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ARTICLE TYPE

'Dry Bases': Carbon Dioxide Capture using Alkaline Dry Water

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An alkaline form of 'dry water'—a 'dry base'—is prepared by the high-speed mixing of aqueous solutions of metal carbonates or organic amines with hydrophobic silica nanoparticles. Despite being mostly water, the dry base looks and flows like a powder, and adsorbs CO₂ rapidly without any mixing because of its high surface-to-volume ratio. Unlike normal aqueous base solutions, dry bases can be non-corrosive because they do not readily wet surfaces.

Rising levels of CO₂ in the atmosphere are a major environmental concern. The combustion of fossil fuels accounts for a large percentage of all anthropogenic CO₂ emissions, and carbon capture from such sources has been widely debated. There are a number of potential materials for CO₂ capture.¹⁻⁵ Perhaps most well developed are liquid amines⁶ such as monoethanolamine (MEA) and diethanolamine (DEA). However, liquid amines have some drawbacks, such as the energy cost for regeneration, solvent boil off, and corrosion to the plant that is caused by the amine.¹⁻⁴ Typically, 10–30 wt. % aqueous solutions of the amine are used because more concentrated solutions lead to excessive corrosion.⁴ Another way to lower the corrosivity and the regeneration energy is to support or chemically graft amines onto porous solids such as silicas.^{7, 8} However, such strategies can also reduce the amount of CO₂ that is absorbed.¹

'Dry water' is a free-flowing powder composed of water micro-droplets. It is prepared by the high-speed mixing of water with hydrophobic silica nanoparticles, and it contains only 10–20 wt. % silica.⁹ As such, dry water can be thought of as a 'powdered form' of water, or a stabilized aerosol: it looks and flows like a powder (Fig. 1), and it has much higher surface-to-volume ratio than bulk water.

We previously reported the use of dry water to improve the kinetics of methane,^{10, 11} carbon dioxide, and krypton clathrate formation in comparison with bulk water.¹² The finely dispersed water droplets in dry water increase the gas-liquid interface significantly, leading to greatly enhanced kinetics of clathration. We also used the large gas-liquid interface in dry water to carry out hydrogenation reactions without any physical stirring or other mixing.¹³ Again, the reaction kinetics were increased significantly compared to a bulk water control. Another application for dry water that exploits its large gas-liquid interface is sensing.¹⁴

In this report, we describe the use of alkaline dry water, or 'dry base' for CO₂ capture. Like aqueous solutions of liquid amines, aqueous solutions of group 1 and 2 metal carbonates are well known to capture CO₂, in this case as bicarbonates.¹⁵⁻¹⁹ We hypothesised that alkaline aqueous solutions might be rendered into 'dry bases' by high-speed mixing with hydrophobic silica nanoparticles. Hence, there would be a much greater surface area available for CO₂ capture, even in the absence of any mixing, such that the kinetics of gas absorption are increased. We also speculated that there could be further advantages in having these corrosive liquids coated with hydrophobic silica

The formation of a series of dry bases was achieved by direct blending of neat, liquid DEA (**DryDEA**), an aqueous solution of potassium carbonate (**DryK₂CO₃**), or an aqueous solution of an amine polymer, polyethyleneimine (**DryPEI**) with hydrophobic silica nanoparticles at high speed (37,000 rpm) using a simple household blender for mixing, as previously described for neutral dry water.¹⁰ Typically, a 50 % solution of base (either K₂CO₃ or PEI, total mass 90 g) was mixed with hydrophobic silica nanoparticles (10 g). In the case of neat DEA, 80 g of DEA was mixed with 20 g hydrophobic silica nanoparticles. For all of these systems, a free-flowing powder was formed (see example data in Figure 1 for **DryK₂CO₃**; other systems were visually similar).

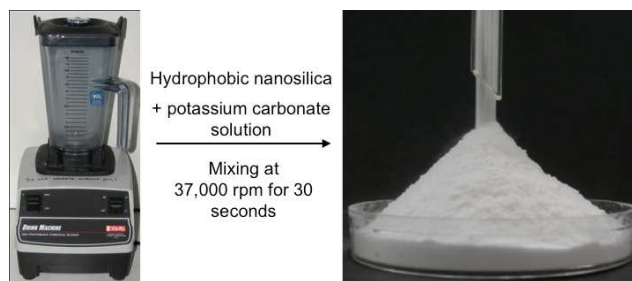


Figure 1 Formation of a dry base, in this case **DryK₂CO₃**, as a free-flowing powder using a standard kitchen blender

The dry base droplets were imaged using an optical microscope. The majority of the droplets were smaller than 20 μm in diameter, similar to those observed for other examples of neutral dry water (see Fig. S2, Supporting Information).⁹⁻¹¹

To measure the CO₂ capture capacity of the dry bases, 5 g of dry base in a 60 mL plastic bottle was exposed to CO₂

using a balloon containing the pure gas. The internal pressure of the balloon was estimated to be from 2–3 bar. The balloon was topped up throughout the experiment to maintain this pressure. The amount of CO₂ captured by the dry base was measured gravimetrically using a balance, and the experiment repeated five times to obtain an average uptake as a function of time. Figure 2 shows the CO₂ uptake of neat **DryDEA** over a period of 1 hour. After 1 hour, the uptake of CO₂ by DryDEA was 17.9 wt. %. This uptake is higher than the theoretical value based on the mass of DEA used. This may be due to the inherent error with weighing, although the value quoted is an average of 5 measurements as indicated by the error bars. Instead, we attribute this to some extra adsorption by the particulate silica used to make the dry water. The silica used has a BET surface area of 120 m²/g and it is likely that this contributes to the uptake. This is around 60 % more CO₂ than absorbed by a stirred sample of neat, liquid DEA, and three times the absorption measured for an unstirred control. (For both controls, an equal mass of DEA was used as contained in the **DryDEA** sample.) The kinetics of absorption were approximated by calculating the time it takes to reach 90 % of the final uptake (t_{90}). The t_{90} of DryDEA is 12 min. This is significantly faster than for the stirred DEA sample (t_{90} = 17 min) or the unstirred material (t_{90} = 19 min). We believe that the lower absolute absorption of the bulk DEA samples and apparent rise to a lower equilibrium level than dry DEA arises from mass transport effects. Attainment of the theoretical maximum uptake requires diffusion of CO₂ through the viscous solution. Over the reported timescale, we attribute the initially fast uptake to reaction at the interface, with slow mass transport then becoming dominant. This also explains why the stirred mixture takes up more CO₂: the absolute uptake is lower than for dryDEA, because again the stirred DEA is very viscous, so stirring is inefficient. We also highlight the reported 60 minute duration: it is likely that uptake might be greater over a significantly longer measurement timescale. For some cases with DEA, precipitation occurred on exposure to CO₂ in the controls. In the dry water samples, this is difficult to probe, but may also be occurring.

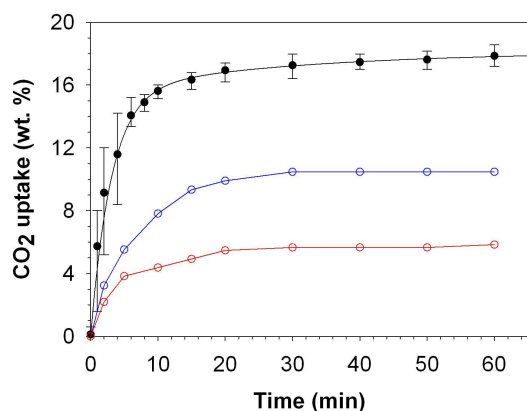


Figure 2 Average CO₂ uptake of **DryDEA** (black) with fitted uptake curve compared to the stirred (blue) and non-stirred (red) control experiments for bulk DEA liquid.

We analysed the sample post CO₂-uptake using solid-state NMR under magic angle spinning (MAS). The ¹H MAS NMR spectra (Fig. S6.1) shows very narrow lines, and suggests that most of the sample is not very solid, but more like soft matter or a liquid. This is in agreement with our hypothesis that the **DryDEA** consists of droplets of liquid DEA surrounded by a silica shell. H₂O and Si-CH₃ signals are detected at 3.7–3.0 ppm and -0.1 ppm, respectively, while the four resonances observed for the DEA (between 0–2 ppm) imply that there are two distinct DEA species present. The ¹³C MAS NMR spectrum obtained under ¹³C direct excitation (Figure 3a) shows a peak at high field (approx -1 ppm), assigned to the methyl of a Si-CH₃ group on the hydrophobised silica nano particles (note that H18 contains Si-CH₃, not Si-OCH₃ groups). The peaks at 163 and 161–150 ppm are assigned to the carbamate and carbonates, respectively.²⁰ Three peaks in the 50–65 ppm region are assigned to the CH₂ groups on the DEA, the larger line width of the 50 ppm peak suggesting that there are two peaks overlapping. Hence, in agreement with the ¹H MAS NMR data, we assign these peaks to two co-existing DEA species, the carbamate and the protonated amine. These data are in agreement with other reports for CO₂ uptake in DEA in solution.^{20, 21} ¹³C Cross-polarisation MAS NMR spectroscopy,²² which is only sensitive to solid state material, shows essentially only the presence of the Si-CH₃ (Figure 3b), again demonstrating that our model of the **DryDEA** is correct and almost all of the DEA behaves as a liquid. The predominant peak between 165 and 150 ppm is assigned to the carbamate. Hence, we suggest that the uptake of CO₂ is via the 2:1 carbamate mechanism.²³ The presence of small amounts of carbonates in the 161–150 ppm region may be due to some promotion by silanols or, more likely due to the presence of water vapour during the experiment, since we did not dry the system before use.

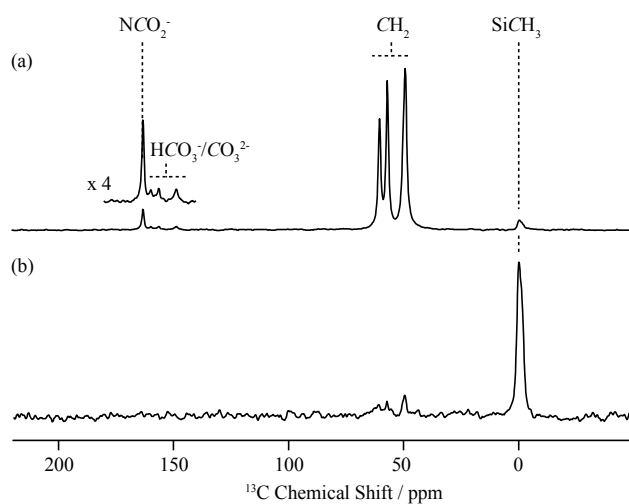


Figure 3 Solid-state ¹³C NMR spectra of **DryDEA** post CO₂ adsorption recorded under MAS rate of 10 kHz. (a) ¹³C direct excitation spectrum. (b) ¹³C cross polarisation spectrum obtained with a 2 ms contact time. The insert at low field shows a magnified view of the spectrum in the 180–140 ppm region.

Two concentrations of potassium carbonate solutions were mixed with hydrophobic silica to form **DryK₂CO₃** (50 % and 33.3 %, respectively). It is not possible to prepare K₂CO₃ solutions more concentrated than 50 %. A solution of 50 % K₂CO₃ with 10 % silica nanoparticles resulted in **DryK₂CO₃(45)**, while the 33.3 % solution gave **DryK₂CO₃(30)**. Figure 4 shows the CO₂ uptakes of these two dry bases compared with stirred and unstirred control solutions of K₂CO₃. The **DryK₂CO₃** samples show greatly improved CO₂ uptakes with respect to the stirred and unstirred control experiments. As expected, the more dilute dry base, **DryK₂CO₃(30)**, showed an average CO₂ uptake (10.1 wt. %) that was lower than the more concentrated solution (14.5 wt. %). The reduction in capacity of **DryK₂CO₃(30)** sample is proportional to the reduced amount of potassium carbonate in the sample. In comparison to **DryDEA**, the maximum uptake of the **DryK₂CO₃** samples is lower but the kinetics of CO₂ absorption are much faster. Both **DryK₂CO₃** samples have a t_{90} value of just 5 min.

Aqueous solutions were also prepared from an amine containing polymer, polyethyleneimine (PEI). A sample with a high molecular weight of 750,000 g/mol was used, since this has an essentially negligible vapour pressure and is therefore less likely to be susceptible toward boil-off during recycling. At this molecular weight, however, bulk solutions of the polymer become viscous and hard to stir using simple stirring techniques. Nonetheless, **DryPEI** could be prepared readily from a 50 % solution of polyethyleneimine (90 g) and hydrophobic silica nanoparticles (10 g) using a kitchen blender, as before. The maximum uptake of CO₂ by the resulting dry base was 20.4 wt. % (Figure 5) with a t_{90} value of 12 min. **DryPEI**, therefore, has similar kinetics to **DryDEA**, but the absolute CO₂ uptake is somewhat higher than either the **DryDEA** material or the two **DryK₂CO₃** samples. The non-stirred PEI solution control shows just 5 % of the uptake of the **DryPEI** sample over the experimental period, demonstrating greatly enhanced mass transport in the particulate dry base material. We propose that this dramatic difference stems from the viscosity of the PEI solutions, which reduces mass transport in the bulk solution. For the same reason, a stirred control experiment was not possible due to the high viscosity of the bulk PEI solution. Hence, our 'dry base' approach allows the use of concentrated, highly viscous polymer solutions that are difficult to work with in their bulk forms.

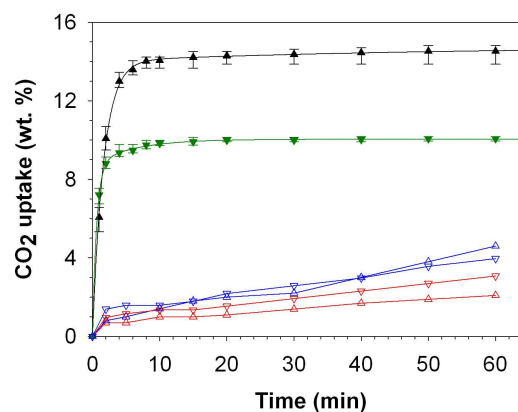


Figure 4 Average CO₂ uptake for **DryK₂CO₃(45)** (black) and **DryK₂CO₃(30)** (green) with fitted uptake curves compared to the stirred (blue) and non-stirred (red) control experiments. ▲ **DryK₂CO₃(45)** (filled) and 50 wt.% K₂CO₃ solution controls (open), ▼ **DryK₂CO₃(30)** (filled) and 33.3 wt.% K₂CO₃ solution controls (open).

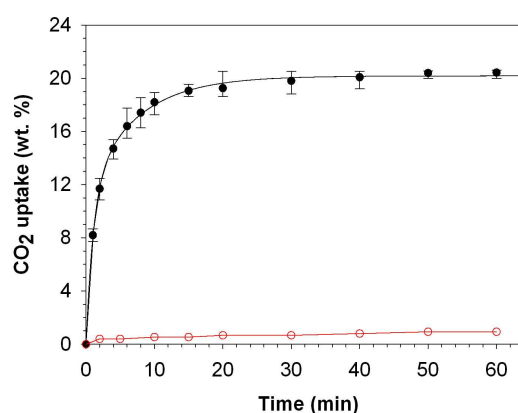


Figure 5 Average CO₂ uptake of **DryPEI** with fitted uptake curve and non-stirred bulk PEI solution control (red). In both cases, a 50 % aqueous solution of polyethyleneimine was used.

DryK₂CO₃ and **DryPEI** have an advantage over the **DryDEA** sample in that the base itself is not volatile (although of course they contain 45-60 % water as made by weight), and is therefore not subject to boil-off, unlike the organic amine. To be commercially relevant, materials will need to be recycled, both to recover the captured CO₂ and to regenerate the material for successive absorption cycles. The temperatures required for regeneration of **DryDEA** and **DryPEI** were measured by thermogravimetric (TG) analysis by absorbing and desorbing CO₂ at a number of different temperatures (Figure 6 and Figure 7; see also Fig. S4 and S5, in the Supporting Information). Due to the volatility of DEA, there is a trade-off between the total removal of all the absorbed CO₂ and the loss of DEA due to boil off (b.p. of DEA = 55 °C). At a temperature of around 70 °C, it was found that the CO₂ could be desorbed without losing significant amounts of DEA. For **DryPEI**, a higher regeneration temperature of 160 °C was required to desorb the CO₂. This temperature resulted in almost all of the water being removed from the sample (a loss of 45 %). No further weight loss was observed after the first heating cycle. To simulate multiple

regeneration cycles, the samples were first exposed to CO₂ (1 bar, 100 mL/min) at ambient temperature (21 °C) for 90 minutes to obtain an initial sorbent capacity before being heated to the recycling temperature to calculate performance; the dry base was allowed to cool to the adsorption temperature of 25 °C to adsorb CO₂. A total of nine regeneration cycles were carried out.

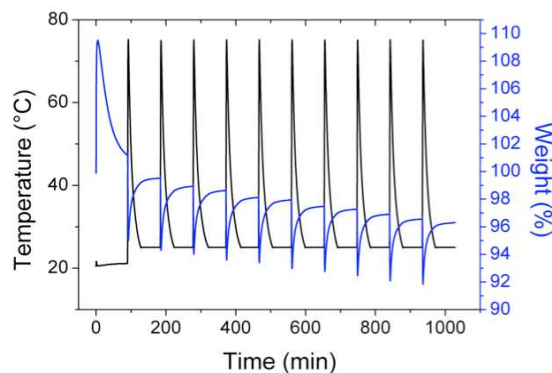


Figure 6 Cycling of absorption of CO₂ at 25 °C by **DryDEA** and regeneration at 70 °C

The recycling of **DryDEA** is shown in Figure 6. Under the constant flow of CO₂, **DryDEA** adsorbs approximately 9 wt % CO₂ under ambient condition. Around 5 % of the DEA is lost upon heating of the sample to 70 °C. Then, approximately 5 wt % CO₂ is adsorbed by the sample under a flow of pure CO₂ after regeneration. This adsorption capacity is significantly lower in comparison with the balloon test conducted under a slight over-pressure of CO₂. After each regeneration, a small amount of DEA was lost, as might be expected for a volatile liquid amine, and this is indicated by the decrease in capacity with successive cycles. After 9 regeneration cycles, a total weight loss of 8 % was observed. This would clearly be an issue in a real-life situation, where the loss of the volatile DEA would likely lead to corrosion issues.

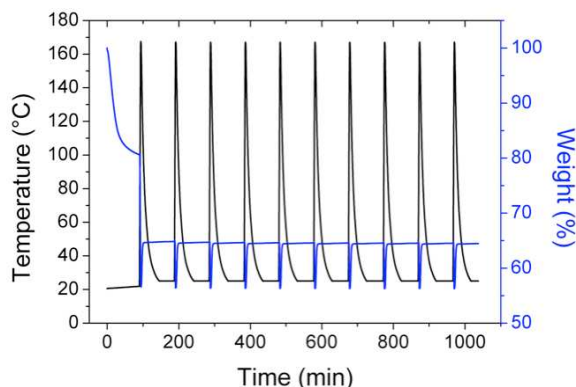


Figure 7 Cycling of absorption of CO₂ at 15 °C by **DryPEI** and regeneration at 160 °C

Despite the initial loss of most of the water under ambient conditions and the constant flow of CO₂, Figure 7 shows that **DryPEI** is much more stable than **DryDEA** in subsequent cycles. The regeneration temperature in this case was 160 °C,

higher than that required for **DryDEA**. Subsequent regenerations show no further loss of sample mass, and a constant CO₂ uptake of around 14 wt % (based on the sample mass after the first recycle) is observed. This is much closer to that observed in static absorption experiments at slightly higher CO₂ pressure (2–3 bar) with no gas flow. These results show, however, that there is a trade-off between absorption capacity and regeneration temperatures: 160 °C is undesirably high, but this might conceivably be modified, for example, by using a different amine-containing polymer.

As typical CO₂ partial pressures for post-combustion capture are between 0.12–0.15 bar at temperatures between 40–80 °C further experiments were carried out on **DryDEA** and **DryPEI** using 15 % CO₂ up to a temperature of 150 °C (Figure 8). Under these conditions, **DryDEA** showed a maximum uptake of 12.8 wt. % at ambient temperature which dropped with increasing temperature. Again evaporation of DEA from the sample was seen at higher temperatures. For **DryPEI**, the maximum uptake of 12.3 wt. % was observed at a temperature of around 92 °C, slightly higher than the target absorption temperature. Much lower uptakes were observed at temperatures of above 120 °C, indicating that regeneration of the sample may be possible over a narrow temperature range. In comparison to **DryDEA**, much less evaporation was observed for **DryPEI**.

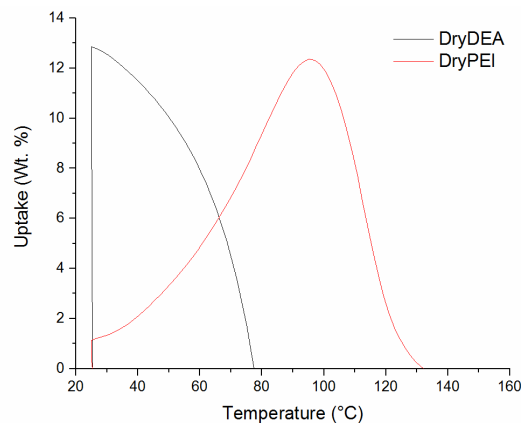


Figure 8 Uptake of 15 % CO₂ in N₂ between ambient and 150 °C for (black) **DryDEA** and (red) **DryPEI**

These liquid bases are surrounded by a shell of hydrophobic silica nanoparticles that renders the whole droplet surface hydrophobic. We therefore expected that there would be little direct contact between the alkaline solution and any external surfaces, such as the containment vessel for the dry base. We speculated that this might in turn reduce the corrosivity of the encapsulated base, and be a potential answer to the issue of high corrosivity of alkaline solutions in carbon capture plants.

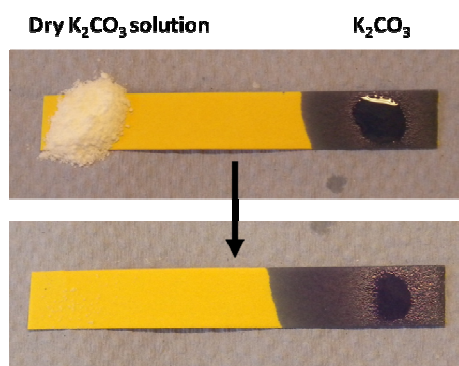


Figure 9 Dry bases are rendered hydrophobic by their hydrophobic silica coating, and they wet surfaces much less readily than the corresponding bulk alkaline solutions. This is illustrated here using indicator paper: unlike the bulk alkaline solution, the dry base does not cause a pH change. For the same reason, dry bases do not dissolve metals, such as aluminium foil (Fig. S3.2), that are placed in contact with them. These dry bases are therefore rendered much less corrosive than their bulk solution counterparts, at least for non-volatile bases.

This was demonstrated by simple contact experiments. For example, **DryK₂CO₃** is hydrophobic and does not ‘wet’ surfaces such as pH indicator paper, unlike the corresponding K₂CO₃ solution (Figure 9). Likewise, aluminium foil dissolves readily over the course of 4 h when immersed in bulk K₂CO₃ solution, but is unaffected by immersion in **DryK₂CO₃** of the same pH, even after 18 h. While aluminium is clearly not used as a containment material in powerplants, these results indicate that the corrosivity of the dry bases might lead to fewer corrosion issues than the corresponding alkaline solutions themselves. Corrosion is often cited as a disadvantage of liquid amine technologies.²⁴ Hence, a dry base, if implemented on a large scale, might in principle allow the use of more concentrated base solutions while also extending the lifetime of the carbon capture plant. More rigorous long-term testing on relevant materials, such as stainless steel, is required to substantiate this.

Conclusions

‘Dry bases’ are interesting candidates for CO₂ capture or, in principle, for other applications where it is desirable to place gases in intimate contact with alkaline solutions without any active physical mixing. In comparison with bulk alkaline solutions, dry bases demonstrate greatly enhanced CO₂ uptakes, faster kinetics, and, in some cases, can be regenerated and recycled multiple times. Preliminary tests also show that involatile dry bases are much less corrosive than their bulk liquid counterparts. The preparation of dry bases is simple (Fig. 1), requiring no specialized equipment. However, a number of scale-up challenges exist: dry water and dry bases can have a low volumetric density (0.15 – 0.96 g/cm³, depending on the precise preparation conditions and water contents). As a result, the volumetric CO₂ capacity, as opposed to the gravimetric capacity, might be less competitive, and volumetric capacities may be of greater importance for large scale applications where the physical

footprint of the plant is paramount. Also, these low-density, low-viscosity, and highly compressible powders might not translate directly into equipment that is designed to be used with standard non-compressible liquids, or with solid adsorbents. Nevertheless, dry bases combine rapid mass transport in the absence of mixing with low corrosivity in a unique way, conferring in some respects the properties of solid particulate absorbents on alkaline liquid solutions.

Acknowledgements

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Notes and references

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- [†] Electronic Supplementary Information (ESI) available: including experimental details, microscope images, particle size analysis, corrosivity tests and ¹H MAS NMR. See DOI: 10.1039/b000000x/
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