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DOI:

[10.1039/c2jm12592g](https://doi.org/10.1039/c2jm12592g)

### *Document Version*

Early version, also known as pre-print

### *Citation for published version (Harvard):*

Drage, TC, Snape, CE, Stevens, LA, Wood, J, Wang, J, Cooper, AI, Dawson, R, Guo, X, Satterley, C & Irons, R 2012, 'Materials challenges for the development of solid sorbents for post-combustion carbon capture', *Journal of Materials Chemistry*, vol. 22, no. 7, pp. 2815-2823. <https://doi.org/10.1039/c2jm12592g>

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# Materials challenges for the development of solid sorbents for post-combustion carbon capture

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*Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X*

*First published on the web Xth XXXXXXXXX 200X*

DOI: 10.1039/b000000x

In an effort to reduce the energy penalty and cost associated with current state of the art carbon capture technologies, a range of 2<sup>nd</sup> and 3<sup>rd</sup> generation CO<sub>2</sub> capture technologies are being developed. One of these technologies, based on solid sorbents for the gas separation in carbon capture, has the potential to significantly reduce the energy penalty and avoid some of the problems associated with the current state of the art capture technologies. However to realise this potential, two developments are required, new porous materials and plant integration processes. This application note describes the performance requirements and challenges posed to the development of functional materials for this application. The key challenges for materials development and requirements in terms of: operating conditions, gas composition, stability and lifetime required to make solid sorbents a viable large scale CO<sub>2</sub> capture process are described herein. Examples of potential future research and breakthrough materials currently being developed will be discussed.

## Introduction

Recognising that fossil fuels will continue globally as part of a diverse energy mix for some time<sup>1</sup>, targets and strategies have been developed to reduce greenhouse gas emissions, for example the European Unions Sustainable Energy Technology (SET) Plan.<sup>2</sup> Rapid development and implementation of these strategies will be required if the warnings of potentially damaging climate change reported by the Intergovernmental Panel on Climate Change (IPCC) are to be avoided<sup>3</sup>, a task that is made more challenging when set against the significant global increase in energy demand.<sup>1</sup> A strong economic case for urgent action to reduce greenhouse gas emissions has also been made in the 2006 Stern report.<sup>4</sup> Europe is committed to an 80% reduction in greenhouse gas emissions by 2050<sup>5</sup> and similar emissions reduction targets have been proposed and committed to on a global scale.<sup>6</sup> In relation to electricity generation, carbon abatement technologies have been proposed to achieve these ambitious targets for large-scale fossil fuel, e.g. coal and gas, power plants.<sup>5</sup> More specifically, emissions reductions are proposed to be achieved by: increasing efficiency (up to 20% reduction on CO<sub>2</sub> emissions); co-firing biomass with coal (up to 10%) and employing carbon capture and storage (CCS) technology which could reduce emissions from power stations by as much as 90%, and the potential to contribute up to 28% of global carbon dioxide mitigation by 2050.<sup>5</sup>

Carbon capture and storage is the subject of significant research, development and demonstration activity on a global scale. The key objective of which is to achieve full scale commercial deployment of the technology within the next 10 years<sup>7</sup> followed by potential deployment of between 6 and 80 GW of CCS plant (low or high penetration scenarios

respectively) by 2030 in the European Union alone.<sup>2</sup> The background, process and challenges of CCS have been described elsewhere<sup>3</sup> and would be beyond the scope of this application note to discuss in detail. In brief, CCS is a technology that allows the continued use of fossil fuels without release of CO<sub>2</sub> into the atmosphere by separation and purification of the gas from the combustion or gasification process for long term disposal, for example by geological storage. A range of CCS technologies: pre, post-combustion capture and oxyfuel combustion are currently under development. At the core of each of these technologies is a gas separation, essentially; CO<sub>2</sub> and N<sub>2</sub> in the case of post-combustion capture, CO<sub>2</sub> and H<sub>2</sub> for pre-combustion capture and O<sub>2</sub> from air for oxyfuel combustion. Each of these gas separations will be performed at a range of different physical conditions (e.g. temperature, overall pressure and CO<sub>2</sub> partial pressure) depending on the CCS technology and point in the process where it is applied.<sup>3</sup> To be successful CO<sub>2</sub> capture technologies need to operate with a minimum energy penalty on the host power plant, at reasonable capital and operating expenditure, have an acceptable plant footprint and perform to achieve capture targets and produce CO<sub>2</sub> of high enough purity to meet the requirements and legislation for subsequent transport and storage.<sup>8</sup>

The topic of this application note is the development of functional materials for post-combustion carbon capture. The current technology of choice, amine solvent scrubbing, uses aqueous solutions of alkanolamines to achieve CO<sub>2</sub> separation from flue gas.<sup>9-11</sup> These solvents are operated through a temperature swing cycle to selectively capture and release CO<sub>2</sub> by the formation of reversible carbamate species.<sup>12</sup> Whilst this technology is the current state of the art and will be used in the first generation of carbon capture plant, the technology has a number of drawbacks in terms of complexity

in operation, high pH solvents leading to corrosion of metal piping, and the energy-intensive regeneration of the solvents.<sup>9</sup> This high energy usage of this process ultimately results in an up to a 10% point reduction in plant efficiency,<sup>13, 14</sup> and a significant increase in cost of electricity.<sup>15</sup> This has led to the proposal of a range of potentially more efficient and less energy intensive second and third generation capture technologies,<sup>16</sup> examples of which include; advanced solvents,<sup>17, 18</sup> solid sorbents,<sup>19</sup> membranes,<sup>20</sup> and ionic liquids,<sup>21, 22</sup> amongst others.<sup>16</sup> These different capture technologies and materials are at various stages of development and proximity to commercialization. The ultimate aim of these alternative capture processes is to meet the energy and cost reduction targets set by, for example the US Department of Energy<sup>16</sup> and European Union SET plan<sup>23</sup> which are proposed accelerate the global uptake of CCS.

This application note is principally concerned with post-combustion capture using solid sorbents at low temperature (between approx 25 and 100 °C), one of the most promising technologies described above. The key aim of this application note is to provide a valuable resource to scientists developing materials for this application. To achieve this aim, the key challenges for materials development and requirements in terms of; operating conditions, gas composition, stability and lifetime required to make solid sorbents a viable large scale CO<sub>2</sub> capture process are described. Finally, examples of potential breakthrough materials currently being developed will be discussed.

## Solid sorbents for CCS

The development of a solid adsorbent capture technology is one of the most promising alternative capture technologies.<sup>16</sup> A key motivation for the development of solid adsorbents for carbon capture is the potential energy saving shown by theoretical studies. These studies suggest that an adsorbent system with a cyclic capacity approaching or better than 3 mmol g<sup>-1</sup> could significantly reduce the energy requirement of post-combustion capture by 30-50% compared with amine solvent systems.<sup>24</sup> However, at present the proposed capture efficiency improvements are theoretical and require the development of materials and processes to make them a reality, a not insignificant challenge. A general framework for the performance of adsorbents for post-combustion capture of CO<sub>2</sub> has been defined by The National Energy Technology Laboratory in the US.<sup>25</sup> These targets refer to the intrinsic performance of the material as well as the process itself:

1. The ultimate target for a sorbent capture process is a reduction of 30-50 percent of the energy required for a wet (MEA) process.
2. The sorbent should achieve a minimum CO<sub>2</sub> delta loading of 3.0 mmol g<sup>-1</sup> under flue gas conditions.
3. The sorbent must adsorb and desorb CO<sub>2</sub> within a narrow temperature envelope (e.g. 40 to 110 °C) in the presence of water vapour at atmospheric pressure.
4. The sorbent is durable and stable within the plant operating conditions and retain its high CO<sub>2</sub> capture capacity over numerous absorption and regeneration cycles.

5. The sorbent must perform and be durable in the presence of water vapour and other acid flue gas constituents.

A wide range of materials have been developed for this application. An extensively review of materials development would be beyond the scope of this application and has been reviewed elsewhere.<sup>19</sup> The principal classes of porous materials under development are summarised below:

- 1 Supported amines – amine polymers physically associated with the surface of a porous material, for example polymers or inorganic supports.<sup>26-28</sup>
- 2 Immobilized amines – similar to above but with amine functional groups bonded to the surface of a porous material, for example silica and carbon.<sup>29, 30</sup>
- 3 Activated carbons – with and without surface modification to increase selectivity and capacity.<sup>31-33</sup>
- 4 Hydrotalcites, with and without surface modification<sup>34, 35</sup> and zeolites.<sup>36</sup>
- 5 Inorganic-organic hybrid materials, such as Metal Organic Frameworks (MOFs).<sup>37</sup>

Of all the materials developed and tested the challenge still remains to develop materials that achieve these performance targets and are fully stable under the conditions of post-combustion flue gases<sup>38</sup>, and as such still poses a challenge to materials scientists.

## Defining the Challenge for Materials

The following section details the conditions and operational requirements of solid sorbents for post-combustion capture applications. Within each of the following sections challenges for materials development with respect to flue gas conditions, performance targets and operation conditions, as well as desirable physical properties will be discussed.

### Flue Gas Composition

Although post-combustion capture is ultimately the separation of CO<sub>2</sub> from nitrogen, this is not conducted in a clean gas stream. Most post-combustion capture applications at present are targeted towards coal fired power plant. As coal is not a pure hydrocarbon, containing a wide range of heteroatoms and inorganic components, the gas from its combustion will contain a range of gaseous and solid components. This gas composition will vary depending on the fuel type used and the location of the capture unit in the powerplant, for example before or after flue gas desulphurisation and NO<sub>x</sub> reduction technologies.<sup>39</sup> Example composition and physical conditions of a post combustion flue gases from coal combustion before and after flue gas treatment, as well as from natural gas combustion where these materials may also find an application, are presented in Table 1. It is evident from these example gas compositions that CO<sub>2</sub> will be present at a low volume concentration (3-15%), and thus, given the flue gas will be emitted at close to atmospheric pressure, a low partial pressure. As a result materials with a high selectivity for CO<sub>2</sub>, and potentially a high surface affinity to CO<sub>2</sub> will be required.

**Table 1.** Example flue gas composition from coal<sup>39, 40</sup> and gas<sup>3</sup> combustion (values are quoted as vol% unless otherwise stated).

Component	Coal <sup>1</sup> (no FGD/DeNO <sub>x</sub> )	Coal (after FGD/DeNO <sub>x</sub> )	Natural Gas
N <sub>2</sub>	75-80%	75-80%	75%
CO <sub>2</sub>	12-15%	12-15%	3%
SO <sub>2</sub>	1800 ppm	10 - 70 ppm	<10ppm
NO <sub>x</sub>	500 ppm	50 - 100 ppm	50ppm
H <sub>2</sub> O	5-7%	5-14% <sup>8</sup>	7%
O <sub>2</sub>	3-4%	3-4%	13-15%
CO	<100 ppm - occasionally 5000ppm	<100 ppm occasionally 5000ppm	<5ppm
Hg / As	ppb	ppb	0
Particulates	10 -20 mg Nm <sup>-3</sup>	10 - 20 mg Nm <sup>-3</sup>	not present
Pressure (MPa)	0.1	0.1	0.1
CO <sub>2</sub> partial pressure (MPa)	0.012-0.015	0.012-0.015	0.005-0.01

The composition and physical condition of flue gases present a challenging environment in which the adsorbents will need to operate. Water and oxygen will always be present in the flue gases irrespective of the fuel combusted. As their removal prior to the capture process will involve a significant energy penalty, any solid sorbent for carbon capture will have to meet the performance requirements and be stable in the presence of these components. This leads to one key difference between amine solvent systems and solid adsorbent systems where water poses a lesser problem for an already aqueous system.

The presence of water vapour will define which materials can be used based on their stability. As an example metal organic frameworks (MOFs)<sup>41, 42</sup>, covalent organic framework (COFs)<sup>43</sup> are crystalline microporous materials which can exhibit exceptionally high surface areas and gas sorption capacities and as such have been proposed as potential materials for CCS. However, these materials can be very unstable in the presence of moisture. The IRMOF series and the more recently produced COF materials are particularly unstable (e.g., loss of porosity at room temperature in air).<sup>44</sup> Clearly materials of this type would be unsuitable for CCS application. If such materials are to be used more stable types are required, for example one class of MOF known as zeolitic imidazole frameworks (ZIFs), which are reported to have significantly improved stability over other classes of MOF.<sup>45</sup>

In addition to the stability of a material in the presence of water vapour, its effect on the CO<sub>2</sub> adsorption process will also be significant. Whilst in some cases evidence suggests that the presence of water may be beneficial to CO<sub>2</sub> uptake in terms of increasing the capture capacity of immobilized amines,<sup>26</sup> which are often tolerant to moisture.<sup>46</sup> Water can also act in competition with CO<sub>2</sub> for porous sites<sup>47</sup> or be absorbed by the materials themselves. This can lead to significant decrease in capacity as well as heating of a material as a result of the heat of absorption of water. Ideally materials developed for CCS applications will either react beneficially or be unreactive in the presence of water vapour.

Oxygen, commonly present at 3-4 vol % in coal derived flue gases, is known to lead to degradation of amine solvents when applied to CCS. Whilst this is potentially an important reaction, no specific studies of oxidative stability of adsorbent

materials have been published. Based on experience from solvent systems, the oxidation rate for monoethanolamine has been shown to be dependent on both the concentration of oxygen and amine as well as the CO<sub>2</sub> loading.<sup>48</sup> The rate of oxidation has also been proposed to be catalysed by iron present in the scrubber columns as a result of wall corrosion,<sup>49</sup> a reaction that will potentially be avoided in solid sorbent based systems.

Further trace components, for example, other acid gases such as SO<sub>x</sub> and NO<sub>x</sub> in the flue gas can also lead to significant challenges for materials. SO<sub>2</sub> is a particular concern for post-combustion capture from coal and has been noted to decrease the performance of a range of immobilised amine adsorbents, by reacting with the basic surface sites.<sup>38</sup> Whilst the mechanism of reaction of amines with SO<sub>2</sub> has been reported for solvent systems<sup>50</sup> little is published for this interaction with adsorbent materials. Degradation of amine solvents by SO<sub>2</sub> is minimised by reducing the concentration of the gas as far as possible using flue gas desulphurisation.<sup>39</sup> However, whilst the concentration of these components in the gas stream are low after treatment to levels required for amine capture (Table 2), they will still react competitively or and potentially irreversibly with sorbents containing basic functional groups.

### 70 Performance targets and operating conditions

The cyclic capacity of a solid sorbent is a critical performance parameter. However, it is important to further define the operating conditions at which these targets are to be met (Table 2) and the materials challenges these pose. Overall, these relate to materials as well as process challenges for the development of the capture technology.

Performance targets for the cyclic CO<sub>2</sub> capacity of adsorbent materials have been proposed from theoretical studies<sup>24, 51</sup> form the technology to achieve significant energy penalty reductions when compared to solvent based systems. These studies indicate that a target cyclic capacity would be something approaching or greater than 3 mmol g<sup>-1</sup>. The key to this definition is that it refers to the cyclic and not the equilibrium capacity of the material and can be defined as:

$$[CO_2]_{cyclic} = [CO_2]_{ads} - [CO_2]_{desorb}$$

The temperature and partial pressure of the adsorption and desorption phase of the capture process, which will ultimately determine the cyclic capacity, will be a function of the conditions of the gas at capture and also the regeneration technique applied. Examples of which include temperature, pressure or vacuum swing cycles. For a temperature swing process, capture will be at a low partial pressure and temperature (Table 1) whilst regeneration will be at a higher temperature (80 – 130 °C) and involve a higher partial pressure of CO<sub>2</sub>, close to atmospheric as the gas desorbs.

**Table 2.** Proposed operating conditions for capture plant based on a temperature swing adsorption process.

Performance Parameter	Target
Operating Temperature (°C): adsorption	40 – 60 °C
: desorption	85 – 140 °C
Cyclic capacity	>3 mmol g <sup>-1</sup>
Rate of adsorption	Order of seconds
Operating pressure	1015 mbar
Pressure drop of capture plant	Ideally < 2 psi
CO <sub>2</sub> product purity	>95 %
CO <sub>2</sub> capture (of total emissions)	>80 %

The temperature of the gas stream for CO<sub>2</sub> capture, around 40 °C – 75 °C after flue gas desulphurisation (FGD) and the low partial pressure of CO<sub>2</sub> (Table 1) has driven the development of adsorbent materials. Many adsorbents perform well at ambient temperature and with CO<sub>2</sub> at atmospheric pressure, for example, standard activated carbons and zeolites. However, as these materials operate via weak physisorption and Van der Waals interactions, adsorption capacities decline rapidly with increasing temperature and under reduced partial pressures. As a result such materials will not achieve the required capacity at typical flue gas temperatures.<sup>28, 31, 32</sup> In an attempt to increase cyclic capacity and achieve sufficiently high gas separation factors, chemical adsorption has been adopted using porous media enhanced with basic surface functionalities to increase adsorbent-adsorbate bonding. This has mainly been achieved either by impregnation of porous substrates, by surface modification or by nitrogen enrichment, to introduce basic functional groups (see introduction). Immobilised amine groups are most commonly used with chemical adsorption of CO<sub>2</sub> and react by the formation of a reversible carbamate ion<sup>52, 53</sup>. Supported amine polymers and surface immobilized amine groups have resulted in some of the more successful adsorbents for CO<sub>2</sub> capture.<sup>24, 26, 27, 54</sup> However, this can sometimes be at the expense of beneficial textural properties and thermal stability.

Another key factor to consider for cyclic capacity is that the dynamic / breakthrough capacity of the sorbent is also crucial. In application, regardless of the configuration of the capture plant used, whether it be fixed, moving or fluidised bed the contact time between adsorbent and adsorbate is likely to be in the order of seconds or less. Therefore, the working capacity in a dynamic system is going to be a function of the rate of adsorption as much as the equilibrium capacity. As a result, fast reaction kinetics are crucial when the large, rapidly flowing gas volumes of power plant are considered, as an example flow rates associated with an 830 MW unit producing a flue gas flow rate in the order of 140 Nm<sup>3</sup> s<sup>-1</sup>.

Whilst the cyclic capacity of the sorbent material is a crucial parameter, the actual process for regeneration at large scale and the impact of this process on materials performance, stability and lifetime has received significantly less focus. However, this cannot be ignored as the regeneration conditions, usually involving elevated temperatures, will impact significantly on these performance values.<sup>28, 55</sup> Many of the cyclic capacities that are reported also tend to be based on regeneration using nitrogen as a sweep gas, for example<sup>27</sup>. This system would not be used at large scale as this results in

a gas composed of dilute CO<sub>2</sub> in nitrogen, essentially the same as the flue gas. At scale, regeneration of solid sorbents can be achieved through temperature and pressure swing cycles, as well as using a sweeping gas to promote desorption. In post-combustion capture processes, where the flue gas is at close to atmospheric pressure, pressure swing cycles can only realistically be achieved through the use of a vacuum to provide the pressure differential. Previously it has been demonstrated that adsorbents can be regenerated using vacuum to facilitate pressure swing adsorption (PSA) with or without heating.<sup>56-58</sup> Temperature swing adsorption (TSA) is the most likely technique to be used for post-combustion capture using solid sorbents. TSA exploits the fact that CO<sub>2</sub> capacity decreases significantly with increasing temperature, for example TSA regeneration of amine based adsorbents has been achieved in nitrogen, CO<sub>2</sub> and also under vacuum conditions.<sup>28</sup> The temperature of these cycles will be determined by the flue gas conditions requirements of the plant as well as the chemistry, stability and performance of the sorbent. It has previously been reported that regeneration temperature when using CO<sub>2</sub> as a stripping gas can have a significant influence on the lifetime and stability of the amine based adsorbents. With temperatures above 130 °C resulting in a secondary reaction between the amine and CO<sub>2</sub> to form a potentially irreversible urea complex.<sup>28</sup> Possible strategies to avoid such reactions could be to use adsorbent materials with a lower CO<sub>2</sub> sorption enthalpy, therefore requiring lower regeneration temperatures to avoid secondary reactions. For example, the use of adsorbents composed of predominantly secondary amine groups can lead to the need for decreased regeneration temperatures.<sup>59, 60</sup> However, there will always be a trade off between adsorption kinetics and regeneration energy, and therefore a balance may need to be sought. Recently the presence of water vapour has also been demonstrated to eliminate these secondary reactions<sup>46</sup> reviving the potential of using CO<sub>2</sub> as a sweep gas for regeneration. Recent work has also explored the potential of using steam as a sweep gas to regenerating adsorbent materials for carbon capture.<sup>61</sup>

The regeneration energy for adsorbents can be calculated by Equation 1<sup>38</sup> which clearly demonstrates the importance of the materials physical and chemical properties as well as performance. Critically it defines that the temperature difference between capture and regeneration ( $\Delta T$ ), the specific heat capacity of the adsorbent ( $C_S$ ), adsorption capacity ( $L$ ) and the heat of adsorption ( $Q_r$ ) all influence the regeneration energy. This clearly demonstrates how developing materials with increased CO<sub>2</sub> loading ( $L$ ), low specific heat capacity ( $C_S$ ); and lower heat of adsorption ( $Q_r$ ) can lead to a more efficient capture technology.

**Equation 1.** Regeneration energy,  $Q$  (kJ) as a function of mass (kg)  $m_c$  for cyclic adsorbents.<sup>38</sup> Where:  $m_e$  = mass of equipment (kg);  $T_1$  and  $T_2$  refer to the temperature of capture and regeneration respectively (K);  $C_{p,c}$  = constant pressure specific heat for CO<sub>2</sub> (kJ/kg K),  $B$  is a dimensionless conversion factor.

$$\frac{Q}{m_c} = \frac{m_e}{m_c} C_e \Delta T + \frac{B}{L} C_S \Delta T + C_{p,c} T_2 - C_S T_1 + \frac{Q_r}{m_c}$$

Predictably performance is going to be a trade off between CO<sub>2</sub> loading ( $L$ ) and the heat of adsorption ( $Q_r$ ). Chemical adsorbents, for example immobilised amines, with higher capacity at 40 – 50 °C at low partial pressures of CO<sub>2</sub>, will generally have a higher  $Q_r$  than physical adsorbents. The work of Sjostrom and Krutka (2010)<sup>38</sup> clearly demonstrates how low working capacities (~ 1 wt.%), seen for standard activated carbons and zeolites, results in high theoretical regeneration energies due to the large mass of sorbent required in the system.

### Physical / chemical properties and cost

The previous section has described the performance of materials in terms of capture capacity. However, other challenges exist for these materials in terms of their physical properties. The specific heat capacity of the material as defined in Equation 1 is an important property and will impact on the rate at which the adsorbent can be cooled and heated, and therefore be cycled. This will also influence the energy requirements of the process. It should also be noted that sorbent capacity is predominantly reported on a mass basis, with volumetric capacities are rarely if ever reported. The density of activated carbons has previously been demonstrated to vary greatly and influence significantly volumetric CO<sub>2</sub> capacity, which will ultimately influence bed or plant size.<sup>62</sup> The physical strength of any materials is going to be an important factor, especially if circulating of fluidised bed contactors are to be used. Finally, the cost and potential for large scale manufacture of any materials must also be carefully considered. Given the large scale at which the technology will need to be deployed for use on fossil fuel fired powerplant it is very important that the material costs is minimised. Cost is also linked to the lifetime of the material and the number of cycles it can operate over. This once again highlights the importance of the development of effective processes for the cycling and regeneration of solid sorbents to maximise their lifetime and reduce replacement rates to a minimum.

### Future Developments.

There is a significant global effort on the development and testing of solid sorbent materials applying a wide class of materials<sup>19</sup>, which have performed to a varying degree in flue gas conditions.<sup>38</sup> Future developments will continue on this range of materials. For example, immobilised amines on porous media have proven to be some of the most successful materials for carbon capture and will continue to be developed. Research is advanced on the development and testing of these materials in flue gas environments and improving their stability, especially relating to the chemistry of the amine attachment.

The following summarises the potential and development of some breakthrough materials that show potential for breakthroughs in this application:

Synthetic microporous polymers possess some of the highest reported surface areas<sup>63</sup> and some preparative routes might in principle be applicable to CCS applications,<sup>64</sup> although bond-forming chemistries such as Pd-catalyzed

cross-coupling<sup>65, 66</sup> are likely to be too expensive for scale-up. A key benefit of porous organic chemistries is the very diverse synthetic organic chemistry which is available, both in terms of the wide range of monomers that can be exploited either by direct incorporation<sup>67-69</sup> or by the possibility of post-synthetic modification of networks to include functional groups reactive to CO<sub>2</sub>. Incorporation of functional monomers has been shown to be useful in tuning the isosteric heat of adsorption of CO<sub>2</sub> by these materials.<sup>70</sup> A further advantage of organic polymeric networks over other highly porous synthetic materials such as hybrid inorganic-organic materials is their high moisture stability together with high thermal stability.<sup>63</sup> However, despite recent reports of uptakes of around 3 mmol g<sup>-1</sup> at ambient temperatures,<sup>71</sup> microporous organic polymers have yet to achieve high enough CO<sub>2</sub> loadings under the required conditions to be commercialised.

Hydrotalcites, are clay-like materials consisting of MgAl hydroxides in Brucite-type layered structures, which have already been demonstrated to show potential as adsorbents for CO<sub>2</sub> at high temperatures<sup>72</sup>. Chemisorption of CO<sub>2</sub> occurs upon hydrotalcites, which leads to reasonable rate of adsorption and ability to operate at elevated temperatures, but at present the amount of CO<sub>2</sub> captured is too low for economical operation. They also offer the advantage of being relatively cheap to produce. The capacity of hydrotalcites to adsorb CO<sub>2</sub> has been increased by promoting the structure with potassium, with 0.76 mol/kg CO<sub>2</sub> being adsorbed on a wet basis at 0.4 bar CO<sub>2</sub> pressure at 676 K over an Mg-K hydrotalcite,<sup>73</sup> but further increases in capacity are necessary. This work proposes surface modification of hydrotalcites with aminosilane molecules to increase the basicity of the surface and to capture greater quantities of CO<sub>2</sub>. The techniques used are based on methods proposed by Park et al (2005)<sup>74</sup>, in which layered double hydroxide surface modified with (3-aminopropyl)-triethoxysilane was prepared with the objective of using a surfactant dodecylsulfate to widen the gallery height between the layered structure before the amine was attached. This is particularly important to preserve space for the CO<sub>2</sub> to enter the structure during subsequent adsorption. This concept was further investigated by Wypych et al (2005)<sup>75</sup>, who exfoliated Mg-Al layered double hydroxides in toluene to peel apart the layered structure, prior to grafting with amines. An alternative strategy is to graft the amines on to the hydrotalcite by rehydration after calcination<sup>76</sup>. However the reported use of prepared amine-modified hydrotalcite materials for CO<sub>2</sub> capture is lacking and thus optimization of preparation procedures and measurement of adsorption capacities are being investigated in the current study. The development of techniques for surface modification of hydrotalcites could bring about a step change in the amount of CO<sub>2</sub> captured.

Activated also carbons show potential for application in CCS. Although they have previously been reported to have high regeneration energy compared to supported amines.<sup>38</sup> Research continues into the modification of the surface chemistry of carbons to increase their CO<sub>2</sub> capacity at low CO<sub>2</sub> partial pressures, mainly by surface modification. This can be either through the increase of basic functionality<sup>31, 33</sup> or

by enhancing surface area and gas activation and selectivity on hierarchically porous structures of carbon and oxides.

## Conclusions

The development of solid sorbents for CO<sub>2</sub> capture is an area of significant academic and industrial interest. The composition of the flue gases in post-combustion capture and the requirements for material performance to minimise the energy penalty of the capture process present a significant challenge for materials development. However, given the potential benefits of CO<sub>2</sub> capture using solid sorbents if suitable materials can be developed it is a research challenge that has attracted a large research focus. As described in this application note, materials and process are intrinsically linked in post-combustion capture and materials development without reference to the application is unlikely to yield suitable materials. To date, a wide range of functional materials have been and will continue to be developed with potential to meet the performance requirements. Whilst at present the required cyclic capture capacities can be achieved, one of the main challenges still remains to develop materials that can operate reliably and over a large number of cycles in a flue gas environment, a challenge which will certainly be the focus of future materials research.

## Acknowledgements

The authors would like to thank E.ON-EPSC strategic call on CCS for funding the Step Change Adsorbents and Processes for CO<sub>2</sub> Capture research programme - EP/G061785/1.

## Notes and references

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<sup>f</sup> Based on a medium to high sulphur coal.

<sup>g</sup> The moisture content of post FGD flue gas will depend on whether a wet or dry technology is used. Wet FGDs (such as the common limestone/gypsum technology) typically produce a flue gas at outlet with between 10 – 14 vol% H<sub>2</sub>O.

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