allows the switch to cheaper reactants, avoids potentially hazardous reagents and wastes, and reduces the number of process steps to one.1042 The formylation of amines with CO₂ leads to formamide products which are versatile chemicals and key building blocks.1043 Organic carbonates provide a wide range of potential products ranging from low molecular weight products such as dimethylcarbonate1044,1045 to cycle carbonates1046 and finally polymeric compounds.1047,1048 Beyond the more efficient production of current products, advanced methods for CO₂ conversion could generate novel products enabling environmental benefits such as the novel OME-fuels mentioned above.1066–1068

The systematic identification of such opportunities would be desirable. Systematic design methodologies could help to identify promising targets.1018 In order to support research at early design stages, predictive model approaches need to be developed which would allow to enable the in silico assessment of the potential of novel pathways and products.1036 By employing the quantum-chemistry-based thermodynamic model COSMO-RS, Jens et al.1049 were able to screen more than 100 000 combinations of flowsheet layouts, solvents and chemical storage molecules for the conversion of CO₂ to CO. Incorporating such model-based knowledge into the chemical design process would accelerate the development of novel CCU technologies.

Life-cycle assessment (LCA) of prospective products could help to guide research needs and to provide performance targets.1045,1050 Importantly, LCA should not only be limited to impacts on climate change. Instead, a wide range of environmental impacts should be considered to avoid problem shifting to other impact categories such as resource depletion. These trade-offs need to be analysed even though some CO₂-based products reduce all environmental impacts as shown, e.g., for the novel polyethercarbonate polyols.987 Still, these products are not carbon negative in general and even often not close to carbon neutral due to the need of highly energetic reagents such as hydrogen or epoxides in the case of polyols. Identifying sustainable pathways for the co-reagents is thus a key challenge.1051

In order for life-cycle assessment to take on a guiding role, a methodological consensus has to be reached for the application to CO₂ re-use technologies.1001 Currently, a wide variety of
methodological choices are applied making it difficult to compare results from different studies.\textsuperscript{989} The LCA community can learn from the case of bio-based materials how (difficult it is) to apply LCA to renewable carbon feedstock.\textsuperscript{\textcircled{1052}} To provide a better database for environmental assessment but in particular also for knowledge gaps regarding accurate costing and data on process technologies, large scale projects are helpful demonstrating the industrial application of novel CCU pathways.

Such large-scale projects would also be beneficial to learn about public acceptance of CCU technologies.\textsuperscript{1053,1055} Integrating insight from public acceptance studies into the research and development process could become crucial for the future implementation of CCU. A major role in the transition to low-carbon fuels will be played by politics. Since many pathways are not yet economically viable, incentivising low-carbon fuels would be required. Carbon tax benefits or CO\textsubscript{2} certificates could be related to the re-use of CO\textsubscript{2} as means of climate change mitigation. For this purpose, carbon accounting methods would need to be adapted to provide a benefit from re-using carbon dioxide from the atmosphere or from flue gases. For a production technique for precipitated calcium carbonate, the Court of Justice of the European Union has recently ruled that the CO\textsubscript{2} is chemically bound in a stable product, thus the CO\textsubscript{2} source does not have to account for the CO\textsubscript{2} emissions under the emissions trading system (ETS).\textsuperscript{1055}

In order to contribute its potential share to climate change mitigation, CO\textsubscript{2} re-use has to survive the hype cycle where it might currently be approaching the peak of inflated expectations. Sound and unbiased assessment of the benefits and disadvantages of CCU technologies should help to identify the plateau of productivity.

### 11 Technology learning and associated cost reduction

#### 11.1 The theoretical basis for learning curves

Computer models used for energy-related planning and policy analysis typically employ one of two methods to represent technological change: either the future cost and performance of technologies are exogenously specified by the modeller, or a mathematical model is used to relate the future cost and performance of energy-related technologies to other model parameters. The latter method includes the use of “learning curves” (or experience curves) to project the future cost of technologies.

In 1936, Wright\textsuperscript{1056} observed that the average time required to manufacture a given model of a Boeing aircraft decreased systematically with each unit produced. Wright\textsuperscript{1056} captured this phenomenon with an equation representing what he called a “progress curve” given by:

\[
Y = ax^b
\]  \hspace{1cm} (15)

where, \(Y\) is the estimated average direct man-hours per unit for \(x\) units; \(a\) is the direct man-hours needed to manufacture the first unit; and \(b\) is a parametric constant. Using this equation, Wright demonstrated that the labour input, \(Y\), dropped by 20 percent for every doubling of cumulative output, an 80 percent “progress ratio” where the exponent \(b\) was \(-0.32\).

Wright’s work remained relatively obscure until a decade later, when it was picked up by a group of economists at the then recently founded RAND Corporation, who applied his findings to the production of war materials and described the phenomenon as “learning-by-doing”. Subsequent work by the Boston Consulting Group (1968)\textsuperscript{1057} applied Wright’s equation to the relationship between the average unit price and cumulative production of two dozen selected industrial products. When applied in this fashion to a class of product (rather than to a specific manufacturing process), the “learning curve” equation became referred to as an “experience curve”.

More recently, this formulation (eqn (15)) has been adopted in empirical studies to characterise learning phenomena in a broad range of sectors, including manufacturing, ship production, consumer products, energy supply technologies, fuel technology, energy demand technologies, and environmental control technologies.\textsuperscript{1058} In these applications, the dependent variable \(Y\) is typically the unit price or cost of a technology and \(x\) is its cumulative production or installed capacity. Eqn (15) also can be re-written as:

\[
\log Y = c + b \log x
\]  \hspace{1cm} (16)

where, \(c\) is a constant and \(b\) is the slope of a line on a logarithmic scale. In these applications, the one-factor independent variable, \(x\), is effectively surrogate for all factors that affect the cost trajectory of a technology.

Today, this log-linear form of the learning curve remains the most popular equation used to represent the expected cost improvements of a technology. A characteristic parameter is the “learning rate”, defined as the fractional reduction in cost for each doubling of cumulative production or capacity, and is given by:

\[
LR = 1 - 2^b
\]  \hspace{1cm} (17)

“Component-based learning curves” extend the one-factor learning model to represent the total cost of a technology as the sum of individual component or sub-system costs. This formulation seeks to account for the fact that different components of a complex technology (like a power plant) may have different levels of maturity and different rates of learning. Thus:

\[
Y = \sum_{i=1}^{n} a_n x_i^{b_n}
\]  \hspace{1cm} (18)

where, \(n\) is a specified technology component or sub-system, \(a_n\) is the specific cost of cost component \(n\) at unit cumulative capacity, and \(b_n\) is the learning parameter for technology component \(n\).\textsuperscript{1058} A number of studies use eqn (18) to estimate the future cost of technologies for which there is no direct historical experience, such as power plants with carbon capture and storage.\textsuperscript{1059} The overall plant is broken down into components or sub-sections and the future cost of each component is then estimated based on an appropriate learning rate for that
component. The future cost of the overall plant is then estimated by summing the costs of all components after a specified increment of capacity.

Research over the past few decades also has sought deeper insights into the underlying factors that contribute to cost reductions and technological change. One result is a variety of multi-factor learning models that have been developed to explicitly account for such factors as R&D spending, knowledge spillovers, increased capital investments, economies-of-scale, changes in input prices, labour costs, and other factors. While such models provide more detailed descriptions of factors that affect a particular technology cost, they are not as prevalent as the one-factor model shown earlier, in large part because of data requirements and limitations.

For energy technologies, the most prevalent multi-factor model is a “two-factor learning curve” where the key drivers of cost reduction are assumed to be the cumulative expenditure for R&D on the technology, in addition to its cumulative installed capacity or production. In this formulation, eqn (17) is expanded to explicitly include the effect of cumulative R&D expenditures:

$$\log Y = a + b_{LBD}(\log x) + b_{LBR}(\log R)$$

where, $b_{LBD}$ is the learning-by-doing (LBD) parameter, $b_{LBR}$ is the learning-by-researching (LBR) parameter, $R$ is the cumulative R&D investment or knowledge stock, $\log x$ is the specific cost at unit cumulative capacity and unit knowledge stock, and $Y$ and $x$ have the same meaning as before.

An important caveat on learning curves is that the mathematical models outlined above may not correctly represent technology cost trends in all cases. Historical data show that for a variety of reasons the cost of a particular technology may increase with experience, especially in the early stages of deployment and adoption. Nor do cost reduction trajectories always follow a log-linear relationship. Any use of learning curves for technology cost forecasting must take such uncertainties into account.

### 11.2 Learning rates for fossil fuel power plants

A recent literature review summarised the empirical learning rates reported for different types of electric power generation technologies. Table 9 summarises those results for combustion-based power plants fuelled by coal and natural gas. There is also considerable interest in the future cost of such plants equipped with CCS, as well as coal-based integrated gasification combined cycle (IGCC) plants with and without CCS. Since there is no significant historical basis from which to derive learning rates for these technologies, several studies have used the “bottom-up” component modelling approach outlined earlier to estimate the learning rates of future IGCC, PC and NGCC power plants with CCS based on analogous technologies. Table 9 shows the range of results from such studies.

For CCS technologies, current commercial systems for post-combustion CO₂ capture are often assumed to be technically analogous to post-combustion flue gas desulphurisation systems for SO₂ capture, which had average historical learning rates of 12% for capital costs and 22% for O&M (operation and maintenance) costs, according to previous studies. Using a component-based learning curve (eqn (18)), Rubin et al. derived composite (plant-level) learning rates from 1% to 4% for capital cost and from 2% to 5% for cost of electricity based on 100 GW of new plant capacity with CCS. Using a similar approach, Li et al. projected learning rates of 5.7% to 9.9% for PC plants with CCS in China. For natural gas applications, van den Broek et al. also used a component-based modeling approach to estimate future learning rates for NGCC plants with CCS. The resulting rates ranged from 2% to 7%, with a nominal value of 5%.

### 11.3 Implications for future CCS cost

The research on learning rates cited above suggests that the cost of CCS for power plant applications is expected to fall as such installations are more widely deployed. This is consistent with pronouncements from the Sask Power company in Canada and the NRG company in Texas, which operate the first two large-scale CCS projects at coal-fired power plants. Both companies project a roughly 20 percent cost reduction for a subsequent CCS installation based on the experience to date at the Boundary Dam and Petra Nova power plants, respectively.

Based on modelling studies that employ learning rates from Table 9, the magnitude of future cost reductions for power plants equipped with CCS will depend strongly on the nature and timing of policy drivers to achieve deep reductions in CO₂ and other greenhouse gas emissions. One recent study projected reductions in 2050 of roughly 1% to 40% in the cost of electricity generation for power plants with CCS, and higher percentage reductions in the cost per ton of CO₂ avoided. However, such scenarios assumed increasing levels of a worldwide carbon price (tax) to incent markets for CCS technology. It remains to be seen whether strong policy drivers of this type will emerge to help drive significant reductions in future CCS cost.

### 12 Negative emissions technologies

#### 12.1 Bioenergy with carbon capture and storage (BECCS)

Bioenergy with carbon capture and storage (BECCS) is a CO₂ mitigation technology which combines bioenergy applications with carbon capture and storage. This concept is not consistently defined and can include a variety of industrial and energy technologies with different amounts of CO₂ emissions, such as biomass combustion (dedicated or co-firing) for power production, biomass conversion to liquid and gaseous fuels, bio-refineries, pulp and paper production. Fig. 23 is a graphical representation of the BECCS concept (throughout the literature, the term Bio-CCS is also used as an alternative). In BECCS, CO₂ originating from biomass, which has undergone a conversion process, is capture and stored in geological formations. CO₂ utilisation concepts exist for BECCS as well (BECCUS or Bio-CCUS), where the CO₂ is temporarily fixed in products, such
as fuels, construction materials, chemicals, plastics etc. The concept of BECCS depends on the assumption that biomass binds CO\textsubscript{2} from the atmosphere as it grows and, if captured and stored after conversion, results in a net removal of CO\textsubscript{2} from the atmosphere. Technologies allowing for this net removal are referred to as negative emissions technologies (NETs), and include ocean fertilisation, mineral carbonation, afforestation and direct air capture (DAC) – discussed in Section 12.2.

Sustainability, i.e., carbon neutrality, of the biomass feedstock is a decisive factor in terms of the extent of negative emissions a technology or other mitigation pathway can achieve.\textsuperscript{63} There are several factors that can make true carbon negativity difficult, e.g., emissions from land use change (LUC), production, pre-treatment and transport of biomass, conversion process and CCS process but also the issue of carbon debts, i.e. the amount of time required for carbon offsets to kick in. In comparison, CCS on fossil fuels (Fossil-CCS, i.e., Coal-CCS and Gas-CCS) is quite different, as it can at best lead to zero emissions. Fossil-CCS takes carbon from the geosphere and returns it there, while BECCS takes carbon from the atmosphere, puts it temporarily into the biosphere, and then permanently into the geosphere (assumed there is no major leakage from the storage reservoir). Without a CCS component, processes take carbon from either geosphere or biosphere and transfer it to the atmosphere, so can be at best carbon neutral (biomass resource) or will be net positive (fossil resources). Thus, BECCS can allow offsetting of emissions from sectors where CO\textsubscript{2} reductions are hard to achieve due to technical, economic or political constraints (e.g., aviation, shipping, iron and steel). Many Fossil-CCS plants have the potential to become BECCS plants by switching their fuel feedstock, for example, a coal-fired power plant with CCS converted to co-fire biomass.

There are currently five operating BECCS projects worldwide that capture a total amount of 0.85 Mt CO\textsubscript{2} per year, compared to 16 CCS projects with a capacity of about 31 Mt CO\textsubscript{2} per year.\textsuperscript{4,1066} The Illinois Industrial CCS (IL-CCS) project, capturing CO\textsubscript{2} from Archer Daniels Midland’s (ADM) corn ethanol plant in Decatur (Illinois, USA) and storing it in a sandstone formation, adds an additional 1 Mt CO\textsubscript{2} per year, when operation commenced April 2017.\textsuperscript{1067} The predecessor of the IL-CCS project successfully captured and stored 1 Mt CO\textsubscript{2} per year over three years.\textsuperscript{1068–1070} Thus, the IL-CCS will be the largest BECCS demonstration. Other planned and existing BECCS projects are at significantly smaller scales. The currently operating projects are located in North America, where the main CO\textsubscript{2} source is from ethanol fermentation plants and CO\textsubscript{2} enhanced oil recovery (CO\textsubscript{2}-EOR) is the sink.\textsuperscript{1066,1071} Although the number of existing and planned projects appears promising, hundreds to thousands are needed\textsuperscript{1072} if BECCS is to make a significant contribution to global greenhouse gas (GHG) reduction targets. Necessary steps include the build-up of operational experience and confidence in the technology, as well as verification of the negative emissions potential.

The estimated technical potential for BECCS pathways, including a wide variety of applications in different sectors, varies from 3–20 Gt CO\textsubscript{2} per year.\textsuperscript{49,1066,1073–1080} This is significantly compared to the global CO\textsubscript{2} emissions of currently 36 Gt CO\textsubscript{2} per year.\textsuperscript{1081} The economic potential is usually only a fraction of this, as it considers the cost of resources, their competing use and the reference to fossil fuels.\textsuperscript{1074,1075} It is further limited by the land required to produce the required biomass in a sustainable way (refer to the designated section on land availability). The technical maturity and costs of BECCS are comparable to conventional Fossil-CCS technologies. Economic assessments published in the literature so far, have arrived at a ballpark range of 60–250 US$ per t CO\textsubscript{2} for BECCS.\textsuperscript{6,1066,1076} Large-scale BECCS in power plants tends to be in the upper part of this range, whereas smaller niche applications, like ethanol fermentation, biomethane production and black liquor gasification, are on the lower end. Costs of BECCS are currently estimated to be about half the cost of DAC.\textsuperscript{1082} The important role that NETs play in future climate change mitigation becomes clear when one looks at integrated assessment models (IAMs). IAM studies predict that carbon prices are likely to be up to three times higher if key NETs (i.e., BECCS and DAC) are not available.\textsuperscript{1083} Due to the high uncertainties associated with future technology pathways and their cost development, it is currently not clear where cost effective BECCS deployment will take place.

To provide perspective on BECCS’ potential for atmospheric CO\textsubscript{2} reduction, removing 0.5–1 ppm CO\textsubscript{2} per year would require drawdown of 8–16 Gt CO\textsubscript{2} per year.\textsuperscript{109} Inefficiencies and losses

### Table 9: Reported learning rates for fossil fuel power plants\textsuperscript{1060}

<table>
<thead>
<tr>
<th>Technology and energy source</th>
<th>No. of studies with one factor</th>
<th>No. of studies with two factors</th>
<th>Range of learning rates</th>
<th>Mean learning rate</th>
<th>Years covered by studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>4</td>
<td>0</td>
<td>5.6% to 12%</td>
<td>8.3%</td>
<td>1902–2006</td>
</tr>
<tr>
<td>PC</td>
<td>2</td>
<td>0</td>
<td>1.1% to 9.9%</td>
<td>2.5% to 16%</td>
<td>Projections</td>
</tr>
<tr>
<td>PC + CCS\textsuperscript{b}</td>
<td>2</td>
<td>0</td>
<td>2.5% to 20%\textsuperscript{b}</td>
<td>2.5% to 20%\textsuperscript{b}</td>
<td>Projections</td>
</tr>
<tr>
<td>IGCC\textsuperscript{b}</td>
<td>2</td>
<td>0</td>
<td>–11% to 34%</td>
<td>14%</td>
<td>1980–1998</td>
</tr>
<tr>
<td>IGCC + CCS\textsuperscript{b}</td>
<td>1</td>
<td>0</td>
<td>10% to 22%</td>
<td>15%</td>
<td>1958–1990</td>
</tr>
<tr>
<td>Natural gas</td>
<td>5</td>
<td>1</td>
<td>2% to 7%\textsuperscript{b}</td>
<td>2% to 7%\textsuperscript{b}</td>
<td>Projections</td>
</tr>
<tr>
<td>NGCC</td>
<td>11</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NGCC + CCS\textsuperscript{b}</td>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Values in italics reflect model estimates, not empirical data. \textsuperscript{b} No historical data for this technology. Learning rate values are estimated based on analogies.
along the supply chain play an important role as well. If considering all carbon losses along the chain for BECCS on a switchgrass gasification plant, the aim of storing 1 GtC, or 3.67 GtCO₂, could require a fixation of up to 7.7 Gt CO₂.1084 There are several reasons for the uncertainty in BECCS' potential and cost estimates, e.g., only considering CO₂ but no other GHGs, omitting LUC emissions, insufficient carbon cycle models, lack of underlying data, differences in modelling assumptions, etc.1085

12.1.1 Feasibility of large-scale BECCS deployment. Several barriers to large-scale BECCS deployment exist, among them technical challenges, economics, availability and sustainability of biomass, policy, and public perception. Each issue is worth a detailed investigation of its own. The following sections will focus on the availability of biomass feedstocks and land for production of these, as they are a key requisite for the feasibility of large scale BECCS.

Biomass availability. Biomass broadly denotes material of biological origin that is derived from photosynthesis in a relatively short timeframe. Thus, it excludes material embedded in geological formations and material that is transformed into fossils or peat.1087 There are many different types of biomass feedstocks and they can be classified in many ways, e.g., terrestrial vs. marine, virgin vs. residues, agricultural vs. forest or dedicated vs. waste. One attempt of classification could look like the following,1088,1089 without claiming to be exhaustive:

1. Dedicated energy crops
   (a) Conventional annual crops
      • Oil crops (palm, canola, sunflower, etc.)
      • Sugar/starch crops (sugar cane, sugar beet, corn, all types of cereals, etc.)
   (b) Perennial crops and energy grasses (Miscanthus, switchgrass, etc.)

2. Forestry and forestry residues
   (a) Short rotation forestry (alder, ash, Southern Beech, birch, eucalyptus, paper mulberry, Australian Blackwood, sycamore etc.)
   (b) Short rotation coppice (willow, poplar, etc.)
   (c) Forestry residues
      • Primary (wood chips from branches/tips/poor quality stemwood etc.)
      • Secondary (saw mill by-products: chips sawdust, bark etc.)
      • Tertiary (material from municipal tree management, waste wood etc.)

3. Other residues and wastes
   (a) Agricultural crop residues (straw from cereals/oil seeds, bagasse etc.)
   (b) Municipal organic waste (paper/cardboard, food, garden, textiles etc.)
   (c) Sewage sludge
   (d) Animal manure
   (e) Land fill gas

4. Marine biomass (microalgae/phytoplankton and macroalgae/seaweed)

Although the number of potential feedstocks appears large, competition between different sectors for feedstock and competition with other ecosystem services, such as food production, could significantly limit their availability for BECCS. Fig. 24 shows a tree diagram of different biomass conversion technologies and the variety of end products for each conversion pathway. Currently, there is a high amount of food waste available, especially in developed countries, i.e., 1.3 Gt per year globally.1090 However, this amount could change over time in the long term, through improvements in agricultural
production, storage, processing, distribution and consumer behaviour. Another issue with regards to using some of the above-mentioned feedstocks for large-scale BECCS is their seasonal availability due to harvesting schedules, which makes pre-treatment and storage necessary. Future availability will further depend on improvement in yields, cultivation methods, and growth in demand. Key drivers for biomass feedstock markets and supply chains are crude oil price, climate policy, energy policy, cost of primary energy production, infrastructure and development potential of rural areas.\textsuperscript{1091-1093} Finally, BECCS and other bioenergy applications might experience a feedstock limitation to so-called "additional biomass". This term refers to biomass that can lead to a reduction in GHG emissions without displacing other ecosystem services, such as food or fibre production. Additional biomass includes: biomass grown in excess of what would have been grown anyway, biomass that would otherwise decompose, wastes/residues, and other biomass that does not interfere with important ecosystem services, especially food production.\textsuperscript{1094,1095} Except for wastes/residues and marine biomass, feedstock availability is highly dependent on land availability, which will be discussed in detail in the next section.

\textbf{Land availability.} Land availability for biomass feedstock production is a key driver for large-scale BECCS implementation. Land demand for BECCS is relatively high and largely depends on the selected feedstock. Forest residues need 1.0–1.7 ha per t$_{\text{C,eq}}$ per year (0.27–0.46 ha per t$_{\text{CO}_2,\text{eq}}$ per year), agricultural residues around 0.6 ha per t$_{\text{C,eq}}$ per year (0.16 ha per t$_{\text{CO}_2,\text{eq}}$ per year), and dedicated energy crops 0.1–0.4 ha per t$_{\text{C,eq}}$ per year (0.03–0.11 ha per t$_{\text{CO}_2,\text{eq}}$ per year).\textsuperscript{61} For comparison, other NETs, like enhanced weathering of minerals (EW) and DAC, have significantly lower land demands: < 0.01 ha per t$_{\text{C,eq}}$ per year (0.003 ha per t$_{\text{CO}_2,\text{eq}}$ per year).\textsuperscript{61,1096,1097}

To achieve removal of 3.3 Gt$_{\text{C,eq}}$ per year (12 Gt$_{\text{CO}_2,\text{eq}}$ per year) through deployment of BECCS with dedicated energy crops, 380–700 Mha of land is required,\textsuperscript{61} or 500 Mha, which is in terms of a bioenergy deployment of 100 EJ per year.\textsuperscript{1090} According to other sources, for a range of 26–161 EJ per year, 133–990 Mha of land is necessary.\textsuperscript{1085} For comparison, DAC and EW need substantially lower land areas (below 10 Mha), and afforestation and reforestation (AR) needs a slightly higher amount of land (about 970 Mha).\textsuperscript{61,1084,1097,1098}

The total land area for agriculture in 2014 was 4900 Mha, of which 1,585 Mha was used for arable land and permanent crops, and 3,315 Mha accounted for permanent pasture and meadows. A further 4002 Mha were designated as forest. Of the agricultural cropland, about 300–570 Mha are marginal lands.\textsuperscript{1099-1101} The total current amount of marginal land is relatively uncertain, as it depends on a definition that is rather inconsistent across literature, it ranges between 428–1035 Mha.\textsuperscript{1065,1102,1103} Any land or biomass supply limitation will very likely affect the costs of BECCS. Although current cost estimates for BECCS are lower than for DAC, these costs could rise steeply once land limitations are considered (in this case once removal rates reach 12 Gt$_{\text{CO}_2}$ per year).\textsuperscript{1104,1105}

To meet land requirements for BECCS (i.e., estimated to be 380–990 Mha), two important questions should be addressed: (i) how this land can be provided, and (ii) how much can be freed through other means. As discussed above, marginal lands can be used to partially meet land requirements. Another option that can free significant amounts of land is through dietary changes. The current average diet in the US contains a high amount of animal products (meat, dairy, eggs, fish) and has a land intensity of about 1.08 ha per year per person (of which, 0.74 ha per year is for pasture and 0.34 ha per year for cropland). In contrast, a vegetarian diet requires 0.14 ha per year per person (0.02 ha per year for pasture and 0.12 ha per year for cropland) and a fully plant-based diet needs 0.13 ha per year per person.\textsuperscript{1128} Assuming the current world population of 7.5 billion, a full transition to a vegetarian or plant-based diet could free around 605–685 Mha of cropland and 3165–3315 Mha of pasture. However, the likelihood of human society undergoing such a drastic change in behaviour appears unlikely. In addition, it is important to keep in mind that free allocations between cropland and pastures are usually not possible, i.e., only a certain proportion of pastures will be suitable as cropland. Other, less drastic scenarios estimate that a 40% cut in consumption of animal products by the 2.2 billion people currently on a US-type diet could free 140 Mha of cropland and 500 Mha of pasture.\textsuperscript{1129} Further options to free land are crop yield/livestock productivity improvements or reduction of food waste, as the land area associated with food waste totals ~1400 Mha, for crop and animal commodities combined.\textsuperscript{1090,1111,1112,1130} In conclusion, we could make enough land available for large-scale BECCS deployment, or bioenergy deployment in general, but only with far-reaching changes to our diets and agricultural systems.

\textbf{12.1.2 Key R&D needs for BECCS in the coming 5–10 years.} Although the discussion has focused on land and biomass availability, there are many other challenges surrounding BECCS technologies that need to be addressed if BECCS is to move forward. Table 10 summarises many of those key R&D needs for the coming 5–10 years (this list is not intended to be exhaustive). Research on some of these topics is already underway but most areas could benefit from further quantification to provide more evidence and improve confidence.

\textbf{12.2 Direct air capture of CO$_2$.} Direct air capture (DAC) has gained a lot of interest mostly in popular media,\textsuperscript{1113-1114} because it appears to be an easy fix to our current climate crisis. The concept of placing DAC plants anywhere to remove CO$_2$ from the air provides the mental picture of our atmosphere one day having a CO$_2$ concentration as low as it was prior to the industrial revolution. However, this approach has many technical and economic caveats, primarily associated with the highly dilute nature of atmospheric CO$_2$. 400 ppm, a factor of 100–300 times more dilute than the CO$_2$ concentration in gas- and coal-fired power plants. In this section, we will summarise the technology, economics, and system considerations with an aim to objectively assess the state of DAC today.
In order for DAC to result in a negative CO₂ emissions scenario, it would have to be coupled to CO₂ transport and sequestration infrastructure in order to ensure a positive climate impact. Several companies have emerged with small-scale applications, but their impact on significant and permanent atmospheric CO₂ reductions is minimal owing to their present scale.

There are a range of views regarding DAC as a realistic option for climate change mitigation. In particular, two reports have been published by the American Physical Society and the National Academy of Sciences that discuss the challenges associated with implementing DAC at a scale capable of impacting climate. To the authors’ knowledge, there have only been two studies that have proposed specific designs for DAC systems with estimated costs. In the work of Holmes and Keith, an air–liquid contactor design based upon cooling tower technology was proposed, while in the work of Mazzotti et al., a more conventional contactor was proposed, which may be more suited for flue gas applications. Both designs are unique and the costs for CO₂ capture range between $300 and $600 per tonne of CO₂. House et al. demonstrated the relationship between CO₂ concentration and the energy efficiency of a given separation process and determined that the more dilute a system is, the more unwanted material there is to be processed, leading directly to higher costs with an estimate on the order of $1000 per tCO₂. Although there is general consensus in the community that DAC is significantly more expensive than conventional carbon capture from coal or natural gas-fired power plants, it is described by some as “insurance” against potential CO₂ leakage from geologic storage sites or as a means to offset emissions from dispersed sources such as automobiles, ships, and airplanes.

12.2.1 Technical assessment. In the case of absorption, discussion of the technical challenges associated with CO₂ capture from air requires examination of the equation that describes the flux of CO₂, $J_{CO₂}$, across a gas–liquid interface.

$$J_{CO₂} = c_i k_i E$$

where $c_i$ is the concentration of CO₂ at the gas–liquid interface, $k_i$ is the physical mass-transfer coefficient, and $E$ is the enhancement factor from the chemical reaction. Depending on the reaction conditions, $E$ can take various forms, but in all cases is a complex function of the rate constant. The interfacial concentration, $c_i$, is determined using Henry’s law. Shown in Fig. 25 is $c_i$ as a function of gas-phase CO₂ partial pressure for several solvents, including ionic liquids (IL), piperazine-activated amines (amines-PZ), sodium hydroxide (NaOH), and potassium carbonate (K₂CO₃) as a function of gas-phase CO₂ partial pressure.
pressure and solvent Henry’s law values. The Henry’s law constant is a solvent property that indicates the extent to which CO₂ is soluble in a given solvent. Assuming the concentration of CO₂ in the gas phase is defined as $c_p$, the Henry’s law constant may be defined in a dimensionless form, i.e., $c_p/c_g$, or in a more conventional form, i.e., $c_i/P_{CO2}$, with units of atm·cm⁻³·mol⁻¹. From Fig. 25 it can be seen that for the cases of flue gas from coal and natural gas, $c_i$ is 250 and 150 times that of DAC, respectively for a given solvent. ¹¹⁴⁰

Hence, to force the same amount of CO₂ across the interface for DAC as one would have for the more concentrated cases, $E$ may be up to two orders of magnitude higher to compensate since $k_1$ is a parameter solely influenced by the solvent and its relationship to the packing material. Increased enhancement can be achieved by choosing strong bases with fast kinetics, such as sodium hydroxide (NaOH)¹¹⁴¹ or combinations of piperazine (PZ) with potassium carbonate (K₂CO₃).¹¹⁴² However, the trade-off with having to choose a strong base is the increase in energy required for regeneration.

Due to the increased binding between CO₂ and a strong base, a chemical shift process is required for regeneration rather than a simple thermal- or pressure-swing process. For instance, in the case of NaOH, sodium carbonate (Na₂CO₃) is formed and in order to regenerate NaOH and to produce a near-pure stream of CO₂, one can either react Na₂CO₃ with lime (Ca(OH)₂)¹¹⁴³ or with TiO₂, with the second process (titanate cycle) potentially being less energy-intensive.¹¹⁴⁴ In both reactions, NaOH is regenerated, but a final thermal decomposition step (calcination in the case of calcium carbonate) is also required for producing CO₂.

As expected, similar to absorption separation processes, the low driving force inherent in DAC systems also affects CO₂ separation using solid sorbents. Fig. 26 shows the relationship between pore size and CO₂ concentration in the pore. Due to the low concentration of CO₂ in air, no matter how small the pore is, CO₂ will never saturate the pore. On the other hand, in the case of CO₂ separation from the exhaust of a coal-fired power plant, which is 300 times more concentrated than air in CO₂, saturation of CO₂ takes place in the micropores and smaller mesopores. This state of saturation is an added driving force that can only take place for applications in which CO₂ is sufficiently concentrated in the gas phase.

An alternative way to show that energy increases with decreasing concentration is through examining the minimum work of a given separation process. The relationship between initial CO₂ dilution and the energy required for purification can be shown by estimating the minimum work as a function of initial concentration, capture rate, and final purity. As shown in Fig. 27, the minimum work associated with separating CO₂ from air is approximately 2, 3, and 5 times more energy-intensive than separating CO₂ from the exhausts of natural gas combustion, coal combustion, and coal gasification, respectively.¹⁰⁸ It is also important to note that a reduction in the capture rate combined with a reduction in CO₂ purity will decrease the minimum work, but not significantly. Also, it is important to recognise that by decreasing the CO₂ purity, there...
will be an additional expense associated with compression for transport.

Another technical challenge associated with DAC is the amount of air that needs to be processed to capture a comparable amount of CO$_2$ compared to a power plant. Assuming a capture rate of 50%, one is reducing a volume of gas from 400 ppm down to 200 ppm. In this case a tall contactor is not required, which is different than conventional carbon capture, where a common target is a capture rate of 90% from an exhaust stream with CO$_2$ concentration ranging from approximately 6% to 12%. The degree of CO$_2$ separation increases with column height, as does the pressure drop. The unique “short” design of a DAC plant is a consequence of the low degree of CO$_2$ separation combined with minimising the energy required to overcome the pressure drop. However, there is also a lower limit to the pressure drop that should be avoided. Pressure drop allows for one to control how the flow of the solvent distributes across the system. Inadequate coating of the solvent across the packing material can impact the extent of mass transfer across the gas–liquid interface.

The contactor cross-sectional area can be estimated based upon the amount of air to be processed. For a given DAC plant to capture 1 MtCO$_2$ per year at a 50% capture rate requires processing approximately 80 000 m$^3$ s$^{-1}$ of air. Using a typical air velocity ranging between 2–3 m s$^{-1}$ leads to surface areas on the order of 30 000 m$^2$. This is about 600 times the cross-sectional area of a large packed tower used for CO$_2$ capture from a power plant flue gas. This large surface area requirement for DAC systems may well dominate the capital cost of the plant design. Overcoming the pressure drop across each of these units will require fan power. In conventional carbon capture systems for coal or natural gas exhaust streams, fan or blower power may only comprise up to 3% of the total energy of the separation process, but may in fact dominate in the case of a DAC plant. An added expense is the need for an air filtration system. Due to the complexity of placing filtration units on each of the contactors, likely a central air handling unit would have to be in place prior to air distribution across the contactors.

12.2.2 Economic assessment. There is a wide range of cost estimates for DAC in the literature. Unfortunately, these estimates are not based on detailed process designs, but rather are based on processes with sparse details and many assumptions. A review of the literature by Goeppert et al. reported a range of $20 to $1000 per ton of CO$_2$. Perhaps the most quoted range is $600–800 per t_CO_2 from the American Physical Society study. Many of the lower estimates are from people associated with companies trying to commercialise the technology. The $1000 per t$_{CO_2} estimate comes from House et al.

There is strong evidence that the cost of CO$_2$ capture rises with increasing initial dilution. The CO$_2$ used for commercial markets is from high purity sources such as ammonia plants, ethanol plants and hydrogen production. The reason for this is that starting with high purity sources results in the lowest production costs. This relationship was quantified in an empirical correlation called the Sherwood Plot (see Fig. 28). Reasons for increased cost at lower dilution include smaller driving forces for mass transfer and greater amounts of material to process (see pressure drop discussion below).

Today, the cost of capture from a coal-fired power plant is on the order of $100 per t CO$_2$ avoided. If we knew the scaling factor, we could approximate the cost of DAC. The Sherwood Plot suggests a scaling factor on the order of 100, i.e., the ratio of the concentration of CO$_2$ in the flue gas to the concentration in air. This results in a cost for DAC of $10 000 per t$_{CO_2}$ avoided. Some proponents of DAC claim that the scaling factor should
be based on minimum work, resulting in a cost of about $300 per t CO₂ avoided. The truth probably lies somewhere between these numbers. In any case, the reported costs toward the lower end of the range in the literature (i.e., $20 per t CO₂) just do not seem credible.

To illustrate the difficulty in estimating the cost of DAC systems, we calculate the amount of energy required to move air through the process. Assuming a concentration of CO₂ in air of 400 ppm and a 50% recovery rate, we need to process 2.11 million m³ of air to capture 830 kg of CO₂, approximately the amount of CO₂ produced for every MWh generated at a supercritical coal-fired power plant. Based on air being an ideal gas and assuming no losses in the process, if we had a pressure drop of 0.016 bar (0.23 psi), we would need 1 MWh to move the air. In other words, at this pressure drop, just moving the air would require all the energy released in generating the CO₂ in the first place. This means for a DAC process to be at all practical, pressure drops need to be limited to the order of 6.89 × 10⁻⁴ bar (0.01 psi) and/or that the energy source for DAC needs to be carbon-free. A pressure drop of 6.89 × 10⁻⁴ bar (0.01 psi) is extremely small and it is unclear whether it can be realised in a full-scale DAC system. A better use for carbon-free power today would be to replace fossil-fuel fired power and avoid putting the CO₂ into the air in the first place.

12.2.3 System considerations. DAC is essentially an extension of CCS. Once the CO₂ is captured, and is available at sufficient purity, the options for storage or utilisation are the same in both cases. As shown above, a given technology that is suitable for flue gas CO₂ removal from a coal-fired power plant may not be the equivalent best technology for DAC. Similarly, opportunities that can make DAC more competitive, may not necessary be suitable for CCS. For DAC processes, the resulting gas stream may have a CO₂ concentration as low as 50 vol%. Although too dilute for geological storage, there are several opportunities for dilute CO₂ gas streams (i.e., <50 vol%) to be utilised. For example, opportunities may include, however not limited to, EOR, mineral carbonation, microalgae cultivation and fuel synthesis.

The proponents of DAC make the case that there is a significant advantage to be able to theoretically site a DAC facility anywhere. Specifically, they suggest that it can be located near a storage site (reducing the pipeline cost), or away from populated areas. Siting is a multi-faceted, complex decision. While you may save some money building near a storage site, if there is no industrial infrastructure around, other costs will go up significantly. It is not at all clear that the fact that the feedstock for DAC (i.e., air) is found everywhere translates into any real economic advantage.

Proponents also suggest placement of a DAC plant nearby an EOR site may seem desirable. However, there are usually an abundance of CO₂ sources that are more concentrated nearby EOR operations that can produce CO₂ for much less cost than DAC.

Finally, for DAC to be at all practicable, the systems will need to operate at high capacity factors. Almost no work has been done on long-term operation of these systems. There are trace impurities in the air and since such a large amount of air is processed, they can have an adverse impact on DAC systems. Also, these systems must be able to stand up to the elements. Depending on where they are located, this includes water,
wind, cold, and sandstorms. So far, the DAC literature is silent on these issues.

12.2.4 Future perspective and key research needs. The time scale of DAC implementation is quite slow. If one accepts the high cost associated with concentrating CO₂ from 400 ppm to 90+% purity, the number of DAC plants to be built per year is limited not just from a cost perspective, but also in terms of optimal siting. In addition, once CO₂ is captured, the dilemma of how to permanently dispose of it, is still an issue. Further, due to the slow scale of implementation associated with this approach, the impact that it could have on slowing global warming is limited. First and foremost, conventional carbon capture and storage, the replacement of fossil-based energy with renewables and nuclear power, increasing efficiencies across all sectors, reforestation efforts, and the prevention of deforestation all must be practiced collectively in order to impact climate on a scale that will matter.

13 Commercialisation of CCS: what needs to happen?

This section is intended to provide insights into the challenges facing the development of a viable CCS industry highlighting new approaches and commercial models that could be deployed to realise the full potential of CCS in decarbonising future energy systems at lowest cost. Although based upon experiences from the recent UK CCS Commercialisation Programme and written mostly from a UK perspective with UK experiences from the recent UK CCS Commercialisation Programmes and the scale of the support offered, progress has been minimal. To date, there are two “commercial scale” CCS projects in the power generation sector that are operational, the first is the Boundary Dam project in Canada at 110 MWₖₑₙ output,¹⁸⁸ second is the Petra Nova W.A. Parish CCS project designed to treat a 240 MW flue gas slipstream from a 610 MWₖₑₙ coal-fired unit.¹⁴,¹⁵ The European Union’s ambition for up to 12 CCS projects in operation by 2015¹⁴⁸ supported firstly through the European Economic Programme for Recovery (EEPR) and latterly through the New Entrants Reserve (NER300) programme has failed to deliver a single CCS project.

More success has been enjoyed in the United States through various programmes supported by the US Department of Energy. The Petra Nova W.A. Parish project commenced operation as planned in January 2017.¹⁴ However, Southern Company’s Kemper County IGCC project (lignite power generation at 582 MWₖₑₙ net output) has encountered a number of problems with delivery delays, major technical issues and being significantly over-budget.²¹,²² Consequently, the clean coal component of the project has been suspended.²⁰ In the United Kingdom two competitive CCS procurement programmes for power generation have been run by the UK Government since 2007 with both having been abandoned without success.

The need for CCS as a key part of global strategies to reduce CO₂ emissions may be great³ but so far this need has not been framed in a way that is attractive or rational for the private sector to respond to with investments in CCS projects. The physical and commercial risks associated with the development of large scale CCS projects and the associated CO₂ transport and storage (T&S) infrastructure have so far outweighed the potential rewards on offer, as evidenced by the abandonment of many tens of promising CCS projects around the world.

With the failure of the various government-backed programmes to establish a viable CCS industry and in the absence of any private sector companies willing to expose their balance sheets to full chain CCS projects,¹¹⁴⁸ the question arises: what needs to happen to make CCS a commercial reality? The need for CCS is becoming ever more acute and new approaches to its commercial deployment are needed as a matter of urgency if we wish to meet our carbon targets in the most cost-effective manner.

One of the key attributes of CCS is that it can be applied to all main carbon emitting sectors and is therefore ideally suited to system-wide decarbonisation efforts. A key focus in the early stages of deployment will need to be on the development of CCS infrastructure to which multiple CO₂ sources can connect so as to take advantage of economies of scale and to optimise the development pathway. In the UK regulatory and financial frameworks are already in place for low-carbon power which can be modified to fit CCS. This, together with the large...
volumes of CO₂ available to support large scale CCS infrastructure development, makes the power generation sector, in an increasingly electrical future, the logical first mover sector for CCS.

13.2 The value of CCS

The value of CCS derives from the fact that it is the only technology that can simultaneously address carbon reduction objectives across all main carbon emitting sectors of the economy, without compromising their cost-effective provision of service. These sectors include power generation, industry, transport and heating. 

For many industrial applications there is currently no alternative to CCS for reducing the CO₂ emissions that are inherent to the manufacturing process. The decarbonisation of transport, including road transport, will inevitably involve increases in the numbers of electric vehicles. The resulting demand for electricity can be in part supplied from CCS enabled power stations. CCS in combination with hydrogen production could provide the low-cost route to the decarbonisation of heating as well as support the development of other aspects of the hydrogen economy including the use of fuel cells. CCS is also the only technology that can remove industrial quantities of CO₂ from the atmosphere when combined with power generation from sustainable biomass combustion (so-called BECCS) creating room within carbon budgets for sectors more difficult to decarbonise, such as aviation. Indeed, in the UK, without CCS it is unlikely that the country’s 4th and 5th carbon budgets can be met.

The development of CCS, like all low-carbon technologies, will bring with it some additional costs. In a report prepared by the CCSA together with the TUC, however, it was estimated that the Gross Value Added (GVA) benefits from CCS deployment in the UK would be in the region of £2bn–£4bn per year by 2030, with a cumulative market value of £15bn–£35bn (depending on whether 10 GW or 20 GW of CCS capacity is installed respectively). This is in addition to the creation of between 15 000 and 30 000 jobs.

If CCS is to form a key part of decarbonisation strategies it is important that the benefits of CCS across the economy at the total energy-system level are understood and that the long-term value-for-money case forms a central consideration in developing energy policy.

13.3 The cost of CCS

One of the most frequently expressed concerns regarding CCS is that it is too expensive. Indeed one of the primary reasons given for the discontinuation of the UK CCS competition was the view that the costs to consumers of the first CCS projects would be high and regressive although it was acknowledged that the cost was likely to be higher for the first CCS projects as they provide transport and storage (T&S) infrastructure that could be used by subsequent projects. In the short term the cost of CCS for power generation will continue to be compared to alternative forms of low-carbon power generation even though those alternatives (and their intermittent output) will lead to higher system-wide costs in the long run. In facing up to this challenge any new approaches to CCS commercialisation will need to deliver significant short-term reductions in the costs of first mover projects.

The driving forces for cost reduction have been set out in the CCS cost reduction task force (CRTF) report published in 2013 as part of the UK government’s CCS roadmap, including:

1) investment in large CO₂ storage hubs, supplying multiple CO₂ sites connected through large, shared pipelines, with high load factors;
2) investment in large power stations with progressive improvements in CO₂ capture capability that should be available as from the early 2020s;
3) a reduction in the cost of project capital through a set of measures to reduce risk and improve investor confidence in UK CCS projects; and
4) exploiting potential synergies with CO₂-based EOR in some Central North Sea oil fields.

All of these drivers are as relevant today as they were when the CRTF report was issued in 2013. Based on technology progress in the intervening years and by applying the lessons learnt from the UK CCS Competition, significant reductions in the cost of CCS first mover projects are achievable. Success will depend on the development of large scale anchor projects that invest simultaneously in over-sized T&S infrastructure with third party access rights for follow on projects.

In addition, new commercial approaches will be required to balance multiple key risks (Fig. 29) and see a transfer of some of the CCS specific development and operational risk from the private sector to the public sector beyond that previously envisaged.

The CRTF predicted that the costs for CCS in the UK would be around £161 per MWh for the first mover projects and could approach £100 per MWh by the early 2020s, and achieve a cost significantly below £100 per MWh soon thereafter. The CRTF report was produced as part of the UK CCS roadmap and reflected the expected trajectory of cost reductions as experience and economies of scale grew against reducing capital and operating costs (discussed in Section 11). The UK CCS Commercialisation Programme, itself an integral part of the CCS roadmap, was aimed at attracting developers of first mover projects to invest in full chain CCS projects through a competitive process and offered a package of support in the form of capital grant funding, market price support through a contract for difference (CfD) and a share in the CCS specific risks.

The CRTF predictions for the first mover projects were largely borne out by the subsequent competition projects with the high prices largely a reflection of the adopted approach to risk allocation which crucially placed the full chain technical and commercial integration risk as well as significant CO₂
storage risk with the private sector developers and operators. By adopting new commercialisation approaches that focus on the identified cost reduction drivers and include a modified risk approach that accommodates the lessons learnt from the competition projects, much of the cost reduction potential envisaged by the CRTF for subsequent projects could already be realised for the first mover projects albeit with a transfer of risk to the public sector. This would bring the cost of CCS to levels that are competitive with alternative forms of low-carbon power making CCS more affordable from the outset.

13.4 New approach to CCS commercialisation

13.4.1 CCS risk. The starting point for the development of the CCS industry has invariably been based on the premise that the private sector should deliver CCS and manage all of the technical and commercial integration risks across the full chain. Indeed there are many risks that the private sector is able to manage and price competitively especially where these are within the competences of the developers of the individual chain link elements and can be accommodated within their established business models. There are however certain risks, related to the nascent status of the industry and the lack of proven commercial models across the full chain, that the market will either only accept at a premium or indeed in some cases not accept at all whatever the price.

Based on the UK lessons learnt\(^{1149}\) and the Key Knowledge Deliverables\(^{1156}\) the CCS specific key risks that present the greatest challenges and could most benefit from additional public sector risk support to overcome barriers to CCS development and drive down costs through reduced risk premiums include:

(i) Cross chain default (also referred to as “project on project”) risk;
(ii) Post decommissioning CO₂ storage risk;
(iii) Sub-surface CO₂ storage performance risks impacting on storage rates and capacity;
(iv) Decommissioning cost sufficiency and financial securities related to the CO₂ storage permit;
(v) Insurance market limitations for CO₂ T&S operations.

Risk (i) applies to all individual chain link elements, whereas risks (ii) to (v) apply almost exclusively to the CO₂ storage aspects. Risks (i) and (ii) would in all likelihood need to be absorbed by the public sector potentially for the lifetime of a specific CO₂ T&S system, whereas risks (iii), (iv) and (v) may be time limited and transferrable back to the private sector as practical experience is gained and operating confidence increases. By introducing commercial models that entail a transfer of these risk categories to the public sector, not only can barriers be removed that have thus far prevented the private sector from investing in CCS, but also project financeability would increase and the risk premium added to the cost of capital funding would be significantly reduced.

With private sector confidence in the deliverability of CCS being at a low ebb presently, together with the current lack of appetite to invest in the development of storage capacity where all of the risks (i) to (v) apply, there is a strong argument for the public sector to take direct responsibility for the realisation of the T&S infrastructure. The creation of a publicly owned national transport and storage company (NT&SCO) to provide secure long term CO₂ storage capacity, as recently recommended in a report by the parliamentary advisory group on CCS, chaired by Lord Oxburgh,\(^{101}\) would provide much needed certainty and boost confidence in the deliverability of CCS. Such a company would provide a strong counterparty and a significantly de-risked T&S infrastructure to potential private sector developers of generation and capture (G&C) assets. The use of public sector financing for the T&S assets would also bring benefits by lowering the overall cost of finance and as a consequence the cost of transporting and storing the CO₂.

The Oxburgh report goes a step further and also considers public ownership of the G&C assets with a view to privatisation after a period of successful operation. Private sector investment at a later stage would still require sufficient financial shielding from shortfalls in the availability of the T&S infrastructure (cross chain default risk). This could be achieved through permitted unabated operation with assured revenue stream mechanisms for example through continuation of CfD payments or through switching to capacity market payments. Combining both CfD and capacity payment mechanisms for a single generator would however require amendments to current regulation. The private sector investor would also need to be shielded from liabilities associated with continued payment of T&S capacity reservation and use-of-system fees should the G&C assets suffer prolonged outages for example through contracting for capacity on a pay as you use basis with limitations of liability for non take-up.

Whether or not it is necessary for the public sector to take responsibility for the delivery of the G&C assets rather than the private sector will depend upon confidence in the deliverability of CCS in the UK and the degree to which CCS specific key risks are transferred to the public sector, whether that occurs at the outset or at a later stage following initial operations. Whichever route is followed it will be important to leverage the skills and competences of the private sector that has established a good track record in the delivery of power generation assets since privatisation of the electricity markets in 1990.

Though there are many ways to structure the commercial arrangements between the various stakeholders in a CCS...
network including direct public sector engagement, regulated asset based models, etc. Success will depend upon the appropriate balance of risk between the private sector and the public sector taking into account the listed CCS specific key risks. It will also be important that models form a robust template for the long term development of the CCS industry that is most likely to develop along the lines of clusters of users alongside CO₂ T&S services providers with a clear transfer of liability for the CO₂ to the T&S service provider, potentially a NT&ScCo in the UK, at the factory boundary (Fig. 30).

The use of Enhanced Oil Recovery (EOR) to boost production levels in the mature fields of the North Sea holds out the prospect that CO₂ will, at some point in the future, command a material financial value potentially increasing the rewards available for the storage element of CCS. There is currently however no indication that these rewards would be sufficient for an EOR operator to underpin the associated development risks of the upstream elements of the CCS chain. It is more likely that EOR will develop in the North Sea once CCS is established in the power generation sector using sub-surface geological storage sinks, and hence only after reliable and predictable flows of CO₂ become available off-shore.¹¹⁵⁷

13.4.2 Economics of scale. In order to benefit from economies of scale, future programmes for the commercialisation of CCS should be based on the establishment of a large scale anchor project with 10–15 MtCO₂ per year T&S capacity. The aim should be to maximise the clean power output to reduce the unit cost of CCS per MWh. CO₂ intensity in terms of tCO₂ per MWh should be as low as possible to minimise the scale up factor for the CO₂ capture technology. This would also be advantageous in minimising the initial capacity reservation in the T&S system allowing more capacity for follow-on third party users thus achieving a critical mass as soon as possible. Based upon these considerations and given the current status of CO₂ capture technology in terms of proven operation at commercial scale, the optimum anchor project should feature a ca. 1 GW gas combined cycle plant with post combustion capture technology currently available competitively from a number of suppliers.

To maximise the future benefit of the established T&S infrastructure, the anchor project should be sited in a CO₂ intense industrial cluster. In the UK, there are several such clusters, located mostly along the east coast. This would also reduce transportation distances to the vast potential for CO₂ storage sites in the Central and Southern North Sea. Keeping pipelines short and avoiding overland pipelines as far as possible will help to keep costs down and avoid protracted, complex and costly easement negotiations with a number of landowners.

13.5 Funding of CCS

The funding of CCS requires that a predictable and secure revenue stream is available to cover the costs of CCS and allow the developer to meet all of its financial needs. This will invariably require non-market derived sources of income and/ or beneficial tax incentives for the generation of low-carbon power with CCS and the long-term storage of CO₂.

In the UK, power generation is currently the only sector for which existing regulation and financial frameworks are in place to support low-carbon technology through market price support mechanisms established through the electricity market reform (EMR) and as enshrined in the 2013 Energy Act.¹²³ CCS is recognised as a low-carbon technology and as such qualifies for financial support through the CfD mechanism. Minimising the need for legislative adoption is an important factor in facilitating CCS rollout.

13.5.1 Contract for difference. The allocation of funds from the Levy Control framework (LCF) for CCS projects is key for the development of CCS projects with power generation. The revenue certainty provided through a CfD linked to a strike price for clean power generation is fundamental to the financial viability of a CCS project. However, clarification of the LCF budget (£7.6 billion in 2020/21)¹¹⁵⁸ available to CCS following the recent cancellation of the UK CCS Commercialisation competition, as well as the detailed terms and conditions of the CfD, is required from government.

The development of a CCS project can take several years with costs running into several tens of millions of pounds. It is crucial therefore that the CfD allocation process provides developers with a high degree of certainty that a fully funded CfD will be available at the right strike price once they are ready to take a final investment decision on their projects. Even with such certainty however, a degree of public sector compensation of CCS project development costs is likely to be needed to mitigate to some degree the perceived political risk in such development programmes.

Much of the system-wide value of CCS derives from its ability to operate as flexible generation capacity alongside base load technologies like new nuclear and intermittent renewables. The CfD however as currently designed encourages base load operation as the marginal costs of production can always be covered. If the full value of CCS is to be realised mechanisms should be developed that reward flexibility.

The term of the CfD for CCS projects is set at 15 years in the generic CfD contract. By increasing the term to 20 years, significant reductions in the strike price can be achieved. Other design aspects that warrant further development include valuation and reward for negative emissions (BECCS) and application or alternative mechanism for industrial EII projects for which there is currently no CfD equivalent.

13.5.2 Alternative funding mechanisms. Part of the reason that the strike prices anticipated for the two preferred bidder projects under the second UK CCS commercialisation programme were relatively high, compared to alternative forms of low carbon power generation, lies in the fact that they carry the costs of oversized infrastructure for future users. As long as this approach is taken the leveraging effect that this has on the required strike price for a relatively small clean power output capacity will disadvantage any anchor project in a simple numerical comparison with strike prices of established alternative forms of low-carbon generation. If the potential benefit for follow-on projects is not taken into account in terms of prepaid and de-risked T&S infrastructure leading to significantly lower strike prices for such follow-on projects then this bias is likely to continue to prevent the CCS industry from developing.

Alternative funding mechanisms across the full chain could be considered that would eliminate this bias. Currently, an
The unabated fossil fuel power generator can emit CO₂ to atmosphere for a relatively low cost and, along with its customers, be forever freed from any future liability for the CO₂ from the moment it leaves the stack. The CCS-enabled generator carries the cost of development of T&S infrastructure for its own and future users' needs and has long-term liability for the safe and secure storage of the CO₂ captured. Under the principle of the polluter pays consideration should be given to spreading the costs of the T&S infrastructure over all fossil fuelled power generators and potentially other CO₂ emitters either through a hypothecation of carbon floor price levies, a carbon tax, or a form of CCS obligation certificate similar to the renewables obligation certificate first introduced in 2002 that was instrumental in supporting the early deployment of renewable technology in the UK.99

Such an alternative approach to funding of the T&S infrastructure would significantly reduce the strike price required by the CCS enabled generator to a level more competitive with alternative forms of low-carbon generation. It would also ensure that the value that CCS brings at the total energy system level in terms of decarbonising the economy is paid for more broadly across society and provide the economic drivers for further decarbonisation technology development using tax (or similar levies) as a behaviour modifier.

13.5.3 Other financial support

Grant funding. Grants provided by government as a means of promoting CCS projects bring many benefits. In addition to reducing the financial commitment from the private sector for CCS projects, it also demonstrates government CCS delivery commitment to developers, suppliers and financiers, etc. There remains however the question of how best to deploy grant funding, with most programmes providing grant funding to the developer of a single full chain project. Providing the grant in this way does not change the risk profile of the project, but serves only to reduce the developers' financial exposure to full chain risks regardless of their nature including many business as usual risks. For future programmes it is worth considering targeting any grant funding to those risks in the full chain where there is a lack of market appetite particularly relating to the storage element. Deploying grant funding in this way for a multi-user store, without the requirement for a return on investment built in to the T&S capacity reservation and use-of-system fees, would provide several G&C and EII developers with low-cost CO₂ T&S services representing a far better outcome for the public funding deployed.

Loan guarantees. Many private sector developers of a G&C asset including independent power producers (IPPs) are likely to look to limited or non-recourse debt finance structures (project finance) as the preferred approach to capital formation. The providers of project finance will in turn evaluate the credit worthiness of a CCS enabled power generation project on its stand-alone merits i.e. the ability of the project to meet its debt service obligations even when operating under certain adverse physical or economic conditions. The revenue certainty provided by the CfD mechanism, contracted through the low carbon contracts company (LCCC), is very attractive from a project finance perspective. However, to reach an investment grade rating in order to secure such finance, the investor group will need financial shielding from the risks associated with the transport and storage of CO₂, as already discussed.

As additional support the availability of government backed loan guarantees for example through the UK Guarantees Scheme (UKGS) would help to increase the credit rating of a G&C project in turn reducing the cost of financing. The combination of the CfD, cross chain default risk support and loan guarantees could increase the credit rating of a G&C project sufficiently to open up the possibility of long-term funding from institutional investors and/or the debt capital markets further reducing the cost of capital.

13.6 Outlook for the commercialisation of CCS

To date, efforts around the world to develop a commercially viable CCS industry have largely failed despite the levels of
government intervention and support that have been considered. If this trend is to be reversed the lessons of the past need to be learned and new approaches developed.

The private sector is very unlikely to deliver fully integrated CCS infrastructure and projects without increased public sector support and clear government policy that supports CCS. It is imperative therefore for governments to take firm decisions on whether or not CCS technology will form a key part of their long-term low-carbon future energy strategy.

Where the case for CCS is made, a clear and stable CCS energy policy with a comprehensive roadmap for delivery will be required. This is necessary to build confidence in the deliverability of CCS and to attract the necessary private sector investment. In the UK a new strategy for CCS commercialisation is needed as a matter of urgency as each year of delay in deployment substantially increases the costs of decarbonisation of the UK economy in future years.

CCS can support carbon reduction efforts across all major carbon emitting sectors and represents an essential component of the low-cost pathway to energy-system-wide decarbonisation. Development of CCS will create some costs; however a vibrant CCS industry will bring significant GVA to the economy as well as generate substantial employment potential.

For CCS to take off as a commercially viable and financeable proposition, the public sector will need to accept more of the development and operational risks that have thus far proved to represent unsurmountable barriers for the private sector, most notably in terms of commercial integration of the full chain and the development and operation of storage sites in a multi-user environment.

By optimising the structure, scale, location, technology choices and introducing new commercial models with modified risk reward structures, on the basis of increased public sector allocation of certain CCS specific key risks, the cost of CCS can be reduced significantly. Strike prices that are competitive withalternative forms of low-carbon generation should be achievable including for the first mover anchor projects.

In the UK, the creation of a government backed national CO$_2$ T&S company, with responsibility for the development of T&S infrastructure guaranteeing the long-term availability of CO$_2$ storage capacity for G&C and EI I users, would be necessary for the successful development of the CCS industry. The availability of a de-risked T&S infrastructure would provide a much firmer basis for the private sector to develop G&C and EI I assets in the UK.

The financial viability of CCS in the power generation sector currently requires a source of funding out with that which can be derived solely from market trading to cover the extra capital and operating costs and provide investors with an adequate return for the risks involved. In the UK, the CfDs available to CCS-enabled power generators are a good example of how this can be achieved. As the market adjusts to further penetration of low carbon generation technologies, as CCS design and operating experience grows and capital and operation costs reduce, the additional funding required via the CfD will reduce accordingly. If CCS is to be successfully deployed by EI I operators a comparable mechanism will need to be devised.

In order to reduce the costs of the first mover projects, large scale power generation anchor projects (ca. 1 GW) connected to multi-user T&S CCS infrastructure should be envisaged from the outset. CCS technology is ready for large scale deployment.

The benefits of CCS are economy wide however the costs have invariably been seen as the responsibility of the developer operator of a CCS project. Alternative funding mechanisms could be considered to spread the costs of CCS infrastructure across all major emitters. This would align with the principle of the polluter pays and also reduce the cost to the consumer of the low-carbon electricity generated.

UKGS financial guarantees should also be considered to support UK developers of G&C assets in securing the finance needed for their investment bringing increasing project credit ratings and reducing costs.

If the lessons of previous unsuccessful CCS development programmes are learnt and the remaining challenges to full commercialisation resolved though new commercial approaches, there is every chance that CCS will be able to play its envisaged key role in supporting the cost effective decarbonisation of energy use across the economy starting in the early 2020s.

14 Political economy of CCS: what needs to happen?

Compared to other leading alternatives for mitigating climate change such as nuclear energy, biofuels and renewable energy, carbon dioxide capture and storage (CCS) technologies is a relatively new and unfamiliar option for large-scale decarbonisation and, as such, the politics and economics are not yet settled. Debates over CCS have been embryonic and fairly tepid when compared to nuclear power for example, where entrenched views and social movements have led to vocal political opposition since the 1960s; these or biofuels, where non-governmental organisations (NGOs) have provoked heated disputes over potential competition with food and impacts on biodiversity and sustainability. Even renewables, which are generally viewed more favourably on a national level, have also seen significant opposition, usually local, with opponents sometimes criticised for being driven by not-in-my-backyard (NIMBY) concerns. In all cases, there have been longstanding government support mechanisms in the form of large scale R&D, subsidies and other support mechanisms, reflecting interests coalescing in support (or opposition) to specific options over the course of years and decades.

By contrast, CCS has largely been far removed from attention of not only the public, but also of politicians and other key stakeholders. Despite this wider neglect, the Intergovernmental Panel on Climate Change (IPCC) has led efforts to consolidate and disseminate knowledge on the subject and have highlighted the benefits (and to a lesser-extent the challenges) of large-scale deployment. Other leading analytical organisations such as the International Energy Agency (IEA) or the UK’s Committee on Climate Change (CCC), have found CCS to be critical to efforts to meet aggressive
decarbonisation targets at least cost. For example, the CCC finds that without CCS, the cost of meeting the UK’s 2050 targets would be twice as high as if CCS were to be included.\textsuperscript{39} As discussed in the introduction to this paper, the IPCC Fifth Assessment Report describes how leaving out CCS would result in far higher costs for an aggressive decarbonisation strategy than would be the case if similar limitations were imposed on other low-carbon technologies (e.g., costs would be on average 138% higher under a 450 ppm scenario if CCS were unavailable, compared to 7% higher if omitting nuclear power, 8% for limited penetration of solar/wind and 64% for bioenergy).\textsuperscript{35} Even more tellingly, when asked to solve such a stabilisation scenario, in the electricity sector only 5 models can even solve without recourse to CCS, compared to 36 models with CCS. In the industrial sector, only 3 models could solve (compared with 22 with CCS).

Indeed, there were many reasons to expect that deploying CCS technologies would be relatively straightforward in political economy terms. CCS is the rare option that could address many important policy goals simultaneously including: addressing concerns over security of supply by providing both base-load and flexible low-carbon power; appealing to major influential stakeholders in industry; and allowing for the possibility of decarbonising existing and planned infrastructure in major developing countries. Moreover, CCS is fairly unique in providing viable options for hard-to-reach sectors including process industries such as chemicals, cement, steel as well as offering a potential pathway for negative emissions technologies (NETs) with biomass energy plus CCS (BECCS). Still, in spite of the advent of a few individual projects, driven by local context and incentives, CCS has had, at best, a chequered track record over the past decade.\textsuperscript{39}

Research into CCS dates back to the 1990s although the constituent parts have been tested over the course of many decades. Yet, CCS did not emerge as a potential energy option for low-carbon development until the 2000s. The IPCC Third Assessment Report (TAR) of 2001 did not devote more than one paragraph out of its 58 page Technical Summary to CCS. The first serious effort by the international scientific community to investigate the technologies was when the IPCC issued a 443 page Special Report on CCS in 2005 at the same time as the issue was receiving attention from many national governments and international institutions.

The optimism of 2005 was followed by a series of announcements and cancellations by both government and industry, but more recently, over the course of just the past two years, a number of operational large-scale projects have emerged. The full-chain (capture, transport and storage) exemplars that store roughly 1 million tons or more of CO\textsubscript{2} per year have come on line include the Boundary Dam project in south-eastern Saskatchewan and the Shell Quest project in northern Alberta in Canada, the Petra Nova project in Texas, Emirates Steel in Abu Dhabi.\textsuperscript{1165} Other new projects slated to launch in 2017 include the Illinois Industrial CCS project (1 Mt\textsubscript{CO\textsubscript{2}}), which claims to the first biomass energy with CCS (BECCS) project, the Gorgon LNG facility in Australia (capable of up to 4 Mt\textsubscript{CO\textsubscript{2}}) and other CCS projects in Canada associated with the Alberta Trunk Line project. Prior to Boundary Dam beginning operations in 2014, however, the only large-scale efforts had been storage projects such as Sleipner and Snøhvit in Norway and In Salah in Algeria, which all used CO\textsubscript{2} from gas processing facilities.

Looking forward however, the pipeline slows and little new CO\textsubscript{2} capture capacity is expected between 2018 and 2022. Moreover, according to the IEA, very few national commitments on the advent of the 2015 Paris Climate Conference (i.e., intended nationally determined contributions or INDC), even mention the possibility of using CCS.\textsuperscript{1166} In spite of its scant coverage in the IPCC's 2001 TAR, the reduction potential by 2020 was estimated at 150–750 Mt\textsubscript{CO\textsubscript{2}} primarily in the power sector, ‘split equally between coal and gas, and between developed and developing countries’. According to the Global CCS Institute, in 2020, large scale capture will amount to only 40 Mt\textsubscript{CO\textsubscript{2}} per year, virtually all of which will be in developed countries and the vast majority will be from gas processing and for use in enhanced oil recovery operations. The question therefore is how to explain this uneven and slower-than-expected rollout of CCS, first, the slow progress, followed by a spurt of new projects and then a drying up of projects before lessons can be learned from the first projects?

### 14.1 Stakeholder views

CCS has largely remained a technological and future-oriented solution and as a result, most firms and NGOs have kept a ‘watching brief’ on the issue but have not been involved deeply in advocacy (either in favour or against), with a few exceptions. In the early 2000s, under the leadership of John Browne, BP was the first major industry advocate for using CCS and sought to build a series of ‘decarbonised fossil’ (DF) plants, including DF-1 at Peterhead in Scotland, DF-2 at a petroleum coke plant in Carson, California, DF-3 at Kwinana in Australia and DF-4 at Hydrogen Power Abu Dhabi.\textsuperscript{1167} All of these projects failed for a variety of reasons including government reluctance to pick winners and local opposition. The one small success was the In Salah storage project at its facility in Algeria, which stored 1 Mt\textsubscript{CO\textsubscript{2}} from 2004–2011. When Tony Hayward took over as CEO in 2007, however, BP largely abandoned its role as a strong advocate.

In the meantime, other large energy firms became more deeply involved in supporting the technology, notably, Shell and Statoil. Other firms, which had taken a more active role in the expectation of growing demand for CCS include oil field services firm Schlumberger, which set up a carbon services division, power equipment manufacturers such as Alstom (now GE), and chemicals firms with air separation capabilities such as Air Products and BOC. Still, many other leading firms such as ExxonMobil or Halliburton have shied away from significant involvement. Finally, despite the initial focus being almost entirely on power sector decarbonisation, virtually all electric utilities (including those that had been early leaders and enthusiasts such as Vattenfall in Europe and AEP in the US) have given up on CCS due to a lack of political and financial
support. Most recent projects have been led by oil and gas companies. For example, in the most recent UK Competition, the two finalists were not led by electric utilities, which were effectively junior partners. The one clear exception is the Boundary Dam project where SaskPower, as a Crown Corporation (owned by the provincial government) has a very different set of incentives and governance structure than any private sector power company.

The environmentalist view is probably best summarised by a 2006 position paper by the Climate Action Network Europe umbrella group, which argued that CCS ‘may have a role to play’ but ‘climate policy cannot wait for any one technology’ and ‘CCS must not divert public investments or political attention away from renewable energy and energy efficiency’.1168 There have been some NGOs that have taken a more positive stance. In 2011, a number of small to medium sized NGOs – Bellona and ZERO in Norway, Green Alliance, E3G and Sandbag in the UK, Pembina Institute in Canada, the Climate Institute in Australia and the Natural Resources Defence Council, Clean Air Task Force and World Resources Institute in the US – came together to form an ENGO network on CCS. The distribution of these NGOs also reflects the countries where CCS has received the greatest attention and support. The largest NGOs, such as WWF and Friends of the Earth, have taken a relatively positive if muted view, given the large diversity of their national branches.

Other NGOs, notably Greenpeace, have been more critical voices. For example, the only major example of open advocacy against CCS was their 2008 report False Hope.1169 Their concerns were that: (i) CCS ‘won’t deliver in time’ (i.e., before 2030); (ii) underground storage is risky and poses significant liability; (iii) CCS wastes energy, is expensive and undermines funding in sustainable solutions; and (iv) the world already has the solutions to the climate crisis in the form of renewables. Linked to these concerns is a view that CCS simply perpetuates fossil fuels, which is compounded by many of the first projects being part-financed by using the captured CO₂ for enhanced oil recovery (EOR). Still, there is little evidence that NGO opposition has done much to shift support (for or against) CCS on specific projects or at a national level.

The one area where opposition has made a difference is when local concerns derailed the prospects of CCS, specifically in onshore projects in Germany and the Netherlands. For example, the effort by Shell in 2007–2010 to develop a pilot storage site at Barendrecht (outside of the Netherlands) in the face of significant public opposition ultimately led first to the project being abandoned and then to all onshore storage in the Netherlands being banned.1170,1171

14.2 The politics of CCS

Governments have been, if anything, less consistent in their support of CCS technologies than non-state actors. There have been a handful of countries or jurisdictions, all of which are reliant on fossil fuels, where CCS has moved up the political agenda to the point where it emerged onto the wider political stage. In Canada, resource-rich provinces of Saskatchewan and Alberta took the lead, and in the US, projects were pushed forward in Texas, Mississippi and Alabama, despite these regions being most sceptical of the need for action on climate change. In Europe, although domestic politics were more favourable towards climate action, the common denominator of the leaders, Norway, the Netherlands and the UK was that they were Europe’s main natural gas producers. Australia, whose economy is almost completely dependent on resources, even tried to assert overall leadership by creating a Global CCS Institute funded at A$100 million per year.

Nevertheless, here had been some indications that, even in leading jurisdictions, the politics of CCS would not be as easy as some had assumed and that turning expert consensus into action faced some serious political and economic obstacles. Although, as noted earlier, CCS is largely unknown to the public and many stakeholders, there have been cases where the subject has become politically salient, notably in these resource-rich economies and if CCS becomes an issue then there is a danger of being on the losing side.

Norway was the first nation to take CCS seriously as the government made the decision over whether CCS would be mandated on all fossil-fired generation, which at the time only involved a single gas-fired plant.1172 The technology continued to rise up the national agenda to the point where, in 2011, Jens Stoltenberg, the prime minister, declared CCS would be Norway’s “Moon mission”.1173 The first major effort was focused on Statoil’s Mongstad oil refinery, one of the largest point sources in the country, first on a test centre to be followed by full-scale capture. Unfortunately, the costs of Mongstad rose dramatically, leading to the larger ambitions for full-scale capture at Mongstad being first delayed in 2011 and then abandoned in 2013 (after an expenditure of over $1 billion) although the large Test Centre Mongstad continues.1174 This failure and criticism from Norway’s Auditor General for cost overruns led the Norwegian government to completely revisit its approach to CCS before being relaunched in 2016, with a commitment to have a full-chain project operating by 2022.1175 There has been, therefore, fairly consistent support from one government to the next although with some division over specific details.

CCS became an issue in provincial elections in both Alberta and Saskatchewan with differing outcomes. In Alberta, the long-serving Conservative government had advocated for CCS. During the 2015 election campaign, the climate sceptic Wildrose Party opposed any further spending on CCS and promised to cancel the Quest project. Ultimately, the socialist New Democratic Party (NDP) won the election and although they had been sceptical of CCS and preferred renewables and carbon pricing, once in power the new left-wing government continued to support the project. In Saskatchewan, Brad Wall, the right-leaning premier who had championed CCS throughout his term, highlighted the Boundary Dam project in launching his 2016 re-election campaign. In response, the opposition NDP sought to highlight cost overruns and technical problems at Boundary Dam. Ultimately, Wall was easily re-elected with a 62% mandate and increased his majority to 51 of the 61 seats in the Legislative Assembly.
In some cases, the shift that followed an election was more dramatic. In Australia, the Tony Abbott Government cut the CCS budget by some 70% in its first budget (cutting A$460 million out of A$650 million), after having campaigned against Labour’s climate-friendly agenda. In a stealthier manner, with a brief note to markets, the new majority Conservative government in the UK abandoned the 1 billion competition that had been initiated in 2011 when the Conservatives were in coalition with the Liberal Democrats.

In other cases, the barriers were more institutional than political. The MIT Future of Coal study in 2007, led by Ernie Moniz, the condemned the US Government’s reliance on small-scale storage projects and called for 3–4 large-scale storage projects of greater than 1 million tons per year and significant investment in major demonstration projects. Yet, as Secretary of Energy under President Obama, Moniz was unable to push through any major project, hemmed in by Congressional recalcitrance to take action on climate change and vested interests in the form of the existing Department of Energy (DOE) regional partnerships, each of which touted the benefits of their own small-scale storage experiments.

At a more technical level, governments can over-specify or poorly specify the rules and conditions and thereby reduce the viability of projects. The UK, which had been considered a leader in policy design pre-2015, has seen no less than three failed efforts to fund large-scale CCS demonstration projects. The first failure, BP’s DF-1 project at Peterhead, failed in the early 2000s because the UK Government did not want to ‘pick winners’, which led to a first CCS competition. According to its own National Audit Office (NAO), the first Competition failed because of the government’s insistence on mandating post-combustion coal thereby imposing unnecessary constraints on top of a poorly designed procurement process. The second competition was cancelled in late 2015 and the government was criticised by the NAO for failing to properly quantify the costs of delaying large-scale deployment and take that account in their decision and pointed to inter-departmental battles with HM Treasury. The House of Commons Public Accounts Committee also issued a harsh report pointing to the additional cost of decarbonisation without CCS, the hole in the Government’s long-term plans for decarbonisation and the damage to investor confidence from the hasty withdrawal of funding.

Despite the stern criticism from policy circles, the decision produced few political repercussions other than some criticism from the opposition (primarily from the Scottish National Party), but relatively minimal media coverage.

There have, of course, been cases where the problem was primarily technology choice and economics. The Kemper County project in Mississippi, which was intended to be a large 582 MW coal IGCC plant, was driven by interests in providing CO2 to nearby oil fields and taking advantage of the proximity of minemouth coal rather than climate ambition. Like earlier IGCC projects in the 1970s and 1980s which suffered from delays, cost overruns and reliability problems the Kemper project was delayed repeatedly. With costs projected to exceed $7 billion (some $5 billion more than the original estimate) and plagued by years of technical problems, low gas prices and a complicated supply chain, the plant owners, Southern Company, decided to halt the IGCC element and continue operating as a conventional natural gas power plant.

Outside of the core leading countries or regions, the problem has been even more severe, in part because of the perception that CCS is at best of marginal interest and, at worst, would cannibalise support from preferred technologies. The Clean Development Mechanism (CDM) offers an example of the impact of CCS being perceived as being of relevance to only a select few. CDM was designed as a flexibility mechanism under the Kyoto Protocol in 1997 to allow public or private actors to get credit for abatement activities carried out in developing countries. Many of the countries that benefited from CDM projects using existing approaches, for example, those receiving credit for afforestation projects in Latin America, were concerned that if CCS was included in the CDM, they would lose out. As a result, it took from 2005 to 2011 to officially accept even the possibility of using CCS as an option within the CDM and still not a single project has emerged.

Another instance of the marginalisation of CCS can be seen in the European debate, despite early ambitions. The European Union, as an institution, took some encouraging steps, such as issuing a CO2 Storage Directive (Directive 2009/31/EC) to encourage all member states to prepare appropriate regulations for storing CO2 supplemented by other support mechanisms (to which only a handful of member states responded). A zero emissions fossil fuel power plant (ZEP) technology platform was launched in 2005 with an aim to have up to twelve full-chain projects across Europe by 2020.

To that end, the EU created a new mechanism to provide financial support through its NER 300 programme, which reserved 300 million emissions permits from the New Entrants Reserve (NER) for auction. The price of carbon in the ETS collapsed from over €20 to close to €5 and so much of the anticipated funding stream disappeared, but even more importantly, the scope of the NER300 was expanded to include innovative renewable technologies (IRTs). Unlike CCS, virtually every country had one or more small-scale IRT projects to advance. When NER300 projects were finally awarded under the first call, 15 diverse renewables projects in over a dozen member states had been selected, but not a single CCS project was funded.

Here, too, part of the explanation was institutional since the priorities of the European Commission did not necessarily align with those of the member states that were expected to cover most of the bill. For example, the project rated highest of all by the Commission, the Hatfield/Don Valley project did not even make the shortlist of four projects that the UK Government was considering and so the potential of aligning sources of funding was missed.

14.3 Future challenges and opportunities

In the wake of the Paris agreement’s reaffirmation of a 2 °C global target with an aim ‘to pursue efforts towards’ 1.5 °C, a rapid scale up of CCS (including BECCS and CCS for industry)
should be crucial. Yet, the prospects for CCS technologies are problematic (and at a complete standstill in many countries), driven by the political economy challenge of decarbonising fossil fuels as much as by any technological or economic barriers. It is misleading though to describe the problems as primarily one of cost or economics. Some low-carbon technologies such as offshore wind receive generous subsidies of the scale that would be needed for CCS. Other technologies such as nuclear power have existed for over sixty years and yet at least some governments still willingly provide large subsidies.

Undoubtedly, there are important technical, economic and commercial challenges, which help explain the slow rollout of CCS, but the political economy, which initially appeared promising, has proven to be more problematic than anticipated. As Lord Oxburgh has aptly described it, CCS is an ‘orphan technology’.1184 Unlike nuclear power (or onshore wind), there are no strong opponents, but equally there are few if any advocates willing to lobby strongly. If there were to be unambiguous, serious political commitment to meeting a 2 °C target, then all large energy firms would eagerly lobby for CCS, but for most (and many politicians), their preferred alternative is continued unabated fossil fuel use.

A few resource-rich countries such as Canada, the US, Australia and Norway have moved forward with CCS almost independent of (or despite) their level of commitment to climate change. The economic crisis of 2007–2008 and the stimulus spending that followed meant that CCS was carried along, which, in spite of numerous setbacks, allowed a half dozen large integrated facilities to emerge since 2014. Yet, the portfolio of new projects at even an advanced planning stage is diminishing. Given the long time-scales involved and significant possibility of governments or firms or both reneging on commitments, the cupboard is essentially bare.

The recent round of emergent projects offers an important opportunity for learning. Global R&D on CCS is increasing and in some countries, such as Norway and the US, R&D support has been particularly generous. There will therefore be technological progress; the question is whether the political economy dynamic will change. Ultimately, CCS provides a litmus test for how serious governments are in meeting their climate change commitments, the cupboard is essentially bare.

The CCS community is most interested in reducing the cost to capture and dispose of CO2. However, the power generation industry is most interested in selling electricity; anything that significantly adds to the cost to generate power is therefore of priority interest. Furthermore, the power industry as an entity exists to satisfy a given power demand; therefore both Cost of Electricity (COE) terms calculated in eqn (21) assume a fixed net power generation of each plant (to satisfy a fixed demand) regardless of whether CCS is installed or not. Consistent with this perspective, the captured cost numerator calculates the difference in cost to generate one Megawatt-hour of electricity with CCS versus one Megawatt-hour without CCS. Because eqn (21) incorporates all systems-level factors relevant for assessing CCS impact (cost, efficiency and amount of CO2 captured) a major premise of this section is that captured cost is a sufficient proxy for guiding the improvement of CCS R&D.

The effect of CCS on COE can be inferred through examination of:

\[
\text{COE} = \frac{\text{CCF} \times \text{CC} + \text{VOM} \times \text{CF} + \text{FOM}}{\text{MWh}_\text{net} \times \text{CF}}
\]  

(22)

where CCF is the capital charge factor, CC is capital cost, VOM is the variable operating and maintenance, CF is the capacity factor, FOM is fixed operating and maintenance, and MWh_net is the net power generation capacity.

In general, without balance of plant improvements, and compared to a plant without CCS, CCS always increases COE. Practically, CCS adds to all cost terms in the numerator of eqn (22) (CC, VOM, FOM). Importantly, owing to the level of perceived risk associated with a “new technology”, the CCF is also likely to increase, at least for initial projects. Thermodynamically, CCS is proven via an entropy balance to always reduce the power generation term in the denominator (MWh_net).1185

15 R&D priorities for carbon emissions reduction in coal-based power generation

15.1 Benchmarking CO2 mitigation cost

For any process capturing CO2, costs are comprised of the capital to install carbon capture and storage (CCS) equipment, the fixed costs to operate, and the variable cost to operate which includes the electricity the facility would have otherwise generated had CCS not been implemented. The key challenge is to reduce, by the greatest extent possible, the increase in the cost of the decarbonised product, be this a tonne of low carbon steel or cement or a MWh of low carbon electricity. Whilst the perspectives and analyses presented in this section are general in nature, the remainder of this discussion will be constrained to the perspective of CO2 capture with subsequent storage in a saline aquifer implemented in the coal-fired power industry.

Even in this context, there are a number of ways one can choose to calculate the CO2 capture cost that includes all three cost categories mentioned in some form. However, for the purposes of comparing the performance of one CCS technology versus another and for evaluating the most impactful CCS methods (i.e., more CO2 captured) this paper will formulate discussion around the following calculation:

Captured cost

\[
\text{Captured cost} = \frac{\text{COE}_w/\text{CCS} [\text{$/MWh}_\text{net}]}{-\text{COE}_w/\text{CCS} [\text{$/MWh}_\text{net}]} \times \frac{\text{CO2} \text{ captured[tonne per MWh}_\text{net}]}{\text{CO2} \text{ captured[tonne per MWh}_\text{net}]} \times 100
\]  

(21)

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15.2 Establishing a framework to evaluate CCS technology

In practice, there are numerous ways for a power plant to generate the power required to operate the CCS system. There are also
numerous power generation sources of varying CO₂ footprints (nuclear, solar, wind, natural gas, etc.) from which a plant can purchase electricity to operate a CCS system. In the interest of reducing confounding factors in the cost analysis, this discussion will not explicitly consider all options for electricity generation or its source. Instead, we imply in eqn (21) a formulation that the power required to operate the CCS equipment is generated by the base plant with CCS; i.e., when calculating COE of a plant with CCS, one does not use the MW of power generation of a plant without CCS in the denominator. Eqn (21) is then somewhat of an abstract comparison of plants with and without CCS, as it suggests a comparison of COE of one plant that is different in size than another. However, there are three main benefits of such a perspective.

The first benefit is that each CCS technology can be evaluated independently of the method to provide the electrical load to operate it. The second is that each CCS technology is evaluated under consistent constraints to satisfy a given power demand and the resultant penalties in cost and performance. The third is that the balance of plant contribution to COE is calculated assuming the same equipment and costing methods, which more accurately isolates the true cost of implementing CCS (including larger equipment sizes and/or auxiliary equipment). While there a better metrics to assess the true financial burden on the entity installing and operating CCS on any specific plant, the metrics proposed here are ideal for objectively evaluating a range of CCS technologies.

With this in mind, the U.S. Department of Energy (DOE) has proposed near term goals for reducing the cost to capture CO₂ and uses the above metrics in its assessment of the promise these technologies have for mitigating emissions from fossil-based power plants. In this framework, it is convenient to isolate two main factors that drive the cost to capture CO₂: energy penalty to separate and compress the CO₂, which result in a loss of power generation efficiency, and cost penalties, which are those costs required to build, install and operate the equipment. The energy penalty explicitly accounts for the electricity requirements to power the CCS equipment, as such embody the cost of lost power generation and associated lost revenue. Recall, the calculations assume the electricity required to run the CCS system is provided by the same plant fitted with the CCS system. The cost penalties required to operate the equipment do not include this lost revenue or power purchase costs, but instead includes the fixed and variable operating cost of supplies, personnel, maintenance, etc. If one acknowledges this distinction between the two cost types, the R&D efforts can be largely split between performance improvements and equipment/operating cost reductions. Decomposing costs in this manner is convenient from a systems perspective because the balance between performance improvements and their associated installation/operating cost increases can be explicitly analysed and optimised.

In the context of the equations presented above, the U.S. DOE has set a target for captured cost at $40 per tonne of CO₂ and uses the above metrics in its assessment of the promise these technologies have for mitigating emissions from fossil-based power plants. This framework, it is convenient to isolate two main factors that drive the cost to capture CO₂: energy penalty to separate and compress the CO₂, which result in a loss of power generation efficiency, and cost penalties, which are those costs required to build, install and operate the equipment. The energy penalty explicitly accounts for the electricity requirements to power the CCS equipment, as such embody the cost of lost power generation and associated lost revenue. Recall, the calculations assume the electricity required to run the CCS system is provided by the same plant fitted with the CCS system. The cost penalties required to operate the equipment do not include this lost revenue or power purchase costs, but instead includes the fixed and variable operating cost of supplies, personnel, maintenance, etc. If one acknowledges this distinction between the two cost types, the R&D efforts can be largely split between performance improvements and equipment/operating cost reductions. Decomposing costs in this manner is convenient from a systems perspective because the balance between performance improvements and their associated installation/operating cost increases can be explicitly analysed and optimised.

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separation and compression can be offset if implementing the CCS system provides a productive use of low grade heat not utilised in the base plant. Alternatively, changing the base power generation platform can also offset the net energy penalty by producing efficiency gains elsewhere in the process. It should be noted however that even power generation platforms projected to be among the most efficient options for power generation are only about one-third as effective at reducing CO₂ emissions than CCS. So while thermodynamic penalties may be offset by adopting more efficient power generation, the need for implementing and improving CCS is certainly not removed.

Because zero cost equipment is unrealistic, one can also presume a maximum capital/operating cost reduction that will limit the ultimate success of R&D in this category, similar to the thermodynamic limit previously discussed. A maximum cost reduction is less rooted in fundamental theory and therefore is a more subjective limit that depends on technology, material, manufacturing improvement and even engineering intuition. While the exact value of maximum cost reduction will almost certainly be subject to significant debate, as an R&D trajectory brings costs closer to zero, additional gains will become more difficult to attain and should be considered when devising an R&D plan. Fig. 31 assumes an 80% reduction limit on the cost per gross thermal input to the system.

History has shown in many cases (in particular those cases that do not involve manufacturing or materials breakthroughs) that as thermodynamic improvements are made (via more integrated system configurations, better materials, or better devices) that equipment costs, installation costs, and/or operational costs generally increase. See the notional trajectory from Point A to Point C in Fig. 31. This phenomenon suggests some degree of tolerance has typically been required for cost penalties as performance is improved, or vice versa. However, Fig. 31 suggests a limit on tolerance for both types of penalties. Insight in this context can be gained by noting where the line that represents the DOE goal crosses into space that is thermodynamically-infeasible or cost-infeasible. The point at which these crossovers occur correlates to maximum acceptable penalty values on the vertical and horizontal axes. That is, if one penalty is too high, reducing the other such that the cost reduction goals are met requires an impossible value in infeasible space.

15.3 Framing future CCS R&D strategies

The location of the reference technology on Fig. 31 suggests that most likely a combination of both cost and performance improvements are required to reach the DOE goal; at this point additional thermodynamic penalty will ultimately result in an infeasible path to the DOE target, with a similar conclusion for the cost penalties, albeit there seems to be a bit more room for cost excursions when targeting the DOE goal. To date, most R&D for CCS has explored various ways to improve thermodynamics, independent of cost or manufacturing improvements. In fact, some early stage technologies are projecting a 50% reduction in net energy penalty compared to reference technology. This is remarkable, but unfortunately remains insufficient to reach the DOE target.

Cost projections in most of the CCS screening studies done to date carry a fairly large uncertainty range (±30–50%). However even with the error acknowledged in most studies performed, the trends still indicate performance enhancements tend to result in slightly increased capital/operating costs. To date, nearly all of the cost penalties of CCS technology are due to capital and installation costs. This suggests a need for more focused attention on reducing capital cost while preserving thermodynamic improvements. If additional capital cost penalties cannot be prevented, thermodynamic laws may ultimately prevent the CCS industry from reaching the DOE goal. The maturity of readily available equipment and state of the art manufacturing processes has left little room for equipment cost improvements. However, recent progress in advanced manufacturing and process intensification may provide additional options for realising cost improvements. New manufacturing techniques will allow production of multi-functional unit operations which require complexities in geometry that until recently were infeasible to build. Combining simultaneous thermodynamic operations in such a way may allow improved efficiencies in smaller equipment, with less raw material costs. For example, 3D printing techniques have great freedom in building multiple independent, yet adjacent flow paths in one unit operation which may allow nearly arbitrarily close integration of heat exchange, reaction, and mass exchange operations.

Reaching an optimal combination of cost and performance improvements requires a detailed understanding and ability to accurately simulate the underlying thermodynamics and kinetic phenomena in a manner sufficient for holistic optimisation of the entire system. Evaluating a CO₂ capture material in a system optimised for its performance is critical to properly assessing its promise and intelligently informing future R&D pathways. Little work of this extent has been done to date. However, recent efforts in the Carbon Capture Simulation Initiative (CCSI) funded by the U.S. DOE’s Office of Fossil Energy have begun to address this issue rigorously. Understanding the scale at which certain CCS technology platforms outperform others is also critical. The DOE goal of $40 per tonne of CO₂ captured is formulated around a plant that is sized to produce 550 MW of net power generation, which is on the larger size of most point source generators of CO₂. Indeed, over half of the CO₂ from coal fired power generation in the U.S. is produced by power plants smaller than 550 MW, with normalised CCS capital costs that can triple compared to those required for the baseline 550 MW plant. The implication is that achieving the DOE goal of $40 per tonne will become exponentially more difficult at smaller plant sizes.

At large scales, the need for thermodynamic performance improvements will likely dominate, because economies of scale
are healthy. Still, process intensification strategies will almost certainly be required to shrink equipment sizes or collapse some of the larger, single-purpose unit operations into more multi-purpose unit operations that require less material and space for similar performance. However, as point source sizes become one to two orders of magnitude smaller, economies of scale disappear and the cost to capture a unit mass of CO₂ increases dramatically. At those smaller scales, adequately reducing capital costs will likely require a dramatic shift in paradigm to uncover cost effective solutions. Advanced, mass manufacturing strategies will likely be required to generate low capital cost solutions for small scale, modular CCS. Furthermore, the degree to which cost savings can be realized will almost certainly depend on technology platform. Regardless of platform, and in contrast to larger scales, cost savings at smaller sizes are likely to come at the expense of thermo-dynamic performance. Whether process intensification, mass manufacturing, advanced manufacturing or a combination of all three are employed to reduce cost, a firm understanding of which technology platform will be most cost effective at each scale after optimization is first required. An important counter-factual in this context is that, for some hard to reach point sources, it may be preferable to simply offset these emissions via the use of negative emission or greenhouse gas removal (GGR) technologies.

In tandem with the stated need to reduce cost and energy penalties of CCS, simultaneous performance improvements in power generation itself are also critical as they reduce the amount of CO₂ liberated to satisfy a given power demand in the first place. However, the opportunity for improvements in the power generation efficiency of an existing facility is extremely limited without a major repowering effort. This requires a shift in perspective to greenfield designs. To reveal where the most opportunity for improvements in power generation improvements exist, one can extend the exergy analysis used to generate the thermodynamically infeasible region associated with CCS in Fig. 31 to the remainder of the subsystems in a Pulverised Coal (PC) plant with CCS.

The methodology for exergy analysis in McGlashan and Marquis was used to calculate the work lost due to thermodynamic non-idealities in each subsystem of the power plant. In identifying the sources of these non-idealities, one also identifies areas with the most room for improvement. A typical analysis will reveal that for an average PC power plant equipped with amine based CCS, the ordered priority for improvements above the base PC plant is as follows:

1. Fuel chemical energy transfer (50–60% loss of theoretically ideal work)
2. Steam turbine (~10% loss)
3. CO₂ capture and compression (5–10% loss)

Of particular interest is that operating the CCS system results in less of a power penalty than sources of thermodynamic inefficiency elsewhere in the plant. The transfer of coal combustion heat to the steam cycle by far exhibits the largest losses, due primarily to the large temperature difference in the associated heat exchange process. The steam turbine is the next largest source of lost work. The lost work associated with these two processes in the standard coal based power generation

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**Fig. 31** Cost and performance improvement trajectories to meet CCS goals.
platform process suggests the best opportunity to decrease lost work of low carbon power generation (i.e., to increase power generation efficiency) is to first improve the base power generation technology platform, rather than to increase the efficiency of the CCS process.

Indeed, there is great opportunity in greenfield plant designs to integrate advanced power generation with CCS in manners that render CO₂ separation more inherent (e.g., Chemical Looping, Fuel Cells) or that have higher driving forces for CO₂ separation & compression (e.g., IGCC, Pressurised Oxycombustion). Nevertheless, in addition to offsetting CCS penalties with high efficiency power generation platforms, improving the CCS processes not completely inherent in power generation remains critical. Most work to date focuses on CCS processes that extract CO₂ from a flue gas or syngas already generated by the power generation process, and are in that context largely independent of power generation platform. Transformational, low carbon fossil power generation will need to simultaneously generate power and concentrated CO₂ more efficiently. As a result, the current sequential, or even semi-integrated, approaches to CCS are likely to become obsolete in the long term.

In the near term, where applications for CCS to be retrofit abound, developers should continue to preserve the currently projected thermodynamic improvements to CCS. However, kinetic improvements including heat and mass transfer as well as precisely controlled reaction/separation networks should garner more attention to decrease overall equipment size. Furthermore, as most state of the art CCS systems are sequential and/or only semi integrated, there is great untapped potential to apply concepts of process intensification to even near-term CCS designs. The intent here is to transcend the limitations of conventional, generalised equipment designs to produce geometries and configurations for new equipment that are highly specific to and efficient for CCS application. While an increase in equipment complexity has often resulted in an increase in cost, we again mention that the impending revolution in advanced manufacturing has the potential to cost effectively bring this designer equipment to market.

In the long term, as retirement of existing PC plant designs increases, the need to replace them with advanced baseline fossil power generation platforms like those mentioned above will increase. At this point, the power generation industry will need to implement a new paradigm of CCS; one where the line separating power generation from CO₂ capture is significantly blurred.

16 Conclusion
16.1 IAMs and negative emissions
In the context of meeting the climate change commitments of limiting warming to less than 2 °C, most integrated assessment models (IAMs) cannot find a solution without carbon capture and storage (CCS). In other words, CCS is not just vital to the cost-optimal solution, it is vital to the solution, period.

Intergovernmental Panel on Climate Change (IPCC) scenarios associated with a more than even chance of achieving the 2 °C target are characterised by average capture rates of 10 Gt CO₂ per year in 2050, 25 Gt CO₂ per year in 2100 and cumulative storage of 800–3000 Gt CO₂ by the end of the century.

Further, IAMs do not find a decreasing role for CCS over time. On the contrary, the CCS share in primary energy is mostly higher in the second half of the century compared to the first. This undermines the reputation of CCS as a bridging technology and further underlines its importance in IAMs, which seek to achieve ambitious climate targets. In other words, CCS is likely to be important for the long term.

The more stringent our climate targets, the more important bioenergy with CCS (BECCS), and other negative emissions technologies (NETs), become. In 2100, it is more likely than not that BECCS will provide more than 5% of total global primary energy. For a 1.5 °C scenario, the cumulative negative emissions are between 450 and 1000 GtCO₂ until 2100. This is in stark contrast to some 2 °C scenarios, which do manage to reach their target without carbon removal technologies. Thus, in the context of meeting a 1.5 °C target, all the evidence points to an overshoot in temperature, which will need to be brought back under control via NETs. There are no feasible scenarios which do not involve NETs. Importantly, in addition to removing CO₂ from the atmosphere, NETs allow the offsetting of emissions from hard-to-reach areas, like shipping or aviation. Importantly, the dominance of BECCS may well be a function of the lack of other options within IAMs, and therefore incorporating other NETs in IAMs is a priority. Of the range of potential NETs, BECCS and direct air capture (DAC) are two that are of potential significance.

BECCS is currently industrially deployed, with five plants operating worldwide. The technical maturity and costs of BECCS are comparable to conventional Fossil-CCS technologies, with BECCS costs typically estimated to be on the order of half that of direct air capture.

The technical potential for BECCS pathways is estimated to be in the range of 3–20 Gt CO₂ per year. However, it is becoming increasingly clear that the resource requirement to deliver BECCS is case-specific. Between 380–700 Mha of land may be required by 2100, and depending on the choices made throughout the biomass supply chain, capturing 12 Gt CO₂ per year would require between 130–860 EJ. Land availability for biomass feedstock production is a key driver for large-scale BECCS implementation. Land demand for BECCS largely depends on the selected feedstock.

It is finally important to note that the large-scale deployment of BECCS is contingent on first having access to a mature CCS industry. Given the challenges associated with delivering CCS, the additional challenges of securing sufficient sustainably sourced biomass and the policy questions around incentivising and regulating negative emissions facilities would render attempting large-scale BECCS in the absence of a mature CCS industry exceptionally challenging.

The direct capture of CO₂ from the air is possible, but technically and economically challenging, primarily as a result
of the extremely dilute nature of atmospheric CO₂. Owing to the low concentration of atmospheric CO₂, costs of DAC are likely to be very substantial, and perhaps as much as two orders of magnitude greater than CO₂ capture from power plant exhaust gases. However, at the time of writing, a DAC facility is operating on a commercial basis in Switzerland, and is selling the captured CO₂ for utilisation. However, given that the CO₂ is not geologically stored, this does not constitute a negative emissions project.

One key way in which the dilute nature of atmospheric CO₂ affects process design is the required affinity of the sorbent for CO₂ – this would need to be as much as two orders of magnitude greater than is the case for “standard” capture with chemical solvents such as amines. This in turn makes sorbent regeneration that much more challenging and necessitates a chemical shift process as opposed to a simple temperature or pressure swing. DAC costs are likely to be dominated by the requirement to treat vast volumes of air in order to capture a meaningful amount of CO₂ with the capture of 1 MtCO₂ per year necessitating the processing of 80,000 m³ s⁻¹ of air. The actual cost of DAC is likely to be in the range of $600–1000 per t CO₂. In order to have a realistic assessment of the likely utility of DAC, transparent and realistic estimates of the cost of this technology are urgently required. Given the present level of uncertainty, rational decision making or inclusion in IAMs is highly impossible.

### 16.2 Industrial CCS

In addition to decarbonising the power sector, CCS also plays an important role in decarbonising the industry sector. Decarbonising the industrial sector presents a unique set of challenges, in that there are no obvious alternatives to CCS (cf. renewable energy in the power sector) and the international nature of industry. Particularly important industrial sectors are iron and steel, cement, and oil refining, with large integrated mills, for example, emitting 3.5 MtCO₂ per year, on the order of 1.8 tCO₂ per tsteel. Cement production is also a carbon intense activity, with a carbon intensity in the range of 0.6–1.0 tCO₂ per t cement, with approximately 60% of this CO₂ associated with the calcination step, i.e., even if the energy required to operate the process was entirely zero carbon, this would only reduce the CO₂ intensity by 40%.

Decarbonisation of cement production via amine scrubbing has been observed to be ~3 times more energy intense than oxy-firing and the demonstration of full oxy-fired cement production has been identified as a priority for future research, though Calcium looping is another important technology. In the context of industrial decarbonisation, industrial symbiosis, etc., recovering waste heat from neighbouring facilities, has been observed to be key to cost reduction. Owing to their unique skill sets, the application of CCS to any industrial sector is likely to involve the petrochemical industry. Moreover, when it comes to decarbonising the refining sector, this cost is well within the large swings in oil price. Put another way, the end-use sectors can easily afford to pay for decarbonising this sector. However, relative to the power sector, there is a paucity of academic studies of industrial carbon capture, despite the fact that much of the real-world deployment is happening in the industrial sector. This is therefore an area that warrants further research.

### 16.3 Technology development

The rate at which new materials progress from the lab- or bench-scale to the pilot-scale is too slow. It is critical that this rate be increased. One potential impediment is that the current sorbent benchmark is still 30 wt% MEA, which was originally proposed in 1930. However, this option is now significantly outclassed by blends of solvents, such as the formulation of piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP). It is time to update this benchmark, preferably with reference to current industrial best practice. The fact that new materials continue to be compared with an obsolete benchmark is potentially limiting progress in this area. Efforts should also be made to ensure that laboratory-scale work investigates materials under conditions somewhat representative of the real world-high CO₂ partial pressure for desorption, and eventually including the presence of steam and trace and minor species.

Ionic liquids (ILs) have shown some promise as next-generation CO₂ capture solvents, mainly through their highly desirable stability and low volatility, combined with reasonable absorption capacity. However, there are issues with poor gas uptake kinetics, stemming from high viscosity. Also, the high molar mass of most ILs dictates that, even with high molar CO₂ capacities, the mass uptake rate remains inferior to aqueous alkanolamines, particularly at low pressures. It would seem prudent for future research to focus on reducing the molar mass and viscosity of functionalised ILs. By employing functionalised ions (azolate, phenolate, amino acid) there remains the possibility of increased capacity without necessitating higher cost. If future designs can take into consideration cost aspects in combination with reduced capture energy and higher capacity, there could be justification for the use of these novel solvents.

Metal organic frameworks (MOFs) are a promising class of sorbent materials. However, they are not typically manufactured at large scale, and for those that are, they are typically supplied as a powder rather than a structured adsorbent. Developing an understanding of the large-scale production of MOFs in a form suitable for practical application is key to moving these materials forward towards industrial deployment.

There are an immense number of possible materials which could be used for CCS – testing them all at pilot scale is not practicable. The development of high-throughput modelling and simulation approaches which combine molecular- and process-scale information for material screening is therefore vital. Importantly, data describing mass transfer resistance and diffusion limitations are required to enable this, but are particularly scarce.

CO₂ transport remains an over-designed element of the CCS chain, owing to uncertainties around material selection and process operation. A better understanding of the role of CO₂ composition in fracture propagation is vital for derisking this
element of this technology. Importantly, if purity constraints can be relaxed, this can lead to non-negligible reductions in whole-system cost.

When assessing an improvement in CCS technology, it is important to recall that whilst the CCS community want to reduce the cost of CO₂ capture, the owner of the facility from which the CO₂ must be captured prioritise minimising the cost of their low carbon product. This is especially true of the power sector where they are operating to meet a fixed, and largely inflexible, demand.

With existing technologies, the majority of “CCS costs” are, in fact, associated with increases in capital cost, as opposed to operating cost. This implies that whilst a continued focus on improving thermodynamic performance is helpful, priority must be given to research which promises reduced capital costs.

In this context, in addition to improving the CCS process, the value of improving the underlying process, i.e., the power plant is also vital. From a thermodynamic perspective, 50–60% of theoretical losses occur in the conversion of chemical energy to electrical energy. By comparison, CCS is only 5–10% (except for the cases of high temperature cycles, which integrate the capture efficiency loss into the lost work from the conversion of heat to work, and are therefore more efficient). Moreover, as the power plant increases in efficiency, less CO₂ is produced per MWh thus reducing the cost of the starting point. Thus, where new facilities are built, the deployment of state-of-the-art facilities should be a given.

Thus, R&D initiatives aimed at “improving” CCS should take a whole systems approach and focus on reducing the cost per unit of decarbonised product (e.g., steel, cement, power), and how this decarbonised process will, itself, compete in the market, i.e., what will displace what. This may well be distinct from focusing exclusively on minimising the cost of capturing the CO₂.

### 16.4 CO₂ storage

In the past 5 years, great progress has been made in the area of CO₂ storage. Outstanding challenges in the area of CO₂ storage monitoring and verification include the development of technologies to allow for the quantification of the amount of CO₂ stored and plume migration. Approaches for obtaining quantitative insight into the extent to which CO₂ has partitioned into the aqueous phase, or has become residually trapped are also a key research priority. Leak detection and remediation remain key areas for research, hampered by the lack of analogue in the petroleum industry.

A final key area for urgent research is the development of better understanding of regional CO₂ storage capacity, how it changes with use and how this capacity might evolve over time. Indeed, the lack of such insight is a key hurdle to a better representation of CCS in IPCC-type assessments.

### 16.5 CO₂ conversion and utilisation (CCU)

There is a common narrative that CCU can enable CCS. In the US, where the CO₂ transport and storage infrastructure is available and largely written off, this may be true in the case of CO₂ enhanced oil recovery (CO₂-EOR). In this context, the potential of residual oil zones (ROZs) is significant owing to their likely high CO₂ injected to oil recovered ratios. Thus, in the US, the primary objective is driving down the $ per tCO₂ cost so that CO₂-EOR, combined with the existing tax credit scheme, represents an attractive investment in an era of relatively low oil prices.

In other parts of the world, like the UK or EU, the CO₂ transport and storage infrastructure does not exist at the same scale, nor is there a sufficient investment incentive to induce its deployment (e.g., EOR may not be an option). Thus, in these regions, the key barriers are the lack of infrastructure, with the cost of capture a secondary barrier. Consequently, the UK/EU region would be better advised to focus on deploying transport and storage infrastructure and derisking that element of the investment. Innovations to reduce the $ per tCO₂ cost of capture will continue to come from the global academic community, and can be imported on an as-needed basis. Infrastructure cannot, however, CO₂-EOR can potentially enable the deployment of CCS infrastructure. However, the extent to which CO₂-EOR will actually store CO₂ strongly depends on the way in which the EOR operation is managed, and also on the kind of oil which is recovered. It is important, therefore, to carry out thorough life cycle analyses, both attributional and consequential, in order to develop this kind of insight.

The magnitude of the role that CCU might play in climate change mitigation is likely to be very small, relative to that played by CCS. However, CCU might offer very cost efficient options for CO₂ mitigation, even yielding a profit in some cases. One option which might be deployable at scale is the conversion of CO₂ to a fuel product (e.g., via Fischer–Tropsch processes). However, this requires major progress in catalysis and process design, additionally this route does not store CO₂ long-term but would offer carbon-neutral fuels in a best case future scenario. The primary source of cost in CO₂ to fuels processes is that of hydrogen, with the cost of CO₂ coming second. Thus, in order to move CCU forwards, a key area for research is the development of reduced cost approaches for producing renewable hydrogen.

Another key constraint is that, in order to avoid partial decarbonisation scenarios, the CO₂ used must (a) ideally not come from a fossil source, and (b) be recaptured after the, e.g., CO₂-fuel is used. This will have the effect of enabling CCU to be a key element of a coherent circular economy narrative.

### 16.6 Policy considerations

Current and medium-term UK and EU decarbonisation targets are expressed in terms of a percentage of renewable energy. This is essentially confusing ends (sustainable, affordable and reliable energy) with means (deployment of specific technologies) and is distinct to a technology-agnostic aim of deploying low carbon electricity. As a consequence, the deployment of CCS is disadvantaged from a policy perspective. Better would be to define low carbon energy, e.g., 50 g kWh⁻¹, and replace renewables targets with low carbon targets, e.g., x% of power to come from low carbon targets by a given date. This would allow
individual states the flexibility to realise these goals in a locally optimal manner.

It is vital to recognise that, as we move to a more diverse energy system, not all power generation technologies provide the same services to the system, and thus attempting to value them on a basis of levelised cost of electricity (LCOE) is, at best, misguided. Better to evaluate the value of each technology to the energy system on an individual basis, noting that this value varies with the composition of the system. In this context, CCS, nuclear and bioenergy are notable for their ability to significantly reduce CO₂ emissions at a marginal increase in total system cost. Thus, these technologies must compete amongst themselves. In other words; CCS and intermittent renewable energy generators are not competing to provide the same set of services.

It is evident that, despite substantial public and private effort to commercialise and deploy CCS technology, progress is lagging behind what is commonly considered to be required to meet climate targets. This is despite ample evidence that CCS will both reduce whole-system energy costs, and thus the cost to the consumer and also create a significant number of jobs.

One key issue with the CCS commercialisation models that have been followed thus far is that the private sector should manage all of the technical and commercial integration risks across the full CCS chain (capture, transport and storage). Whilst the private sector can manage and competitively price many risks, there is a lack of proven models for commercialising CCS (distinct to the CO₂-EOR industry, which is much more straightforward). This lack of a proven commercial model across the full chain, means that the market will either only accept at a premium, or not accept, whatever the price.

The key commercial risks that require public support are (i) cross chain default, (ii) post decommissioning CO₂ storage risk, (iii) CO₂ storage performance risks, (iv) decommissioning cost and financial securities related to the CO₂ storage permit, and finally (v) insurance market limitations for CO₂ T&S operations. A commercial model that entails a transfer of risks iii-v to the public sector will both remove the key barriers that have thus far prevented the private sector from investing in CCS and also improve financeability and consequently significantly reduce the risk premium added to the cost of capital funding. This model is in line with what was suggested by the 2016 Oxburgh Report.101

However, it is not necessary to have public ownership of the generation and capture assets, and with the transfer of the aforementioned risks iii-v to the public sector, the private sector can likely deliver CCS without any change to existing regulation. This latter element is particularly important; wherever possible initiatives should ideally fall within existing regulatory frameworks.

Whilst the technical elements of CCS are well-understood, and, as has been discussed in this paper, the financial models are becoming increasingly clear, public acceptability and the consequent impact on the political economy are as yet at an embryonic stage. This is despite substantial evidence of the economy-wide GDP and employment benefits associated with the deployment of CCS.

It is misleading to describe the problems with CCS commercialisation as primarily one of cost. Some low-carbon technologies such as offshore wind receive generous subsidies of the scale that would be needed for CCS. Other technologies such as nuclear power have existed for over sixty years and yet, some governments still willingly provide large subsidies. Uniquely for CCS, the political economy has proven to be more problematic than anticipated. Unlike nuclear power or onshore wind, there are no strong opponents, but neither are there advocates willing to lobby strongly. If there were to be unambiguous, serious political commitment to meeting a 2°C target, then all large energy firms would eagerly lobby for CCS, but for most (and many politicians), their preferred alternative is continued unabated fossil fuel use.

Ultimately, CCS provides a litmus test for how serious governments take the challenge of deep decarbonisation. If there is a genuine effort to meet ambitious climate targets then, if the many analyses are correct, the needed shifts in incentives and regulations will mean change in the interests (and the economics) and large-scale deployment CCS will eventually follow.

Conflicts of interest

There are no conflicts to declare.

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