concrete 4change

Carrier optimisation for the mineralisation of CO2 in concrete

CCUS Innovation 2.0

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Key Achievements

Significant developments towards the production of high-capacity inorganic CO2 carriers for use in cementitious materials are detailed in this report. Following the promising results described in the WP1 report on the synthesis of nitrogen enhanced silica-based materials with CO2 adsorption capacities exceeding 8 wt% (>95 % by chemisorption), careful experimental design and optimisation strategy has yielded carriers with improved CO2 sorption properties: higher CO2 capacities and controllable CO2 desorption in-line with the 48h-480h target.

This was achieved through carrier optimisation: where the formulations of the 3 prior carrier technologies (polymer 1-AMINE 3, amine impregnated, and amine grafted silicas) were developed to achieve the specific goals of WP2 and drive the carrier development forward to a point where CO2 delivery to simulated environments can reliably begin.

Scaled-up quantities (minimum 50 g) of carrier (amine impregnated silicas), exhibiting still very ideal sorption properties (in excess of 20 wt% capacity, with very low desorption rates).

Amine grafted materials and Polymer 1-AMINE 3 based carriers were subjected to optimisation through amine-identity screen and grafting loading investigations; both yielding greatly optimised (increases of +5 wt% and +10 wt%) capacities and desorption rates. In-depth chemisorption analysis to investigate the nature of the surface groups formed on CO2 sorption were conducted, evidencing a clear link between CO2 desorption rates and the formation of specific carbamate environments, whose formation is dependent on the density of surface amine content.

Development of doping methodologies with nitrogen and metal-atom doping were investigated through impregnation strategies, achieving highly regulated and controlled release rates, slowed considerably from the parent material.

Encapsulation technologies have been scoped and evaluated, with a large basis of literature to work upon in order to further develop carrier release rates in response to simulated conditions in future work packages. An ideal polymer system and encapsulation strategy have been extensively developed, producing multiple iterations of polymer encapsulated material which fulfils the requirements to achieve consistent release times in air and cementitious environments pending further development in controlling polymer layer thickness.

Work Package 2.1 – Process optimisations: chemical formulation of the carriers' precursors

Amine grafted silicas

Prior investigation into nitrogen enhanced silicas towards to the production of CO2 carriers for C4C was focused on the grafting of amine 3amine 3 to Silica 1. However, there are multiple other amine moieties that can be grafted to Silica 1, that potentially offer increased CO2 adsorption capacities of this class of carrier material. A variety of alternate amines to amine 3 were grafted to the surface of Silica 1, towards the synthesis of CO2 carriers with advantageous CO2 sorption properties for the requirements of C4C.

Further synthetic optimisation on the grafting of AMINE 3.1 to mesoporous silica was also of interest, particularly on regulating surface amine loadings. It was postulated that through varying the levels of water added to the synthesis of AMINE 3.1 carrier materials, the quantity grafted amine could be modulated, and potentially lead towards carriers with higher CO2 adsorption capacities.

Amine impregnated silicas

Given the very high CO2 loadings of amine impregnated silicas, and their relatively simple production, process optimisation of these materials was not focused on in great detail in this work package, in order to allow for greater development of amine grafted silicas and AMINE 3 impregnated polymers in order to improve CO2 capacities. At this time, amine impregnated silicas exhibit CO2 capacities in excess of 18 wt.%, and represent the best in class materials from this standpoint. 'Optimisation' of amine impregnated silicas was, therefore, focused on scale-up to reach in excess of the 50 g target outlined by the deliverables, verifying CO2 sorption capability and investigating replicability in the scaled-up reaction.

AMINE 3 grafted polymers

AMINE 3 grafted polymers based on Polymer 1, a carrier precursor developed in WP1, demonstrated a maximum CO2 capacity of ~4 wt% at ambient pressure, and 11.67 wt% at 10-bar CO2. Only a few initial conditions were evaluated in WP1- demonstrating the ability to produce these materials and their initial characteristics as candidate materials, and only 1 amine was employed in previous studies. Here, to optimise and further develop these materials, multiple AMINE 2 loadings and amine identities will be evaluated with the specific aim to increase the degree of chemisorption of CO2 and increase capacity.

Identification of precursors for extended amine grafting screen

Amine 3.5 Amine 3.5

Amine 3.5Amine 3.5 presented an optimal moity to graft to the surface of mesoporous silica compared to amine 3 (AMINE 3.1), owing to the presence of an extra, secondary amine group on Amine 3.5. As the chemisorption of CO2 by amines relies on the presence of two distinct primary or secondary amine groups to form the pair, Amine 3.5 can facilitate the intramolecular chemisorption of CO2. The capacity for intermolecular chemisorption is also increased by the greater quantity of amine functional groups on the grafted material.

The increased capacity of grafted Amine 3.5 to chemisorb CO2 through intramolecular and intermolecular bonding rendered Amine 3.5 an ideal substrate to graft to the surface of silica for use as a carrier by C4C, as the theoretical CO2 capacity of Amine 3.5@silica is double that of analogous AMINE 3.1@silica.

Amine 3.7

amine 3.7(like AMINE 3.1, but with a quaternary carbon centre near the amine functional group.

Amine 3.7

The sterically bulky quaternary carbon group is hydrophobic and thus poses as a useful functional group to restrict solvent access and reduce CO2 desorption rates in a high pH environment like cement, hence Amine 3.7@silica synthesis was targeted towards slowing CO2 desorption rates from amine grafted silica carriers.

amine 3.9Amine 3.9

While the grafting of amine 3.9does not provide the silica support with the desired functionality for the chemisorption of CO2 through the formation of ammonium carbamate pairs, it provides a grafted surface that is active for further modification. Amine 3.9@silica can be reacted with amine other amines such as AMINE 2 and AMINE 1, in reactions that produce grafted amines on silica.

AMINE 2

Amine 2 is a amine than can react with Amine 3.9@silica to form an amine grafted material bound to the solid support per surface grafted molecular unit.

Like with the grafting of Amine 3.5 to silica, the grafting of AMINE 2 to silica was performed to increase carrier CO2 adsorption capacity. With five amine groups per surface grafted molecule, each surface-functionalised AMINE 2 molecule has a theoretical CO2 adsorption capacity of 2.5 CO2 molecules taking place via inter- or intramolecular chemisorption. Improved CO2 adsorption capacity through this mechanism is desired for a carrier to be used by C4C, while the increased density of amine groups at the silica surface may aid in slowing CO2 desorption, another desired characteristic for a C4C carrier.

AMINE 1

Like AMINE 2, AMINE 1 is an amine that can be reacted with Amine 3.9@silica to graft a high density of amine functional groups to the support.

AMINE 1 is a much larger amine than AMINE 2, and as such the increased quantity of amine groups per grafted AMINE 1 molecule is advantageous considering increasing the CO2 adsorption capacity of amine@silica materials by chemisorption. The extent of branching and the steric bulk of AMINE 1 is also advantageous when considering slowing desorption of CO2 from loaded carrier material, hence investigation into the synthesis of AMINE 1@silica was also conducted by C4C.

Grafted amine loading variation

Amine-grafted silica loading screen with amine 3 (AMINE 3.1)

Further investigation into the synthesis of AMINE 3.1@Si carriers was also conducted, with particular interest in controlling the quantities of grafted amine on the silica-supported material. An ideal route towards controlling surface-grafted amine loading was identified, where the quantity of water added to the grafting reaction would be screened to optimise surface loadings.

Hydrolysation of AMINE 3.1 to the corresponding triol is required for surface-grafting, hence increasing the quantity of water in

Polymer 1-AMINE 3 amine impregnated CO2 sorbents

Optimisation of Polymer 1-AMINE 3 amine impregnated CO2 sorbents was conducted to better understand the relationship between impregnation quantity, and the choice of impregnated amine with CO2 capacity optimisation. The ability to easily control the amine-loading through modulating the degree of impregnated amine allows us to optimise the ratio between the CO2 capturing amine units of the respective adsorbed amine to the stabilising AMINE 3 , balancing the electrostatic charge formed upon the formation of carbamate species.

Amine impregnation quantity study

WP1 demonstrated the effect of changing AMINE 2 impregnation quantity on CO2 capacity: however, this was limited based on the molar ratios of the AMINE 2 amine and AMINE 3 on the polymer surface being similar. Therefore, a wider range of AMINE 2 impregnation quantities were investigated.

Amine modification study

In addition, the impregnation of only two amines (AMINE 2 and amine 3 inspired liq Amine 3 inspired Liq) was investigated in WP1. To further optimise the already high performance carrier material (~10 wt% CO2 capacity with slow desorption rates), an array of other amine materials were selected, based on their availability, cost, toxicity and scalability. These amine materials were impregnated on the POLYMER 1 - AMINE 3 polymer to scope optimum carrier formulations.

AMINE 1 was selected as an ideal substrate based on learnings from WP1 with mesoporous silica materials: it exhibited a high propensity to capture CO2 and extended CO2 retention- thus making it an ideal candidate to study here. It is inexpensive, low-toxicity and abundant, making scale-up a facile process.

Amine 4 impregnation was also investigated, as a tertiary amine it is extensively employed in CO2 capture technologies. As a very low cost and abundant material, the moderate toxicity of AMINE 4 can be mitigated due to its employment as a relatively minor component in the end-carrier product. Certainly, if found to give beneficial performance, AMINE 4 can be modified to give a candidate which exhibits greatly reduced toxicity.

Amine 5was investigated due to its low toxicity (as a bioavailable material) and potential for greater interaction with CO2 due to its additional catecholic moieties, which can interact more strongly with hydrogen bonding networks formed.

As a whole strategy, these chosen amines provide a targeted, intelligent and achievable strategy to optimise POLYMER 1 - AMINE 3 carrier candidates.

Synthetic methodology

Table 1: Material production matrix for synthesis of AMINE 3.1@Si_x analogues

Sample	Silica 1 / g	Toluene / mL	H2O added / mL	AMINE 3.1 / mMOL
AMINE 3.1@Si_0.15	0.25	100	0.15	5

Sample	Silica 1 / g	Toluene / mL	H2O added / mL	AMINE 3.1 / mMOL
AMINE 3.1@Si_0.20	0.25	100	0.20	5
AMINE 3.1@Si_0.25	0.25	100	0.25	5
AMINE 3.1@Si_0.30	0.25	100	0.30	5
AMINE 3.1@Si_0.35	0.25	100	0.35	5
AMINE 3.1@Si_0.40	0.25	100	0.40	5
AMINE 3.1@Si_0.45	0.25	100	0.45	5
AMINE 3.1@Si_0.50	0.25	100	0.50	5

Material characterisation: Amine grafted materials

As previously reported in ‘Work Package 1 – Screen candidate CO2 sorbent (carrier) materials’, TGA was utilised to determine loadings of grafted material on silica. Mass loss between the temperature region of 200-800°C was analysed and used to determine surface loadings of grafted material, and the molecular mass of the degradation products could be used to convert weight loss into molar loadings.

Further method development has taken place towards CO2 sorption analysis by TGA, to distinguish between strongly and weakly adsorbed CO2 by amine-silica carriers. After being heated at 110°C for 1 hour to remove water, carriers were subsequently heated at 25°C for 1 hour, and 75°C for 1 hour under nitrogen to evaluate N2 adsorption capacities that could be used to give better insights into desorption kinetics (will be discussed in section 5 of this report). The gas flow was then changed to CO2, where CO2 adsorption was analysed for 1 hour. The temperature was then decreased to 25°C, and sample mass change was monitored over a duration of 45 minutes. Monitoring sample mass change under CO2 at these

temperatures was designed to rationalise CO2 adsorption by strong chemisorption (75°C), and by weak physisorption (25°C), where after the assumed saturation of strong chemisorbed CO2 at 75°C, sample mass increase after changing the temperature to 25°C could be used to determine quantities of physisorbed CO2. Following CO2 adsorption, the gas flow was switched to nitrogen, and sample mass change was monitored at 25°C for 1 hour to evaluate CO2 desorption, and the sample was subsequently heated at 110°C for 1 hour.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is an infrared spectroscopy technique used to study the chemical composition of powders, films, and other solid materials. It is a non-destructive technique that can be used to analyse samples without any prior preparation. Unlike transmission FTIR, which requires samples to be transparent to infrared radiation, DRIFTS can be used to analyse opaque samples.

In DRIFTS, the sample is placed in a small cup and then mixed with a IR-transparent material matrix, such as potassium bromide (KBr). An infrared beam is then directed at the sample, and the reflected light is collected and analysed by a Fourier transform infrared (FTIR) spectrometer.

The infrared radiation interacts with the molecules in the sample, causing them to vibrate. The amount of light reflected by the sample depends on the frequencies of the vibrations. By measuring the amount of light reflected at different frequencies, we can identify the molecules in the sample.

DRIFTS is a versatile technique that can be used to analyse a wide variety of samples, including:

- Powders - DRIFTS is a particularly good choice for analysing powders because it does not require any prior sample preparation. This makes it a convenient technique for analysing samples that are difficult to handle or that would be difficult to prepare for transmission FTIR.
- Solid materials - DRIFTS can be used to analyse any solid material, regardless of its optical properties. This makes it a versatile tool for analysing a wide variety of samples.

Applications of DRIFTS

- DRIFTS has a wide range of applications, including material characterisation - DRIFTS can be used to identify the chemical composition of materials, including their elemental composition, functional groups, and crystalline structure.
- Studying surface reactions - DRIFTS can be used to study the kinetics and mechanisms of surface reactions.
- Quality control - DRIFTS can be used to control the quality of materials, such as the species on the carrier as well as carbonate presence.

High pressure in-situ DRIFTS analysis was conducted on select samples, to rationalise the nature of CO2 adsorption to high-capacity carriers.

Amine grafted materials- optimisation by varying amine identify

The amine grafted materials were produced as previously detailed in WP1. The appropriate amine materials were purchased from commercial sources and purified where appropriate through distillation. When evaluating the composition of the materials: surface loadings were evaluated as a function of wt% and molar quantity though TGA as previously reported. TGA and autoclave CO2 loading experiments at 1 bar and 10 bar respectively were then performed and materials evaluated according to their performance in CO2 capture.

Amine loading – TGA decomposition

Thermal decomposition TGA was used to evaluate the quantity of surface grafted amines on Amine 3.5@Si, Amine 3.7@Si, AMINE 2@Si and AMINE 1@Si (Table 2).

Table 2: Comparison of grafted loadings on amine-grafted silica materials produced during screen of different amine moieties

Carrier	Grafted loading / wt%	Grafted loading / mMolg-1	Amine groups per grafted moiety	Grafted amine loading / mMolg-1
Amine 3.5@Si	24.96	2.47	2	4.94
Amine 3.7@Si	8.61	0.86	1	0.86
AMINE 2@Si	8.18	0.43	5	2.15
AMINE 1@Si	14.97	0.19	~18	3.42
AMINE 3.1@Si	27.4	4.80	1	4.80

The grafting of Amine 3.5 to silica was effective, with similar grafted amine loadings as previously observed with AMINE 3.1 when grafted to the same Silica 1 substrate. The amine grafted AMINE 2@Si and AMINE 1@Si have a significantly lower quantity of grafted material on the silica surface when compared to Amine 3.5@Si. However, each grafted moiety contains more amine groups. Considering that grafting AMINE 2 functionalises silica with 5 amine groups, and that AMINE 1 functionalises silica surface with ~18 amine groups, the low loading of material doesn't necessarily mean the CO2 capacities will be negatively affected, if

intramolecular chemisorption of CO2 proceeds. Interestingly, Amine 3.7 proved to be a poor substrate for silica grafting, showing low grafted amine loadings.

CO2 adsorption properties – in situ TGA analysis

TGA was also used to determine the CO2 adsorption capacities of Amine 3.5@Si, Amine 3.7@Si, AMINE 2@Si and AMINE 1@Si (Table 3).

Table 3: CO2 Adsorption capacities of amine@Si carriers

Carrier	Grafted loading / mMolg-1	Grafted amine loading / mMolg-1	CO2 capacity / mMolg-1 (chemisorb)	CO2 capacity / wt% (chemisorb)	CO2 retention (48 hr/480 hr)
Amine 3.5@Si	2.47	4.94	2.76 (1.99)	9.50 (8.75)	75.6 % / 66.6%
Amine 3.7@Si	0.86	0.86	0.46 (0.25)	2.03 (1.12)	-
AMINE 2@Si	0.43	2.15	0.38 (0.22)	1.66 (0.96)	-
AMINE 1@Si	0.19	3.42	0.85 (0.68)	3.73 (3.00)	-
AMINE 3.1@Si 1	4.80	4.80	1.42	6.24	65.7 % / 55.3 %

The amine-grafted silicas proved to be poor CO2 carrier materials when loaded at ambient CO2 pressure, demonstrating low CO2 adsorption capacities relative to the quantity of amine that was functionalised on the silica surface. This suggests that at ambient pressure the intramolecular chemisorption of CO2 is not favoured by amine-grafted silicas, and that the chemisorption of CO2 through the formation of ammonium-carbamate pairs is partially dependent on the density of grafted amines at the silica surface.

Amine 3.7@Si also demonstrated a low CO2 adsorption capacity at ambient pressure via TGA, where the steric bulk of the grafted moiety likely prevents the formation of ammonium-carbamate pairs by neighbouring grafted groups. Of the carriers tested in the extended amine-grafting screen conducted here, only Amine 3.5@Si showed improved CO2 adsorption properties over AMINE 3.1@Si.

With a comparable loading of grafted amine groups on the silica surface, Amine 3.5@Si proved to be significantly more effective than AMINE 3.1@Si for CO2 adsorption at atmospheric pressure.

To further investigate the CO2 loading on carrier precursors, loading at 10 bar of CO2 was conducted at 75°C overnight. In line with ambient pressure results, Amine 3.5@Si exhibited the highest CO2 loading- currently representing a best-in-class carrier at high and ambient CO2 adsorption properties. Amine 3.7@si exhibited similarly poor CO2 adsorption properties.

In contrast, AMINE 1 and AMINE 2 grafted materials exhibited significantly increase CO2 sorption capacities at higher pressure when compared to ambient pressure CO2 adsorption. This indicates the bulkier amines block CO2 sorption at the surface due to decreased surface area, which can be overcome by high pressure CO2 loading.

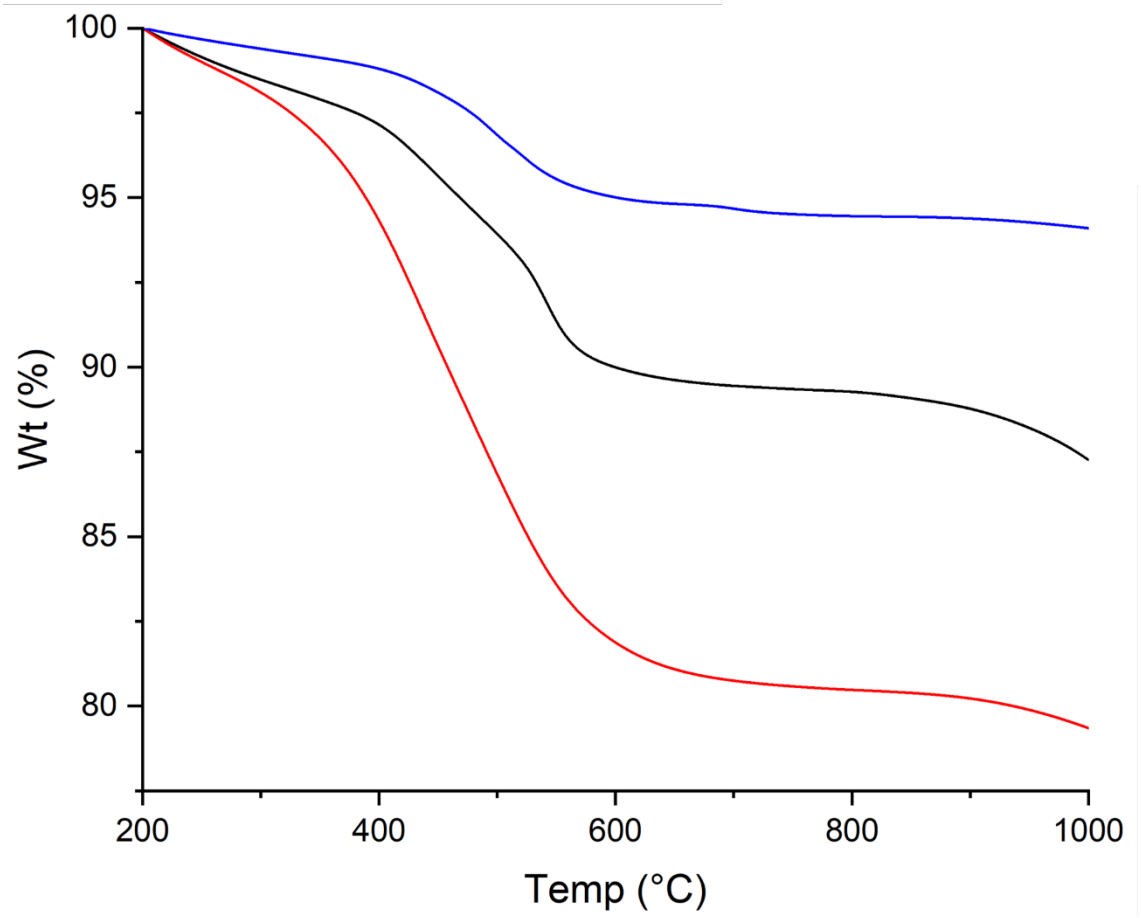
Table 4: CO2 Adsorption capacities of amine-grafted silicas (75°C, 10 bar, overnight)

Carrier	CO2 capacity / %
Amine 3.5@Si	13.8
Amine 3.7@Si	3.2
AMINE 1-P@Si	11.8
AMINE 2-P@Si	10.0
AMINE 3.1@Si 1	8.1

CO2 desorption properties

Desorption of CO2 from Amine 3.5@Si was monitored by TGA following adsorption for 1 hour at 75 °C at ambient CO2 pressure, where the presence of two amine groups per surface grafted molecule was predicted to increase CO2 strong adsorption via intermolecular ammonium-carbamate pair formation, resulting in slower desorption of the strongly bound CO2.

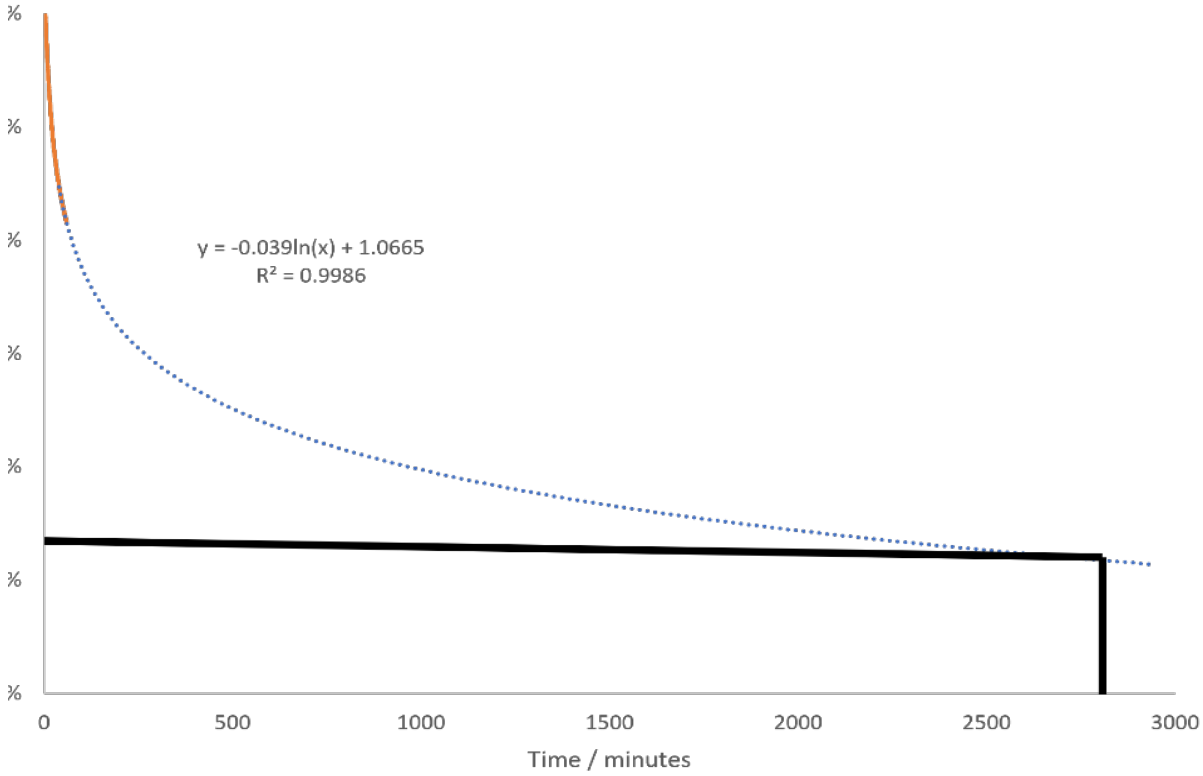
Figure 1: CO2 Desorption profiles of Amine 3.5@Si (red) and AMINE 3.1@Si (WP1, blue).



The grafting of Amine 3.5 to Silica 1 produced a carrier that not only showed a high CO2 adsorption capacity (9.50 wt%, Section 4.5.1.2), but also demonstrated slow desorption kinetics. The desorption profile in Figure 8 shows that after 20 minutes, Amine 3.5@Si retains 95% of previously adsorbed CO2, which falls within the desorption requirements of a carrier to be utilised by C4C. Figure 2 demonstrates the desorption kinetics extrapolated according to an biexponential fit (representing both rapid desorption from physiosorbed CO2 and strongly bound CO2 from chemisorption). The fits were used to calculate the relative quantities of CO2 retained after both 48 and 480 hours under the nitrogen atmosphere of the TGA. These relative quantities provide a good assessment of desorption rates, targeting over 70% retention after 48 s

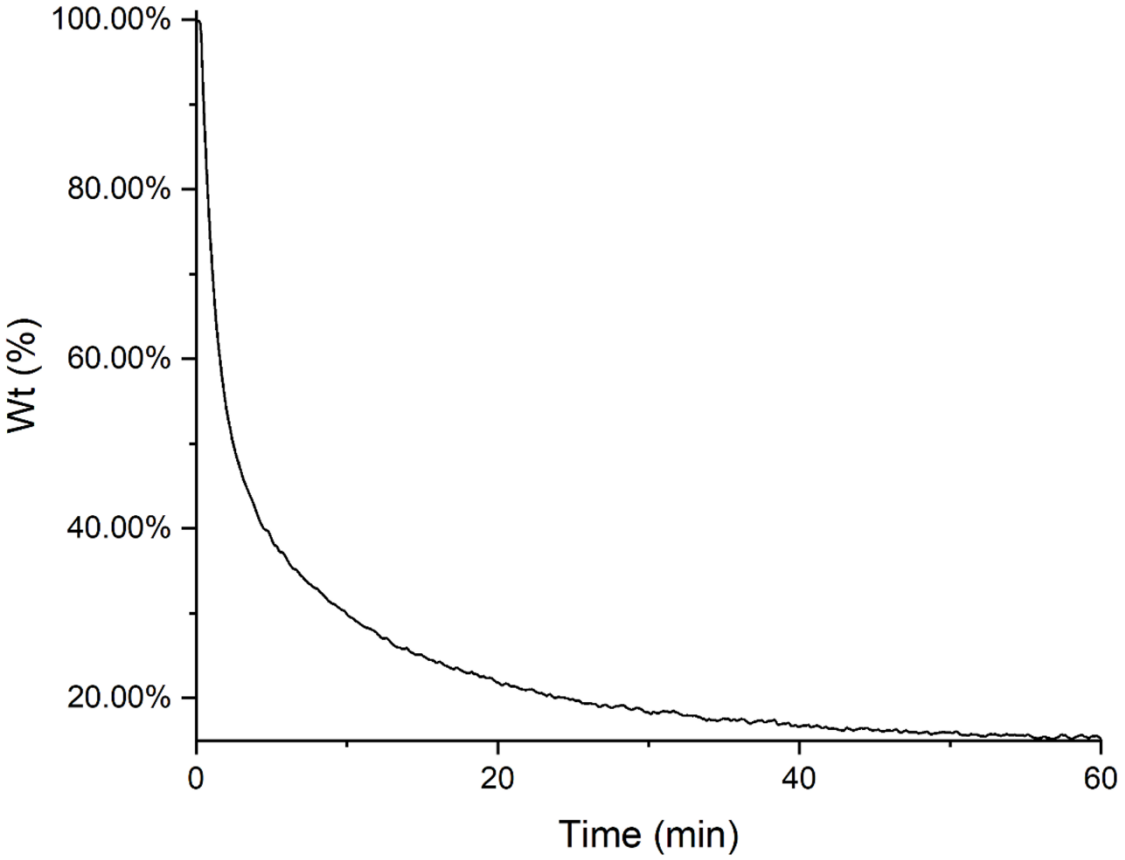
Figure 2 also shows the CO2 desorption of AMINE 3.1@Si prepared according to the same procedure as Amine 3.5@Si (from 'Work Package 1 – Screen candidate CO2 sorbent (carrier) materials'), where slower CO2 desorption is observed for the amine grafted silica. These results in combination with the high CO2 adsorption capacity of Amine 3.5@Si show that it is viable carrier for C4C, and further experimentation on the performance of this carrier at carbonating cement is warranted.

Figure 2: Extrapolated CO2 desorption profile of Amine 3.5@Si



Desorption of CO2 from Amine 3.7@Si was monitored by TGA following adsorption for 1 hour at 75°C at ambient CO2 pressure, where it was initially predicted that the hydrophobic nature of quaternary carbon group of the grafted material would aid in slowing CO2 desorption, particularly in a cementitious environment.

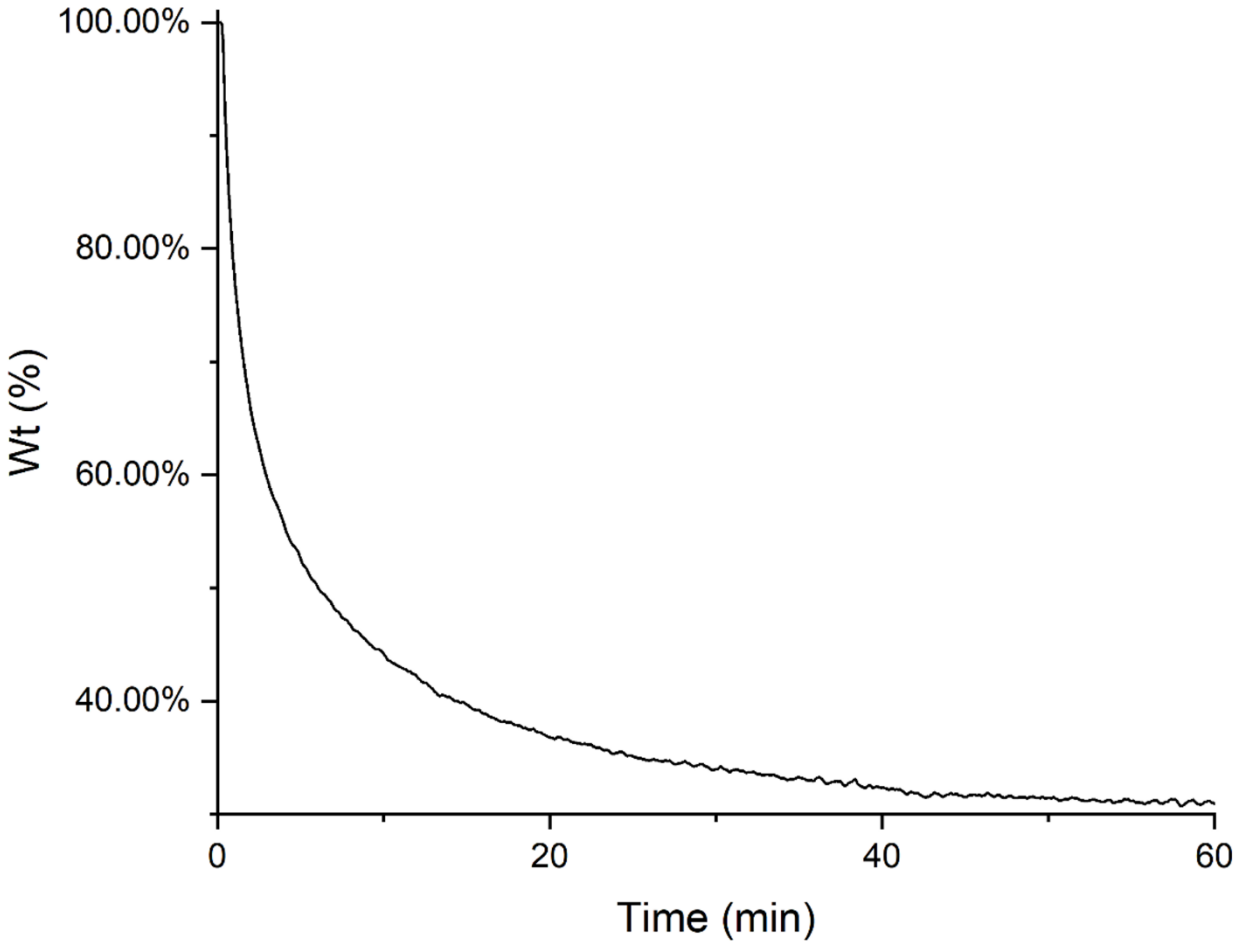
Figure 3: CO2 Desorption profile of Amine 3.7@Si.



The profile in Figure 3 shows that CO2 desorption from Amine 3.7@Si is rapid. After 30 minutes under nitrogen, 80% of the previously adsorbed CO2 had desorbed from Amine 3.7@Si, highlighting that majority of CO2 adsorption by this material is weak. This shows that ammonium-carbamate formation is not the primary mode of CO2 adsorption by this carrier, and that in a cement environment, desorption of CO2 from this material would be expected to be even faster. The low CO2 adsorption capacity of Amine 3.7@Si (Section 4.5.1.2) combined with rapid CO2 desorption kinetics mean that Amine 3.7@Si is not a viable carrier for further study by C4C.

Desorption of CO2 from AMINE 2@Si was monitored by TGA following adsorption for 1 hour at 75°C at ambient CO2 pressure, where it was initially predicted that the high amine density of the grafted moiety would promote the strong adsorption of CO2 via the formation of ammonium-carbamate groups, with strong adsorption resulting in slow desorption kinetics.

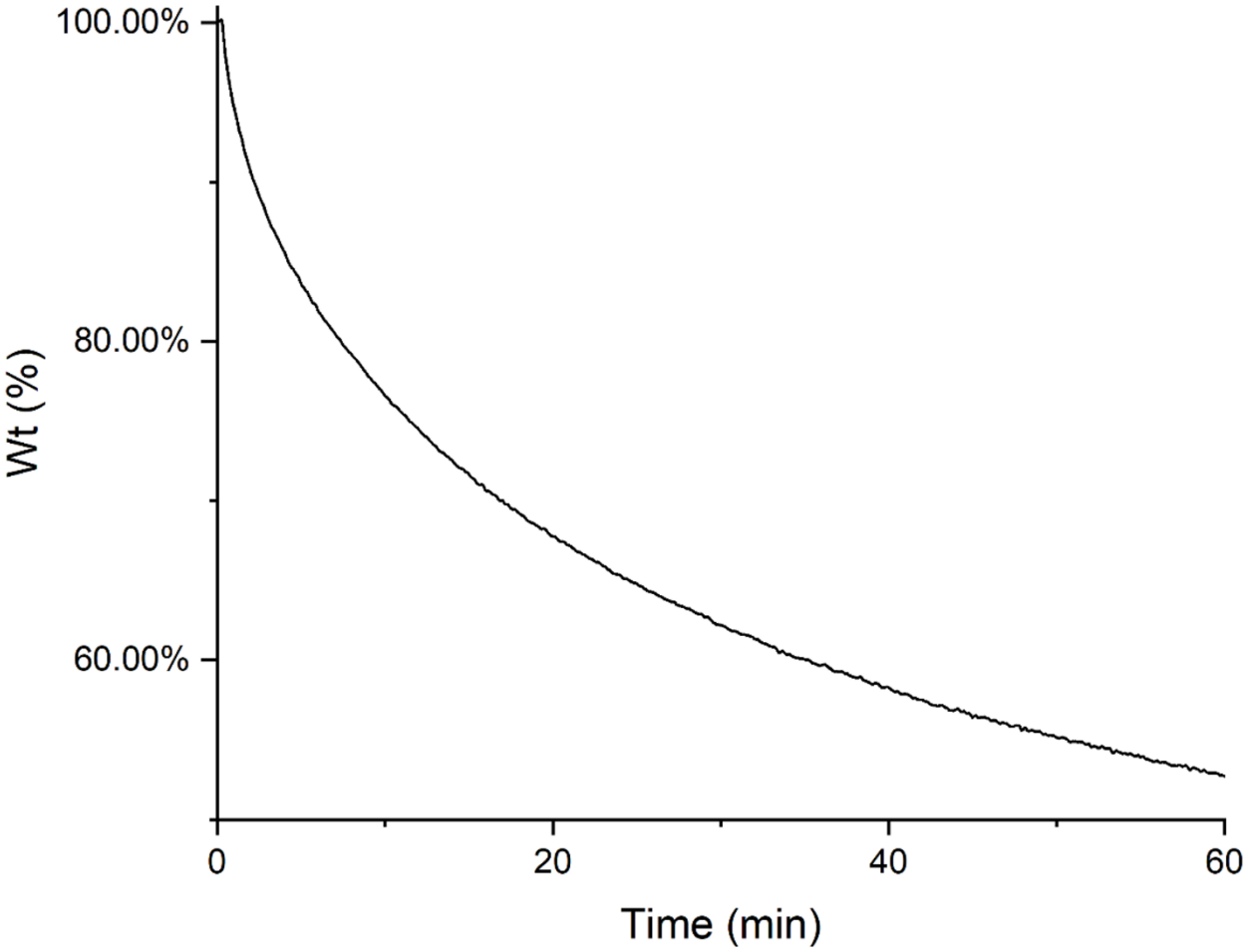
Figure 4: CO2 Desorption profile of AMINE 2@Si.



The grafting of AMINE 2 was proposed to increase the quantity of strongly chemisorbed CO2 to amine-grafted silica carriers, the desorption profile in Figure 4 shows that over 60% of CO2 desorption occurs 20 minutes after exposure to nitrogen. This indicates that the majority of CO2 that was adsorbed to AMINE 2@Si was weakly bound, potentially via the formation of carbamic acid or bicarbonate, with physisorbed CO2 also forming a significant part of the CO2 adsorption profile of this carrier material. As CO2 desorption from AMINE 2@Si was shown to be fast, and that the CO2 capacity was low at 1.66 wt%, this suggests that AMINE 2@Si is not a viable candidate carrier, if loaded at high pressure.

Desorption of CO2 from AMINE 1@Si was monitored by TGA following adsorption for 1 hour at 75°C at ambient CO2 pressure (Figure 4), where it was initially predicted that the high amine density of the grafted moiety would promote the strong adsorption of CO2 via the formation of ammonium-carbamate groups, with strong adsorption resulting in slow desorption kinetics.

Figure 4: CO2 Desorption profile of AMINE 1@Si



Like with AMINE 2, the grafting of AMINE 1 to silica was conducted in search of a carrier material that would slowly release CO2 because of strong adsorption, and AMINE 1@Si does show improved CO2 desorption characteristics compared to the AMINE 2 analogue. However, after 20 minutes under nitrogen, over 30% of adsorbed CO2 desorbs from AMINE 1@Si. A carrier to be used by C4C would require at least 95% retention in CO2 loading after this duration, which be indicative of a majority of strongly adsorbed CO2 by the grafted material. And when the low CO2 loading of AMINE 1@Si is considered (Section 4.5.1.2), combined with the unfavourable CO2 desorption kinetics observed in Figure 12, then it is clear that AMINE 1@Si is not a viable candidate as a CO2 carrier for C4C when loaded at ambient pressure.

Amine loading screen

Amine loading – TGA decomposition

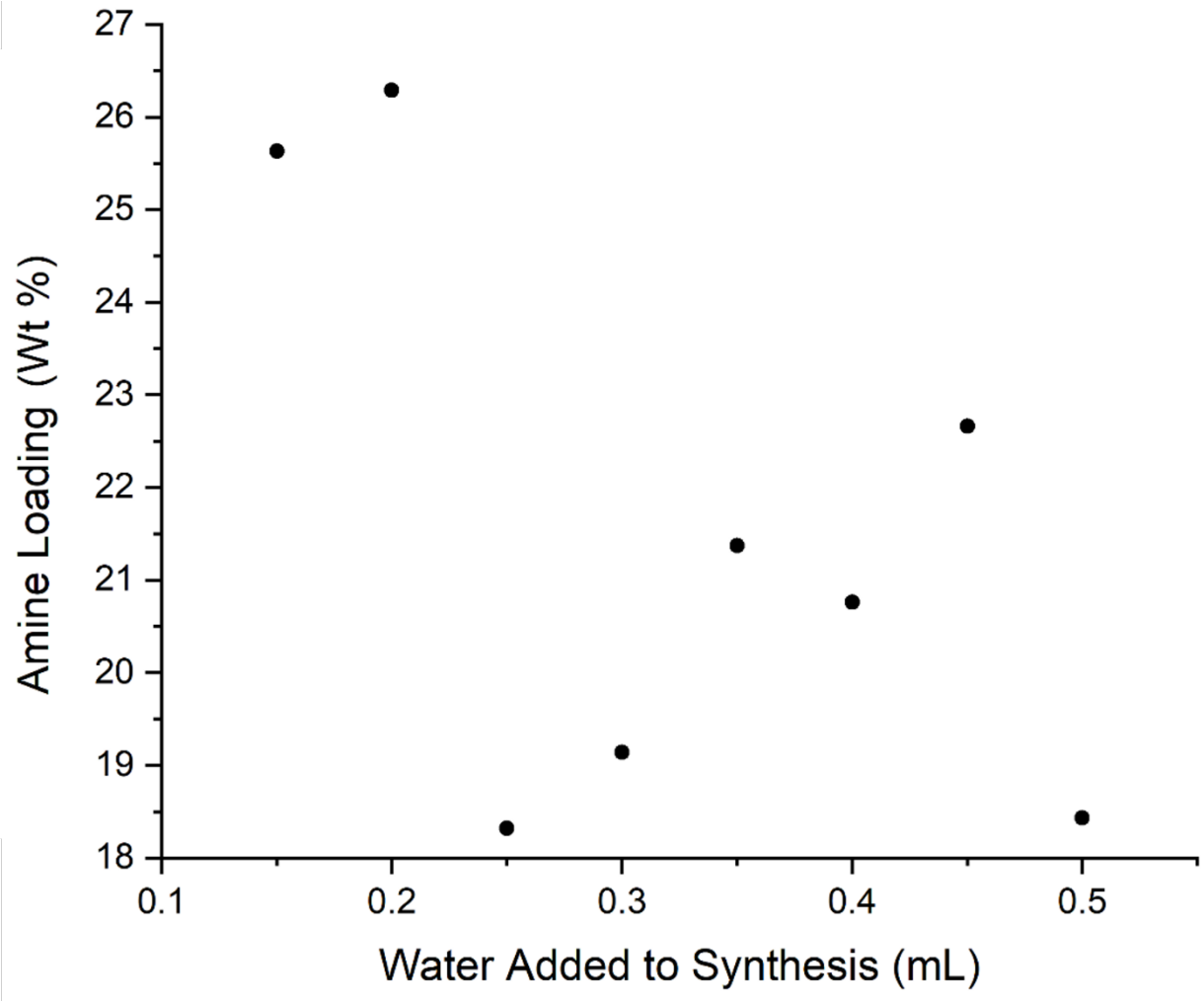
The thermal decomposition profiles of the AMINE 3.1@Si analogues prepared with varying quantities of water in the reaction mixture (AMINE 3.1@Si_x) were obtained from TGA (Table 5). The quantity of grafted amine on the silica surface could be determined and related to the amount of water that was added to the carrier synthesis reactions.

Table 5: Amine loadings on AMINE 3.1@Si_x derivatives

Carrier	AMINE 3.1 loading / wt%	AMINE 3.1 loading / mMolg-1
AMINE 3.1@Si_0.15	25.63	4.42
AMINE 3.1@Si_0.20	26.29	4.53
AMINE 3.1@Si_0.25	18.32	3.16
AMINE 3.1@Si_0.30	19.14	3.30
AMINE 3.1@Si_0.35	21.37	3.68
AMINE 3.1@Si_0.40	20.76	3.47
AMINE 3.1@Si_0.45	22.66	3.91
AMINE 3.1@Si_0.50	18.43	3.18

While some conclusions on the modulation of AMINE 3.1 loading on silica through the introduction of water can be deduced from the results in Table 5 and Table 5 the relationship appears to be complex. The AMINE 3.1@Si_x derivatives prepared with the lowest quantities of water in the reaction mixture (AMINE 3.1@Si_0.15 and AMINE 3.1@Si_0.20) demonstrated the highest amine surface loadings of all the prepared samples. However, when greater than 0.20 mL of water is added to AMINE 3.1@Si syntheses, there does not appear to be a direct relation between water addition and AMINE 3.1 loading on the resultant carrier.

Figure 5: Comparing amine loadings against quantity of water to AMINE 3.1@Si_x derivative syntheses.



The amine loading on AMINE 3.1@Si_0.25 is significantly lower than that on AMINE 3.1@Si_0.20, highlighting how a small increase in water loading in the synthesis can have a significant effect on amine loading on AMINE 3.1@Si derivatives. AMINE 3.1@Si_0.25 to AMINE 3.1@Si_0.45 show a general increase in AMINE 3.1 loading with increasing quantities of water added to the synthesis (omitting AMINE 3.1@Si_0.40), while amine loading on AMINE 3.1@Si_0.50 is the second lowest the carriers examined. From these results, it can be rationalised that AMINE 3.1@Si with high grafted amine loadings can be achieved through the addition of low quantities of water, and that controlling amine surface loadings on AMINE 3.1@Si is challenging after a threshold of water is added to synthetic mixtures.

CO2 adsorption properties – in situ TGA analysis

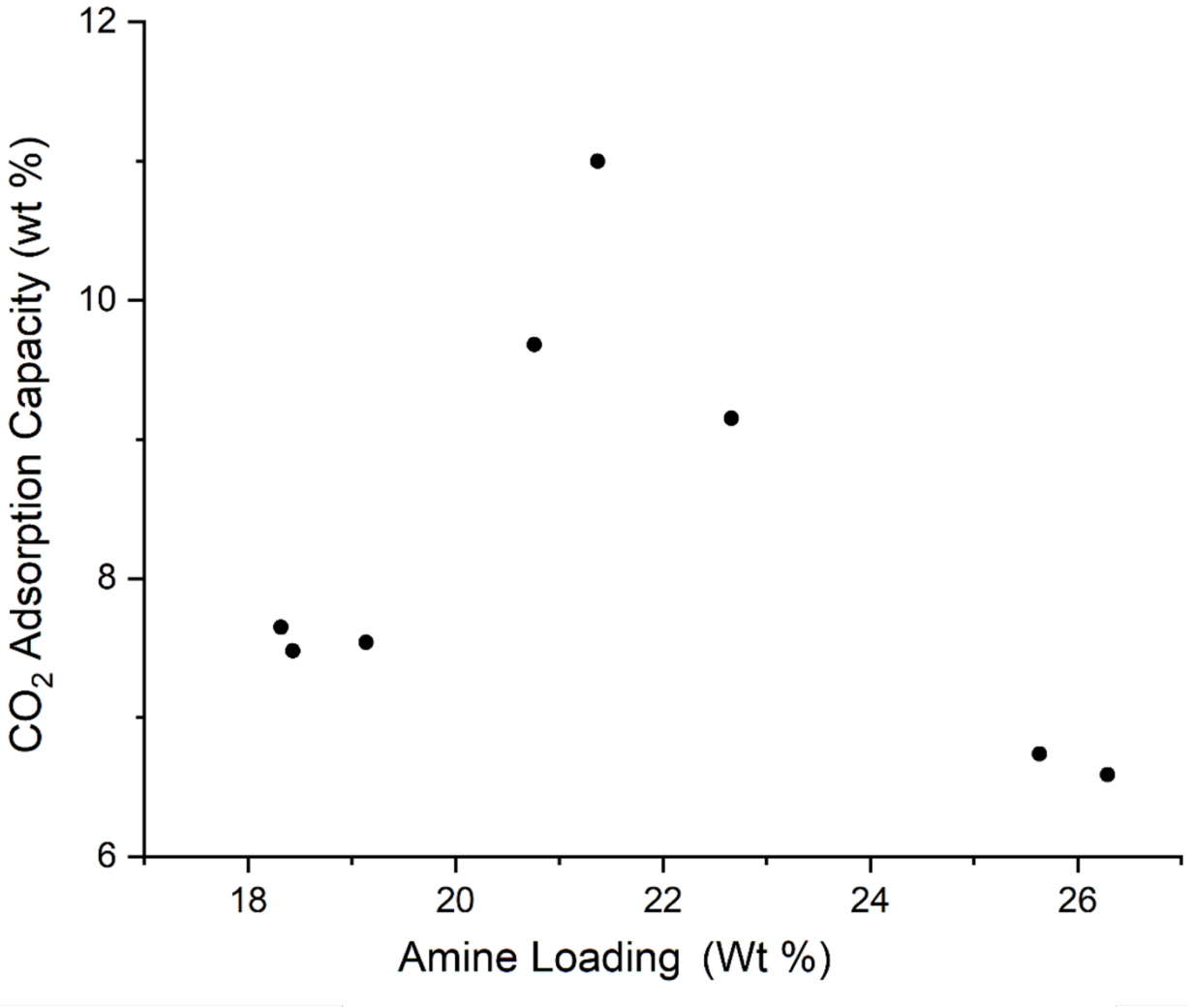
The CO2 adsorption capacities of the AMINE 3.1@Si_x carriers were determined by TGA. There was particular interest in determining how the quantity of AMINE 3.1 that was loaded on this class of material would affect CO2 adsorption capacity, and whether maximum grafted amine loading would correlate to maximum CO2 adsorption capacity. The CO2 adsorption capacities of the AMINE 3.1@Si_x carriers are shown in Table 6.

Table 6: CO2 Adsorption capacities of AMINE 3.1@Si_x derivatives

Carrier	AMINE 3.1 loading / wt%	CO2 capacity / mMolg-1 (chemisorb)	CO2 capacity / wt% (chemisorb)	CO2 retention (48 hr/480 hr)
AMINE 3.1@Si_0.15	25.63	1.53 (1.25)	6.74 (5.50)	71.1 % / 60.2 %
AMINE 3.1@Si_0.20	26.29	1.50 (1.25)	6.59 (5.48)	76.7 % / 67.3 %
AMINE 3.1@Si_0.25	18.32	1.74 (1.49)	7.65 (6.55)	65.1 % / 53.5 %
AMINE 3.1@Si_0.30	19.14	1.71 (1.50)	7.54 (6.59)	69.7 % / 59.3 %
AMINE 3.1@Si_0.35	21.37	2.50 (2.12)	11.0 (9.33)	47.9 % / 34.3 %
AMINE 3.1@Si_0.40	20.76	2.20 (1.87)	9.68 (8.25)	49.8 % / 36.5 %
AMINE 3.1@Si_0.45	22.66	2.08 (1.82)	9.15 (8.02)	79.0 % / 71.6 %
AMINE 3.1@Si_0.50	18.43	1.70 (1.45)	7.48 (6.40)	46.3 % / 32.0 %

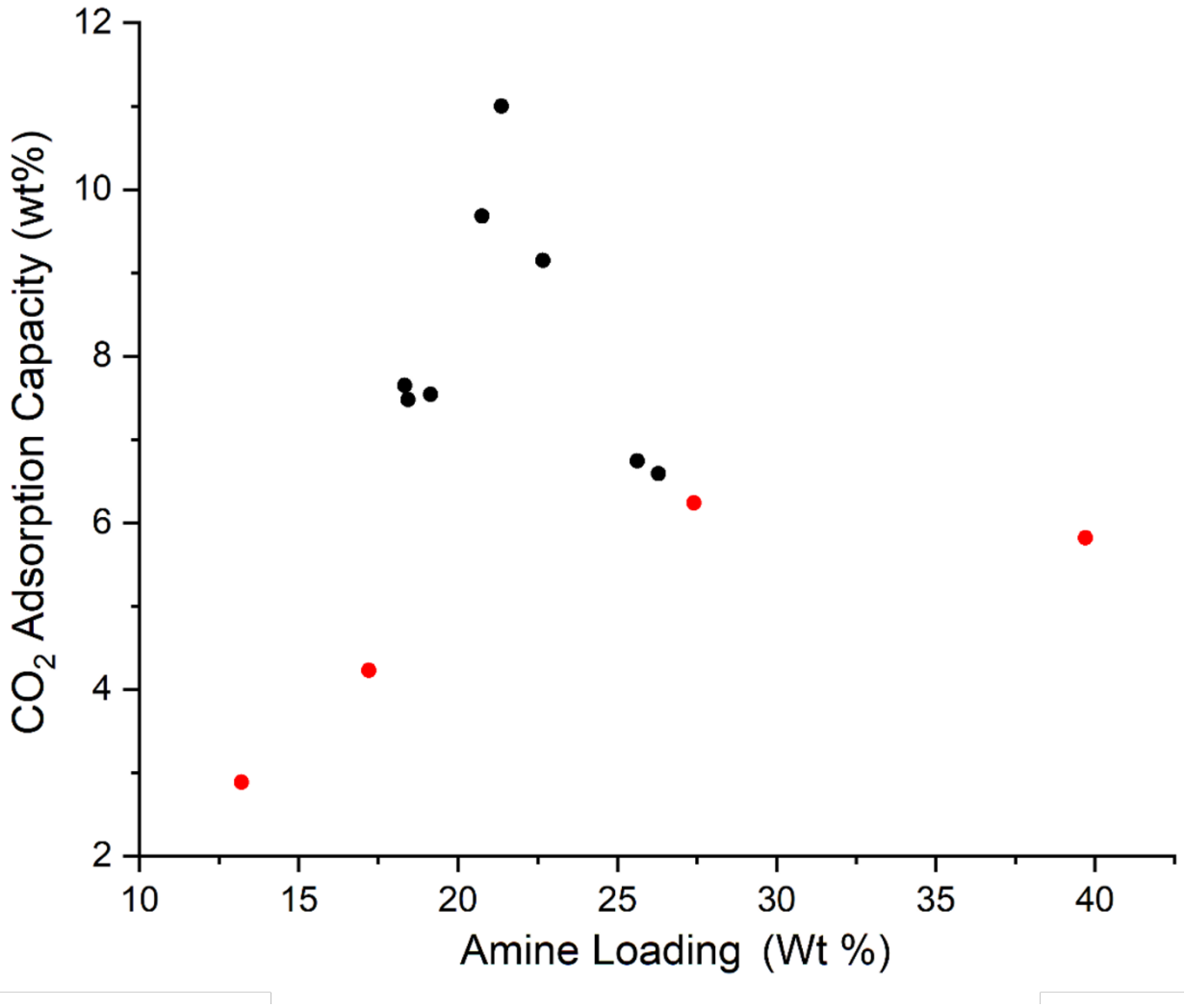
The results in Table 6 suggest that there is an intricate balance between AMTPS loading and CO2 adsorption capacity for the AMINE 3.1@Si_x derivatives, where higher quantities of grafted amine do not appear to be beneficial to CO2 adsorption capacity. AMINE 3.1@Si_0.15 and AMINE 3.1@Si_0.20 had the highest loadings of AMINE 3.1 of the eight analogues that were synthesised, however, they had the lowest CO2 adsorption capacities. This suggests that when AMINE 3.1 loading on Silica 1 is too high, then the porous solid support becomes partially blocked, limiting the accessibility of CO2 to grafted amine that is present within the silica pores, reducing adsorption capacity. The relationship between AMINE 3.1 loading and CO2 adsorption capacity is better visualised by the graph in Figure 14, where an optimum AMINE 3.1 loading for maximum CO2 adsorption capacity of AMINE 3.1@Si_x is clear.

Figure 6: Comparing AMINE 3.1 loading and CO2 adsorption capacities of AMINE 3.1@Si_x derivatives.



Of the eight AMINE 3.1@Si_x derivatives examined for AMINE 3.1 loading and CO2 adsorption capacity, AMINE 3.1@Si_0.35, with a grafted amine loading of 21.37 wt% demonstrated the highest CO2 adsorption capacity (11.0 wt%). AMINE 3.1@Si_x with lower AMINE 3.1 loadings showed decreased CO2 adsorption capacities, which can be attributed to the lower quantity of amine sites present for the chemisorption of CO2 via the formation of ammonium-carbamate pairs. AMINE 3.1@Si_x with higher AMINE 3.1 loadings than 21.37 wt% also showed a reduction in CO2 capacity, due to the assumed blockage of Silica 1 pores due to the increased quantity of grafted material. The four AMINE 3.1@Si derivatives reported on in the 'Work Package 1 – Screen candidate CO2 sorbent (carrier) materials' report, were compared against the eight prepared here (Figure 7).

Figure 7: Comparing AMINE 3.1 loading and CO2 adsorption capacities of AMINE 3.1@Si_x derivatives (black), and AMINE 3.1@Si analogues reported in Work Package 1 (red).



The correlation between the loading of AMINE 3.1 on AMINE 3.1@Silica 1 carries with CO2 adsorption capacity is apparent from Figure 8. When AMINE 3.1 loading on the carrier exceeds 27.5%, it is likely that blockage arising from high grafting loadings restricts CO2 access to grafted amine inside the silica pores, and that CO2 adsorption is nearly exclusively by AMINE 3.1 that is grafted on the external silica surface. This can be deduced from the fact that AMINE 3.1@Si CO2 adsorption capacity is reduced by a very small quantity when AMINE 3.1 loading increases by a large margin from 27.5% to 40%. While AMINE 3.1 loadings that are too low will restrict the formation of ammonium-carbamate pairs, reducing CO2 capacity. AMINE 3.1@Si carriers have an apparent optimum grafted amine loading, between 20 and 23 wt%, for maximum CO2 adsorption capacity.

CO2 adsorption properties – high pressure CO2 loading

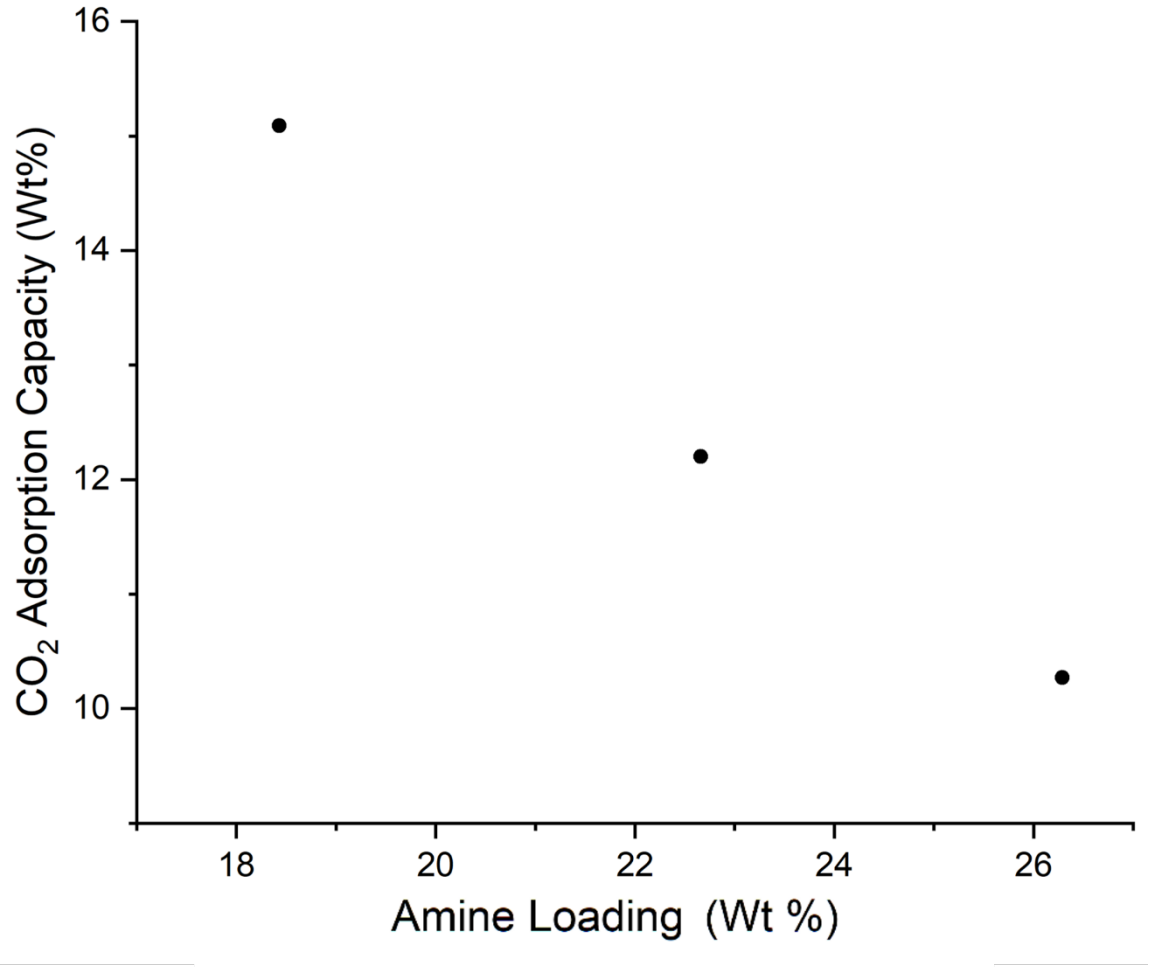
Select AMINE 3.1@Si carriers were also examined for CO2 adsorption capacity under high pressure loading environments. Samples were added to an autoclave, which was subsequently pressurised to 10 bar with CO2. The CO2 loaded autoclave was then heated at 70°C overnight, where after cooling and removal from the autoclave, the difference in mass between the sample before and after CO2 loading was used to determine adsorption capacity.

High pressure CO2 adsorption of AMINE 3.1@Si_0.2 (high AMINE 3.1 loading), AMINE 3.1@Si_0.45 (medium AMINE 3.1 loading) and AMINE 3.1@Si_0.5 (low AMINE 3.1 loading) were examined for high pressure CO2 adsorption.

Table 7: CO2 adsorption capacities of AMINE 3.1@Si-x carriers loaded with 10 bar CO2 at 70°C overnight

Carrier	AMINE 3.1 loading / wt%	CO2 capacity / wt%	CO2 capacity / mmolg-1
AMINE 3.1@Si_0.20	26.29	10.27	2.335
AMINE 3.1@Si_0.45	22.66	12.20	2.772
AMINE 3.1@Si_0.50	18.43	15.09	3.431

Figure 8: Comparing AMINE 3.1 loading and CO2 adsorption capacities of AMINE 3.1@Si_x carriers.

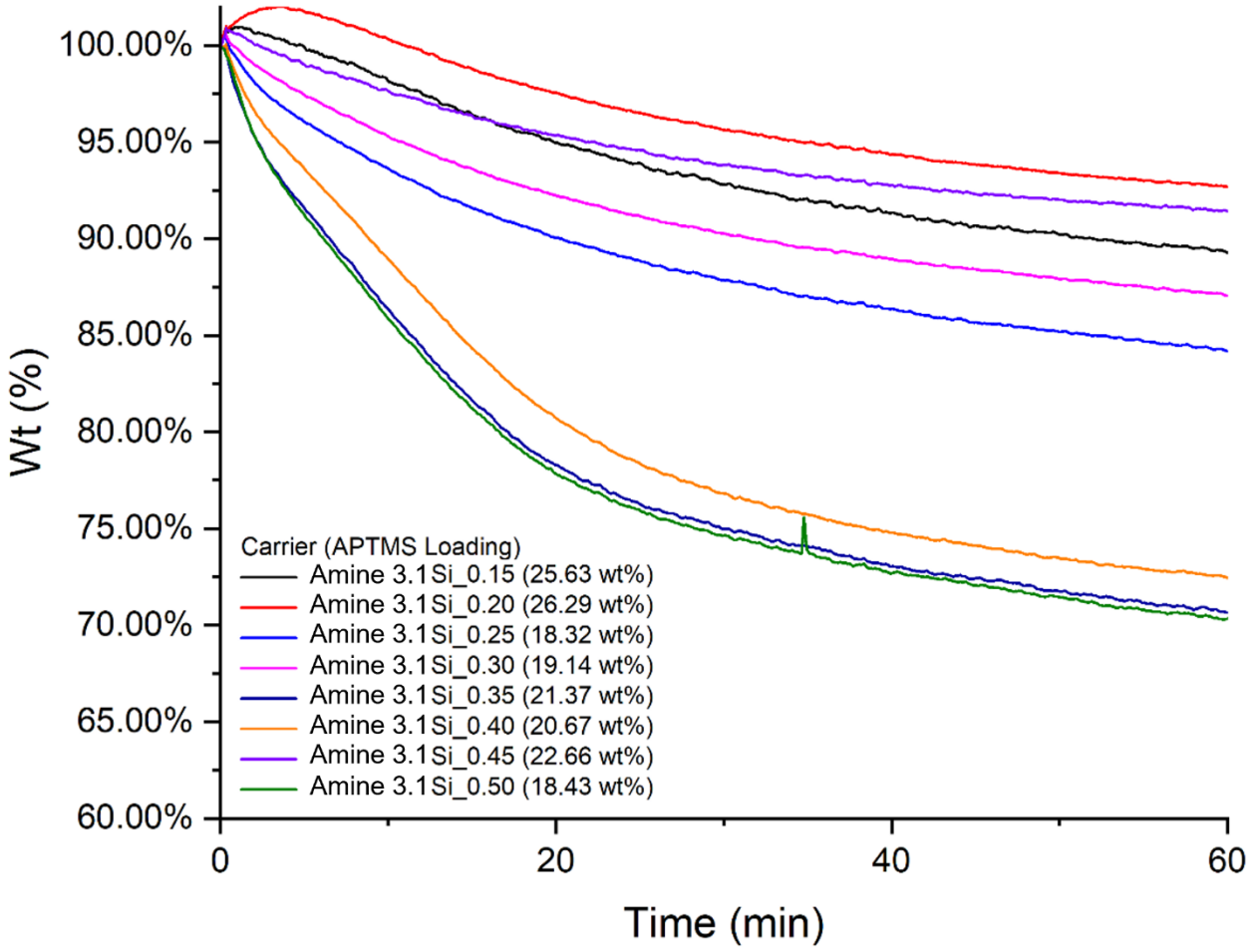


As shown in Figure 16, under high pressure loading environments, there is a negative correlation between CO2 adsorption capacity of AMINE 3.1@Si_x carriers and the quantity of AMINE 3.1 loaded on the silica surface.

CO2 desorption properties

Desorption of CO2 from AMINE 3.1@Si_x derivatives were monitored by TGA, where there was interest in evaluating how the quantity of grafted amine on the Silica 1 affected CO2 desorption kinetics (Figure 9).

Figure 9: CO2 Desorption profiles of AMINE 3.1@Si_x analogues.

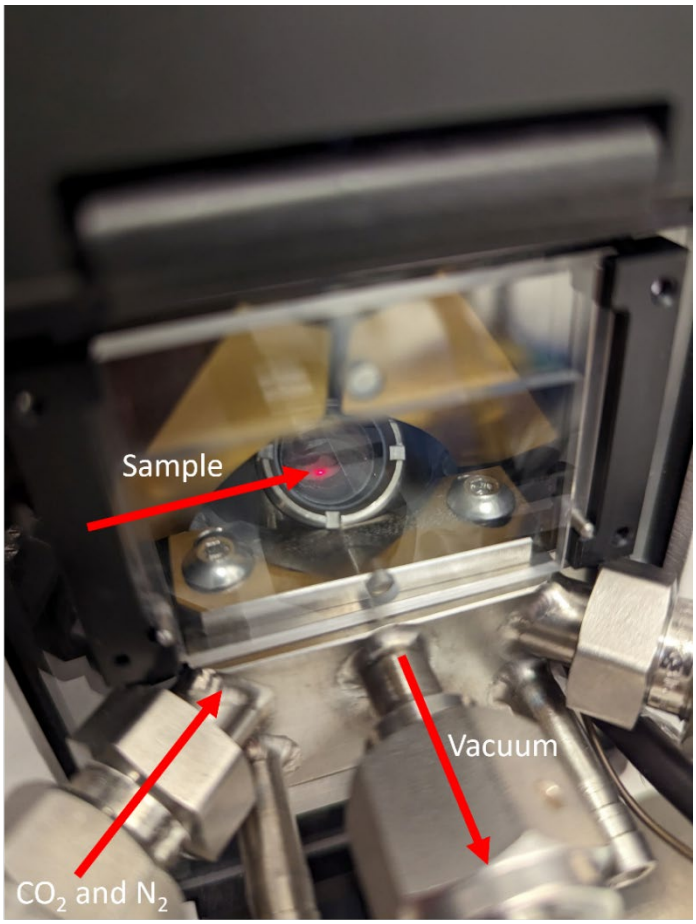


While having the lowest CO2 adsorption capacities, AMINE 3.1@Si_0.15 and AMINE 3.1@Si_0.20 demonstrated very slow CO2 desorption rates. Slow CO2 desorption rates coming from the AMINE 3.1 grafted silica materials with the highest surface loadings can be rationalised by pore blockage. If high grafting concentrations causes silica pore blockage, then CO2 chemisorption at grafted amine sites on the exterior of the support will be prevalent, as there would be no pore access for CO2 physisorption. Hence although the CO2 adsorption capacities of AMINE 3.1@Si_0.15 and AMINE 3.1@Si_0.20 are low, strong chemisorption is prevalent. AMINE 3.1@Si_0.45 also showed slow CO2 desorption and was the AMINE 3.1@Si_x carrier with the third highest grafted amine loading (behind AMINE 3.1@Si_0.15 and AMINE 3.1@Si_0.20), however, this carrier had a high CO2 adsorption capacity of 9.15 wt%. This would suggest partial pore blockage by grafted AMINE 3.1 in this material, but there still being internal amine sites available for CO2 chemisorption. Beyond AMINE 3.1@Si carriers with high grafted surface loadings showing slow CO2 desorption, there isn't a defined relationship between grafted amine loadings and CO2 desorption kinetics. For example, AMINE 3.1@Si_0.25 and AMINE 3.1@Si_0.50 have near identical AMINE 3.1 loadings, but exhibit significantly different CO2 desorption profiles.

Optimisation through intensive surface chemistry evaluation : in-situ FTIR analysis of sorbents to inform further optimisation

In-situ-FTIR analysis was performed using the Harrick Praying mantis High pressure chamber kit with the Shimadzu IrXross FTIR setup and MCT detector to achieve the highest possible resolution and signal quality (Figure 10). FTIR allows for the identification of specific chemical species formed upon CO2 sorption at pressures up to 10 bar at varied temperatures. It was therefore decided to pick 2 differently performing CO2 carriers from this study and replicate conditions within the autoclave CO2 loading experiments. AMINE 3.1@Si_0.35 was chosen due to its extremely high CO2 sorption properties both at atmospheric pressure and 10 bar of CO2, while showing accelerated CO2 desorption in comparison with other AMINE 3.1@Si samples. Amine 3.5@Si was chosen as a comparative substrate for further investigation due to its best-in- class CO2 sorption capacities and desorption rates.

Figure 10: High pressure in-situ FTIR experiment in-action



CO2 sorption was evaluated according to the following regime:

First, the sample was dried by purging with vacuum (1x10-2 mBar) at 110°C to ensure a lack of water vapour within the sample chamber as water vapour exhibits a high IR adsorption coefficient which can obscure signals pertaining to the sample (See Figure 10). Following this, the temperature was dropped to 75°C and the vacuum closed. The port was then switched over to N2 flowing at 0.1 L min-1

First, the chamber cavity was filled with potassium bromide, an IR silent matrix material used in order to accurately evaluate background signals at the different temperatures evaluated. A background measurement was then performed, to allow for subtraction of subsequent measurements against an equilibrium condition, avoiding the misidentification of adventitious signals pertaining to system artifacts. After this, the KBr reference was subjected to 10 bar CO2 at 75°C and a measurement taken- allowing the subtraction of changes in the background due to changes in the beam geometry due to the changes in gas IR cross-section and density within the sample chamber. Temperature was then equilibrated to 25°C and the gas switched again over to N2, whereupon another measurement was taken for the same reason.

The series of preparation experiments is performed before every sample acquisition, in order to accurately subtract signals/artefacts and baseline changes due to the gas-switching and temperature/pressure changes. Following this, the sample (as a 10 % mull with KBr, required in order to avoid signal saturation) was then loaded into the chamber, and dried again at 110°C for 30 minutes, before switching to N2 (1L min-1) where a sample was measured. The sample was then measured against the previous background to give a highly surface-sensitive evaluation of the pre-existing groups. The spectrometer was baselined again, thus enabling us to detect only the changes in spectra during the CO2 sorption process, enabling the identification of the evolved chemical species. Following reduction in temperature to 75°C, The chamber was then cycled to 10 bar of CO2 and the evolution of the spectrum was evaluated over the course of 60 minutes, thus observing species formed on adsorption. The temperature was reduced to 25°C and was then cycled to N2 and the evolution of the spectrum was evaluated again over the course of 60 minutes, thus observing desorption processes where present. Finally, CO2 desorption was promoted by the cycling to vacuum and the residual surface groups were evaluated by a final spectrum. Given it’s prevalence in the CO2 sorption experiment, a very strong signal corresponding to CO2 centred around 2330 cm-1 and 3600 cm-1 can be observed in the adsorption experiment, as well as in the desorption experiment as a remanent of the high quantities of CO2 employed, as it’s adsorption cross-section is extremely high.

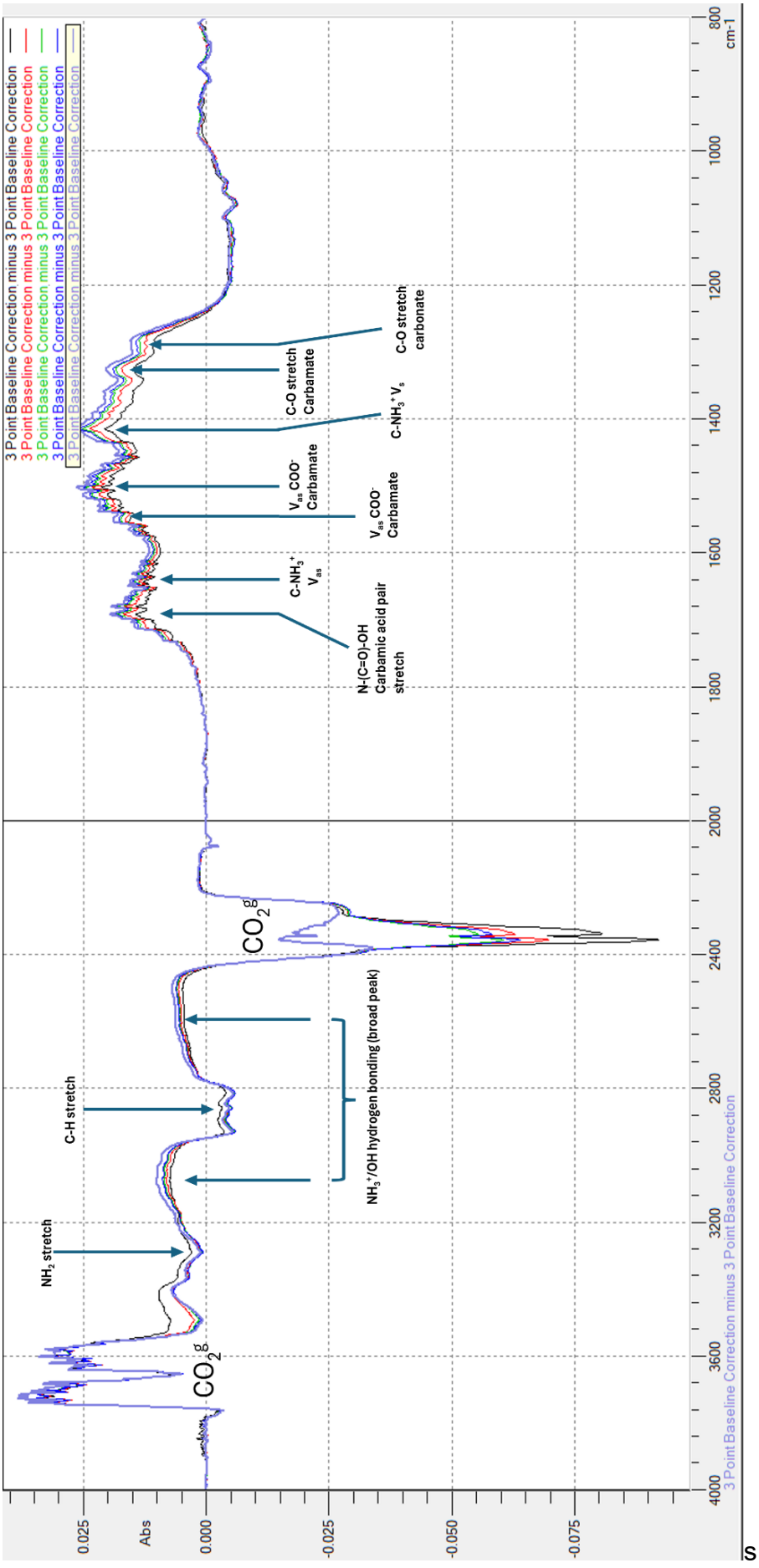
Amine 3.5@Si

Based on literature and company learnings, we are able to identify the spectral evolution of the features as detailed in Table 8. The evolution of the spectrum of Amine 3.5@Si is shown in Figure 11: note that the spectra shown are evolutionary, i.e. baselined to where CO2 were not present, therefore all observed peaks are changes in the spectrum arising from CO2 sorption.

Table 8: Assigned FTIR signals that were used for characterisation of CO2 adsorption by C4C

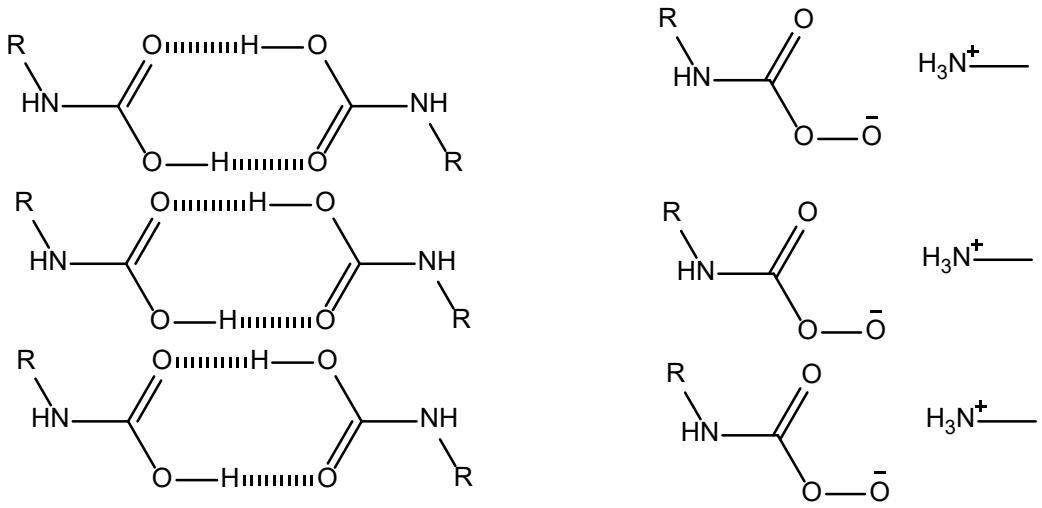
Signal / cm-1	Assignment	Evolution observed during CO2 adsorption at 10 bar
3220	NH2 stretch from amine functionality on AMINE 3.1/Amine 3.5	-ve evolution
Broad peak centred around 3000 cm-1	N-H stretch from -NH3+	+ve evolution
Multiple peaks centred around 2950 cm-1	C-H stretches from alkyl functionalities	-ve evolution
1683	n-(C=O)-OH and carbamate pair	+ve evoltution
1631	C-NH3+ asymmetric stretch	+ve evolution
1568-1575	vas COO- carbamate	+ve evolution
1483	COO- asymmetric stretch	+ve evolution
1409-1486	C-NH3+ symmetric stretch	+ve evolution
1322	COO- carbamate stretch	+ve evolution
1386	C-O stretch - carbamate	+ve evolution
1360	C-O stretch - carbonate	+ve evolution

Figure 6: FTIR spectral evolution of Amine 3.5@Si CO2 adsorption



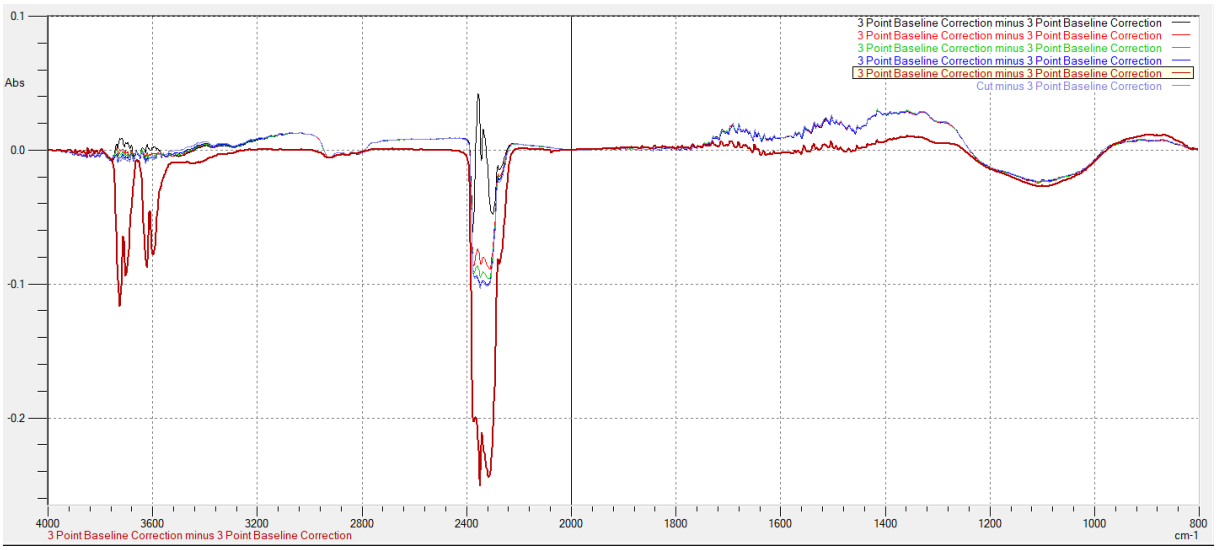
From this experiment we are able to clearly observe the formation of a mixed ammonium carbamate environment, evidenced by the evolution/generation of ammonium (NH3+) and carbamate environments during the CO2 sorption experiment. Interestingly, we were able to identify a particularly blue-shifted carbamate environment at ~1680 cm-1, which from literature can be ascribed to a carbamic acid pair (Figure 12). Given the relatively unstable nature of carbamic acids and their low Pka values (3.72) this could only likely be achieved when representing a dense amine-environment as they are stabilized when near another carbamic acid group.

Figure 12: Formation of carbamates (right) and carbamic acid pairs (left) as evidenced by FTIR spectroscopy.



The desorption process (Figure 13) demonstrated the complete lack of evolution in signals associated with chemisorption of CO2, suggesting that the formed groups are significantly stable under the conditions observed. Even when cycling the chamber to vacuum for 60 minutes, a significant portion of the surfaced-associated ammonium carbamate and carbonates were observed. In the case of Amine 3.5@Si there was no obvious preferential evolution of signals over the course of the 60-minute desorption cycle, nor when cycled to vacuum.

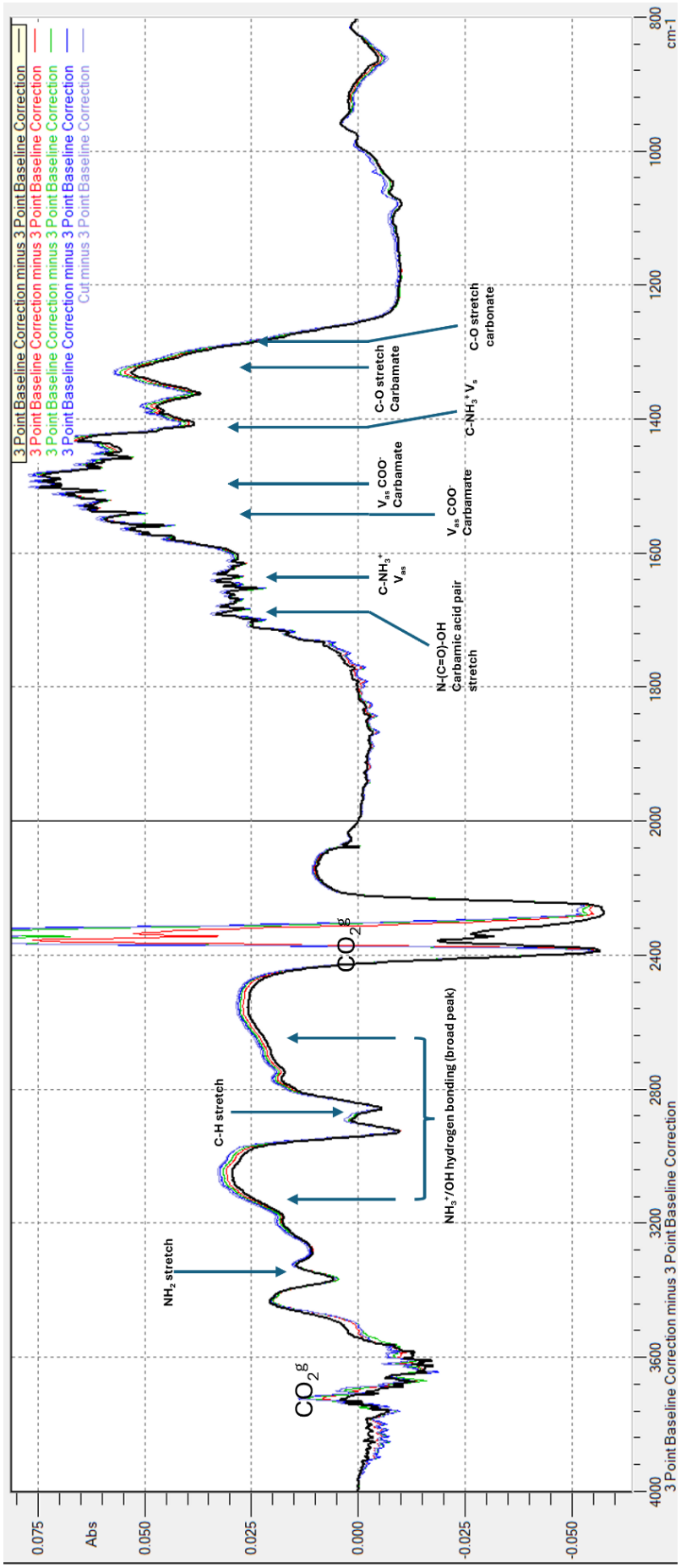
Figure 13: FTIR spectral evolution of Amine 3.5@Si CO2 desorption



AMINE 3.1@Si_0.35 mL

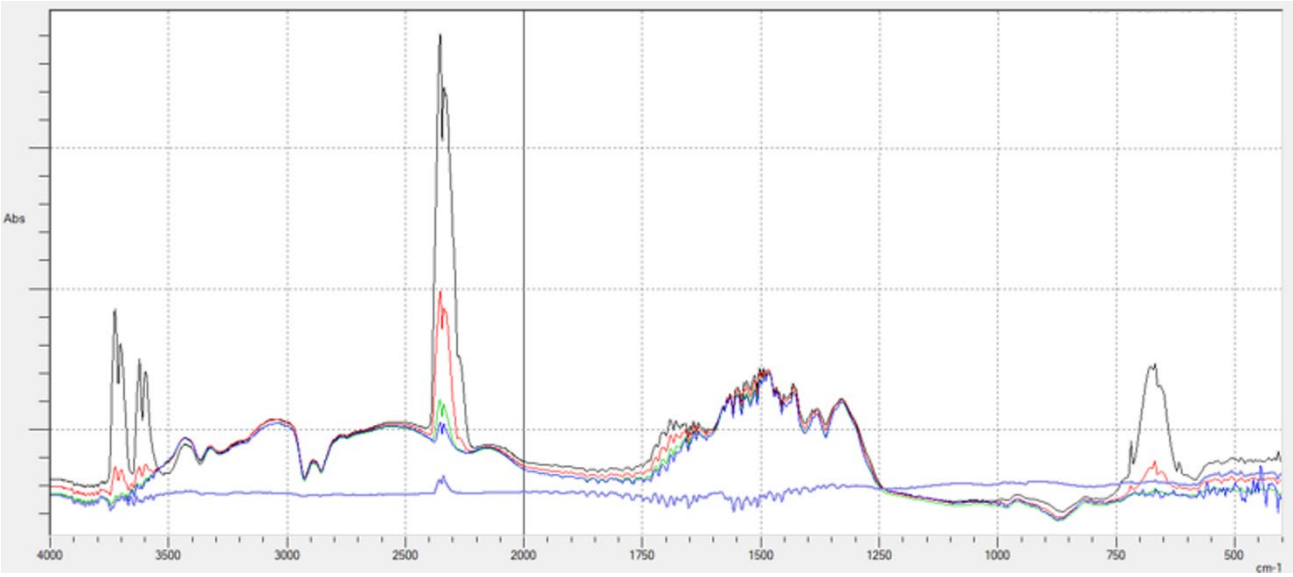
Following CO2 adsorption, AMINE 3.1@Si_0.35 mL exhibited a very similar range of signals corresponding to surface ammonium carbamates and carbamic acid pairs (Figure 14) as seen for Amine 3.5@Si. Comparatively little evolution of these signals was observed, suggesting the rapid saturation of the carrier with CO2 within the course of only a few minutes.

Figure 14: FTIR spectral evolution of AMINE 3.1@Si_0.35 CO2 adsorption



Following desorption under N2 flow at 25°C (Figure 14), an interesting difference can be observed between the evolution of the AMINE 3.1@Si_0.35 mL and Amine 3.5@Si surface chemistries over the course of N2 desorption runs. For AMINE 3.1@Si_0.35 mL, the signal related to the carbamic acid pair was shown to rapidly reduce over the course of 2 hours; a feature not observed for Amine 3.5@Si. Additionally, following treatment at 25°C for 1 minute with high-vacuum the total loss of signals related to CO2 chemisorption was observed.

Figure 14: FTIR spectral evolution of AMINE 3.1@Si_0.35 CO2 desorption



From these investigations, we begin to clarify the relationship between both inter- and intramolecular interactions required for strong CO2 sorption; all related to surface amine density. This supports the hypothesis that when looking at high pressure CO2 sorption, the chemisorption systems are rapidly saturated, with any subsequent evolution likely due to physisorption processes. Furthermore, this research highlights the optimisation performed in the investigation of Amine 3.5@Si as an ideal carrier for the further development within cementitious materials.

Material characterisation – Polymer 1-AMINE 3 amine impregnated materials

AMINE 2 impregnation study

The appropriate quantity of amine was dissolved in methanol, and 0.4 g of the Polymer 1-AMINE 3 precursor was added. The mixture was stirred over 3 hours, and subsequently transferred to a vacuum oven for 40°C under vacuum. The materials were then weighed after drying (Table 9), with recovered quantities closely matching quantitative yields for the materials and resembling the degree to which they were impregnated.

Table 9: Isolated mass of dried POLYMER 1 - AMINE 3-AMINE 2 sample.

Sample	Recovery / g
POLYMER 1 - AMINE 3-AMINE 2 2.5%	0.39
POLYMER 1 - AMINE 3-AMINE 2 5%	0.42
POLYMER 1 - AMINE 3-AMINE 2 13.6%	0.43
POLYMER 1 - AMINE 3-AMINE 2 19.1%	0.48

Material characterisation – scaled up amine impregnated silicas

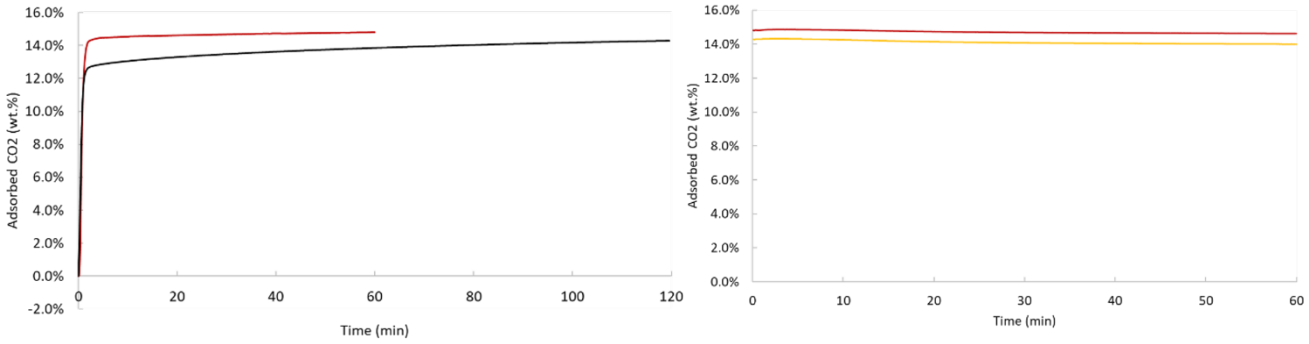
The best performing impregnated silica, Silica 1AMINE 2 50%, was synthesised and characterised as previously reported in WP1 on both small (1 g) and large (100 g) scale. Impregnated materials were washed and characterised by TGA on the previous 1 g scale and 100 g scale to demonstrate the scalability, with amine and moisture content remaining consistent at both small- and large-scale productions (Table 10, Figure 15).

Table 10: Moisture and amine contents of small and large-scale MB AMINE 250%

Sample ID	Moisture Content	Amine Content
MB AMINE 250%-1g	7.36%	44.20%
MB AMINE 250%-100g	8.29%	43.50%

CO2 sorption properties were comparable between small- and large-scale productions of silica 1 AMINE 2 50%, exhibiting comparable (14.2 wt%) CO2 loadings and desorption rates as per the previously reported 1g scale syntheses.

Figure 15: CO2 sorption results for small and large scale reaction products.



These results clearly indicate the scalability of the silica 1 AMINE 2 50% performing sorbent materials, further cementing their place as an ideal CO2 sorbent material.

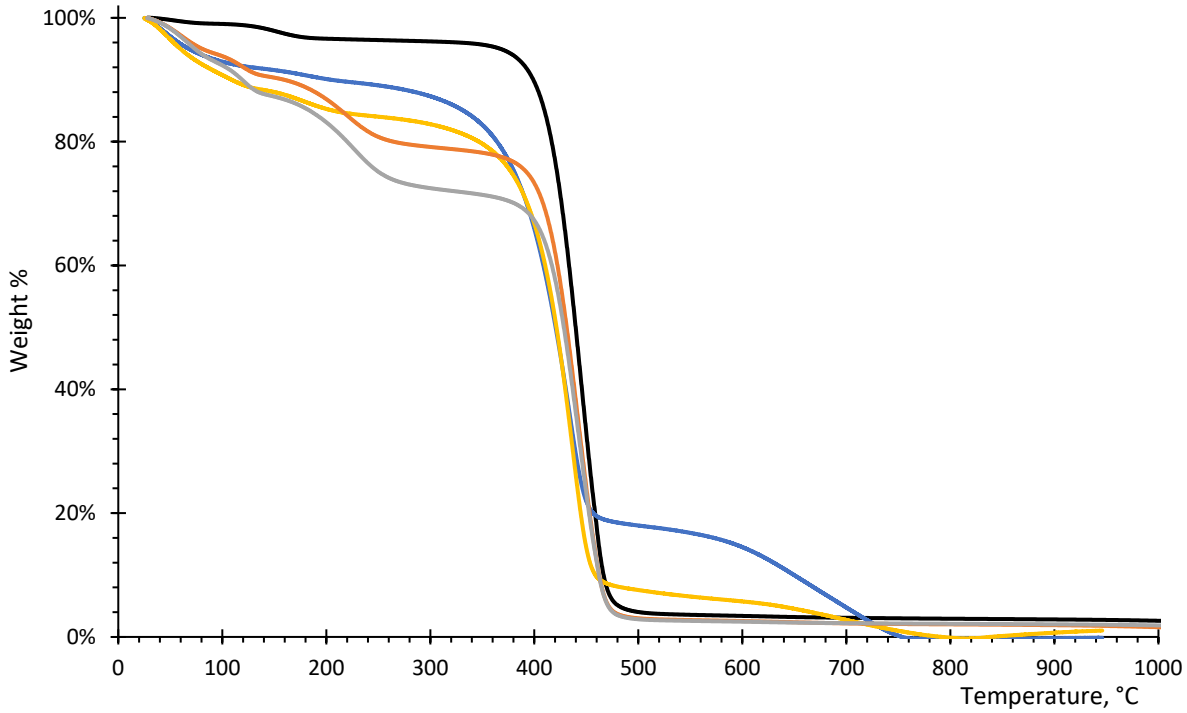
Material characterisation – Polymer 1-AMINE 3 amine impregnated materials

The CO2 sorption experiments were performed using TGA, either Metler Toledo TGA/DSC 3+ or TAI Q500. Impregnated POLYMER 1 - AMINE 3 samples with different amine types and different AMINE 2 loadings were dried at 110°C for 1 h under N2 flow. Then temperature was decreased to 25°C to assess N2 adsorption. Temperature was again increased to 75°C and after 1 h, the gas was switched to ultrapure CO2 for 1h. Then the temperature was decreased to 25°C and after a 45 min temperature stabilisation period, the gas was switched back to N2 to assess CO2 desorption. The CO2 loading was calculated as a percentage of weight against dry weight, which was taken as lowest weight after drying at 100°C and before N2 adsorption at 25°C. The CO2 desorption reading was corrected by subtracting nitrogen loading calculated as the weight gain after 1h under N2 flow at 25°C after drying.

Amine impregnation quantity study

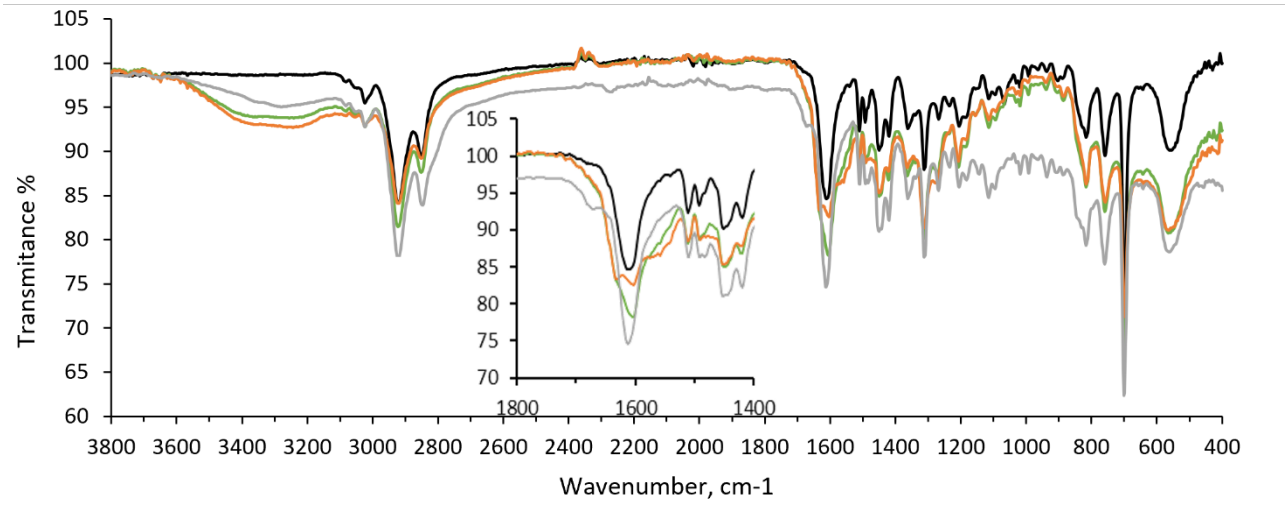
Thermal decomposition study by TGA allows for the comprehensive evaluation and confirmation of the material quantity on the surface of the polymer. In all cases, the increased quantity of AMINE 2 used during the impregnation reaction was reflected in greater mass loss up to 380°C, whereupon the polymer decomposition occurs making it difficult to compare results after this point. Because of this, it is not entirely possible to exactly quantify the amount of AMINE 2 located at the surface of the polymer, however the recovery quantities closely resembled the quantity of AMINE 2 added to the mixture. Nevertheless, it is clear that the amount of AMINE 2 in the functionalisation reaction is reflected in the quantity retained at the surface (Figure 16).

Figure 16: TGA results for Polymer 1-AMINE 3 samples impregnated with AMINE 2. Polymer 1 – Amine 3 (black), Polymer 1 amine 3 – amine 2 2.5% (blue), polymer 1 – amine 3 – amine 2 5% (yellow), polymer 1 – amine 3 – amine 2 13.6% (orange, polymer 1 – amine 3 – amine 2 19.1% (grey).



To evaluate the surface composition, FTIR spectroscopy was employed to evaluate changes in the potential interactions between AMINE 2 and POLYMER 1 - AMINE 3 as the quantity of AMINE 2 on the surface is increased. The FTIR spectra of the AMINE 2 impregnated samples closely resemble that of AMINE 2 (in particular N-H/NH+ stretches at ~3200 cm-1) and the parent POLYMER 1 - AMINE 3 material, especially at low-loadings (Figure 17). However, as the quantity of AMINE 2 on the surface is increased, a shift in the peak at 1610 cm-1 corresponding to the C=N stretch of the AMINE 3 polymer, which is progressively blue-shifted suggesting a significant interaction between the AMINE 3 polymer and the AMINE 2 material. This could suggest that at higher loadings the bond energies of the AMINE 3 base increase, reducing the basicity and producing a potentially more difficult to protonate system, which could affect CO2 capacity.

Figure 17: FTIR results for Polymer 1-AMINE 3 samples impregnated with AMINE 2.



The CO2 sorption properties of the amine impregnated samples produced in this study can be found in Table 11. Ambient pressure CO2 sorption was evaluated by TGA at 25 and 75°C as detailed in section 3.8. CO2 capacities of the lower-impregnation loaded samples POLYMER 1 - AMINE 3-AMINE 2 2.5% and POLYMER 1 - AMINE 3-TPA 5% demonstrated poorer CO2 capacities and similar loadings at ambient pressure, however investigations into high-pressure CO2 loading demonstrated a significant increase in CO2 capacity to a much greater extent that observed for that seen in the higher AMINE 2 loadings. CO2 retention of the POLYMER 1 - AMINE 3-AMINE 2 2.5% condition was shown to be almost total following 1h, representing a significant optimisation over the carriers developed in WP1.

Table 11: CO2 capacities for POLYMER 1 - AMINE 3 samples impregnated with AMINE 2.

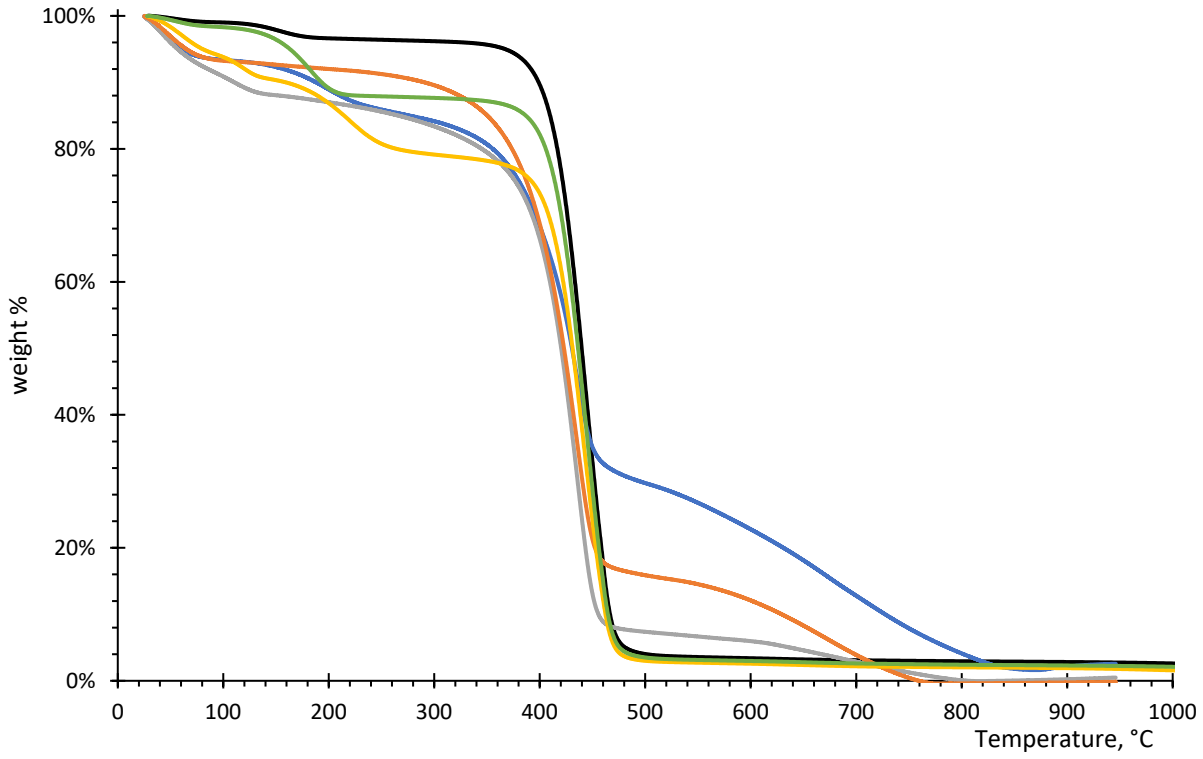
	TGA			Autoclave 10 bar	
	CO2 capacity at 75°C	CO2 capacity at 25°C	Retained CO2 loading after 1 H	CO2 capacity immediate	CO2 capacity after 1 h
POLYMER 1 - AMINE 3-AMINE 2 2.5%	0.9%	1.6%	1.1%	20.8%	20.8%
POLYMER 1 - AMINE 3-AMINE 2 5%	1.9%	2.8%	2.2%	21.6%	13.4%
POLYMER 1 - AMINE 3-AMINE 2 13.6%	2.3%	3.5%	2.0%	10.7%	10.0%

	TGA			Autoclave 10 bar	
	CO2 capacity at 75°C	CO2 capacity at 25°C	Retained CO2 loading after 1 H	CO2 capacity immediate	CO2 capacity after 1 h
POLYMER 1 - AMINE 3-AMINE 2 19.1%	2.0%	2.9%	1.6%	11.7%	10.9%

Amine identity optimisation

Thermal decomposition study by TGA allows for the comprehensive evaluation and confirmation of the material quantity on the surface of the polymer: whereby in all cases, thermal decomposition of the amine was observable up to 380°C, whereupon the polymer decomposition occurs making it difficult to compare results after this point. It is therefore not possible to exactly quantify the amount of amine located at the polymer surface: however, in all cases amine decomposition can be observed at temperatures corresponding to the decomposition temperatures of the parent amine species (Figure 18).

Figure 18: TGA results for Polymer 1-AMINE 3 samples impregnated with amines. Polymer 1 – amine 3 (black), Polymer 1 – Amine 3 – amine 3.4 (blue), Polymer 1 amine 3 – amine 1 (grey), Polymer 1 – amine 3 – amine 4 (orange), polymer 1 – amine 3 – amine 2 (yellow), polymer 1 – amine 3 – liq (green).



In a more effective investigation looking at the changes in surface chemistries of the various amine-impregnated materials, FTIR analyses of the original and impregnated POLYMER 1 - AMINE 3 were conducted using a Fourier transform infrared (FTIR) spectrometer (IRXross, Shimadzu). Impregnated samples show changes in IR spectra compared to pure POLYMER 1 - AMINE 3. Impregnated samples show a broad peak at 3300 cm-1, typical for primary amines. The POLYMER 1 - AMINE 3-AMINE 4 has less pronounced peak, the presence of which can be attributed to residual methanol, as nitrogen is tertiary. The strong C=N peak seen at 1610 cm-1 in pure POLYMER 1 - AMINE 3 becomes wider or splits in two at 1631 and 1558 cm-1 in impregnated samples. The shifted peak at higher wavenumbers is attributed to C=N+ forms of protonated AMINE 3H. Amine 5has an additional O-H bending peak at 1373 cm-1.

Figure 19: FTIR results for POLYMER 1 - AMINE 3 samples nitrogen enhanced. Polymer 1 – amine 3 (black), polymer 1 – amine 3 – amine 1 (orange)

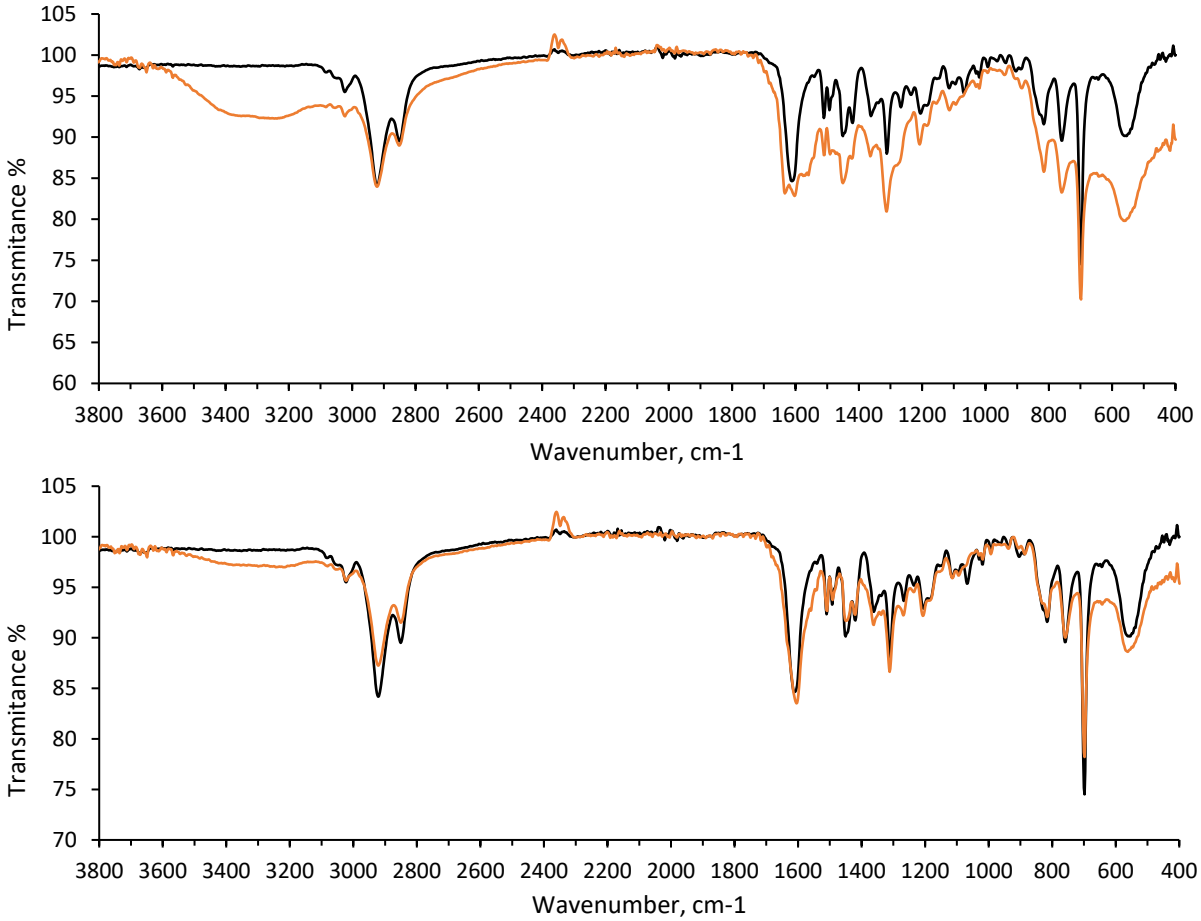


Figure 20. FTIR results for POLYMER 1 - AMINE 3 samples impregnated with nitrogen enhanced. Polymer 1 – amine 3 (black), polymer 1 – amine 3 – amine 4 (orange)

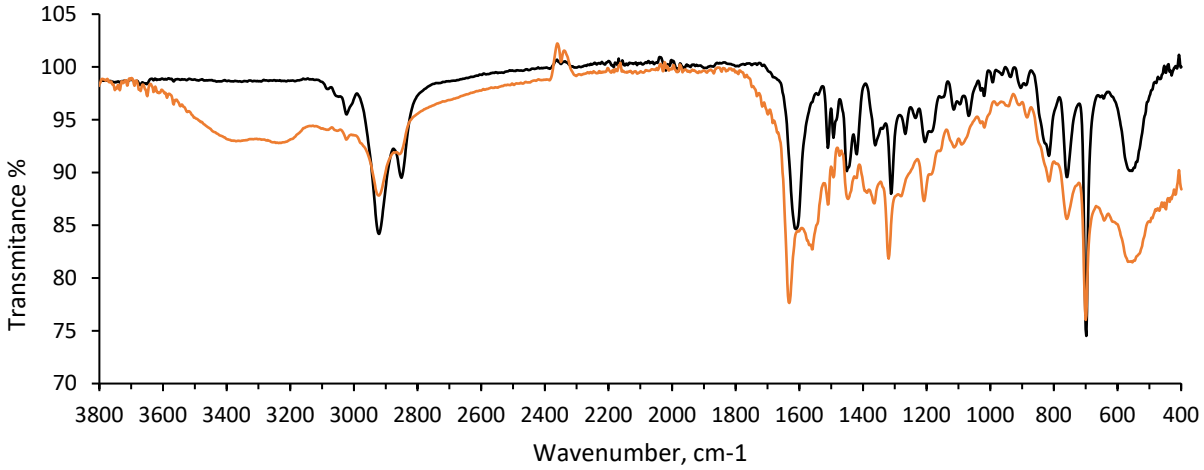


Figure 21. FTIR results for POLYMER 1 - AMINE 3 samples impregnated with nitrogen enhanced. Polymer 1 – amine 3 (black), polymer 1 – amine 3 – amine 3.4 (orange)

FTIR evaluation clearly demonstrates the presence of the respective amines on the POLYMER 1 - AMINE 3 precursors, confirming functionalisation and evidencing their production as specified. The CO2 capacity at 75 and 25°C and CO2 loading after 1 h desorption under N2 flow is given in Section 3. Figure 22 shows CO2 desorption profiles versus time. From normalised CO2 desorption (Figure 20), it is clearly seen that impregnation of POLYMER 1 - AMINE 3 with amines slows down CO2 release. The slow release of CO2 may be attributed to stable carbamate salt formation. Impregnation with AMINE 1 results in highest CO2 uptake as well as slowest release. Amine 5decreases CO2 uptake and does not affect desorption rate considerably. AMINE 4 being a tertiary amine protected by ethylene groups also has insignificant effect on desorption rate and CO2 loading is even decreased. Although nitrogen in amine 3 unspired liq also is tertiary it is more exposed than in AMINE 4 and can contribute to higher loadings, however its CO2 retention is poorer than that of AMINE 2 and AMINE 1. The performance of different amines according to CO2 release rate is as follows: AMINE 1 – AMINE 2 – IMI – AMINE 4 – DA.

Table 12: CO2 capacities for POLYMER 1 - AMINE 3 samples impregnated with amines.

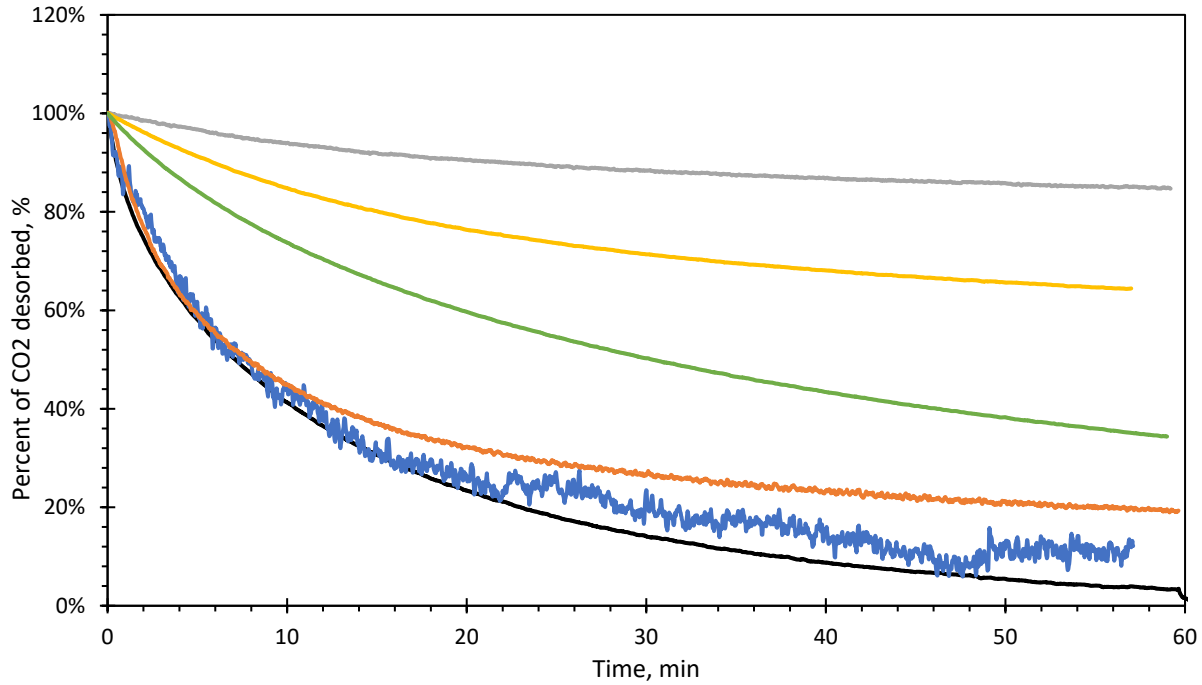
	TGA			Autoclave 10 bar	
	CO2 capacity at 75°C	CO2 capacity at 25°C	Retained CO2 loading	CO2 capacity immediate	CO2 capacity after 1 h
Polymer 1-AMINE 3		3.7%	0.3%	4.7%	3.5%
Polymer 1-AMINE polymer 1 - AMINE 1	2.6%	3.8%	3.0%	17.1%	16.5%
Polymer 1-AMINE 3-Amine 3.4	0.0%	0.4%	0.0%	14.1%	11.1%
Polymer 1-AMINE 3-AMINE 4	0.1%	0.5%	0.1%	22.5%	18.1%
Polymer 1-AMINE 3-Liq		3.9%	1.2%	9.3%	8.5%

Carrier	CO2 capacity (75 °C)	CO2 capacity (25 °C)	CO2 retention (48 hr/480 hr)	Time for 100% CO2 desorption
Polymer 1-AMINE 3	-	3.7%	-	72.1 min
Polymer 1-AMINE 3-AMINE 1	2.6%	3.8%	64.6 % / 52.4 %	-

Carrier	CO2 capacity (75 °C)	CO2 capacity (25 °C)	CO2 retention (48 hr/480 hr)	Time for 100% CO2 desorption
Polymer 1-AMINE 3-Amine 3.4	-	0.4%	-	624.7 min
Polymer 1-AMINE 3-AMINE 4	0.1 %	0.5%	-	417.1 min
Polymer 1-AMINE 3-Liq	-	3.9%	-	261.1 min

Carrier	CO2 capacity (immediate)	CO2 capacity (after 1 hour)
Polymer 1-AMINE 3	4.7%	3.5%
Polymer 1-AMINE 3-AMINE 1	17.1%	16.5%
Polymer 1-AMINE 3-Amine 3.4	14.1%	11.1%
POLYMER 1 - AMINE 3-AMINE 4	22.5%	18.1%
Polymer 1-AMINE 3-Liq	9.3%	8.5%

Figure 22: CO2 desorption for POLYMER 1 - AMINE 3 samples impregnated with amines. Polymer 1 – Amine 3 (black), Polymer 1 – Amine 3 – amine 3.4 (blue), Polymer 1 – Amine 3 – amine 1 (grey), Polymer 1 – Amine 3 – amine 4 (orange), Polymer 1 – Amine 3 – amine 2 (yellow), Polymer 1 – Amine 3 – liq (green)



For high pressure experiments, samples were placed into autoclave, flushed for 1 min with ultrapure CO2, closed and pressurised to 10 bar with ultrapure CO2 and left for 3 days. After opening, the weight of each sample was recorded immediately and after 1h using precision balance. The weight gain after autoclave and weight change was attributed to CO2 and calculated as a weight percent of sample's weight before autoclave, assuming adsorption of moisture and other gases are negligible compared to CO2. All impregnated samples adsorbed considerably larger CO2 amounts than at 1 bar. Surprisingly, AMINE 4 impregnated sample adsorbed the most CO2, even though at 1 bar its capacity was negligible. Similarly, DA adsorbed considerable 14%, more than equivalent AMINE 2, even though at 1 bar its capacity was lower than that of pure POLYMER 1 - AMINE 3. This suggests that amines form a dense layer that CO2 cannot penetrate at 1 bar. Among AMINE 2 impregnated samples, the POLYMER 1 - AMINE 3-AMINE 2 2.5% and 5 % adsorbed more CO2 than those impregnated with higher AMINE 2 loadings.

From these results it is apparent that both amine identity and impregnation quantity are effective ways of controlling CO2 release from AMINE 3-PS based carriers. However, AMINE 2 impregnation still appears to give the optimal results.

Results summary

During the optimisation process detailed in WP2.1, several key developments have been made:

- The synthesis of large-scale amine impregnated carriers on a 100 g scale was demonstrated, exhibiting comparatively high (>14% CO2) loadings, showing the compatibility of this carrier stream with large scale production
- Amine grafted silicas materials were further optimized through the evaluation of the ideal synthesis conditions (via the surface loading screen), achieving extensively improved CO2 adsorption capacities (up to 11%). Further optimisation with other amine materials led to the best-in-class amine grafted silica: Amine 3.5@Si, achieving 13.8 wt% adsorption and extremely high CO2 retention.
- Polymer 1-AMINE 3 was subjected to a similar optimisation process with the loading screen exhibiting particularly enhanced CO2 sorption properties: up to over 20 wt% CO2 capacity compared to previous iterations. Modulating amine identity also appeared to yield a AMINE 1 impregnated Polymer 1-AMINE 3 which exhibited greatly slowed desorption of CO2 in comparison to the AMINE 2 modified materials, albeit at a cost in CO2 sorption capacity.

In all cases, further interactions of materials will continue to be developed as the focus and requirements of the project develop further: with a specific focus on stability and CO2 retention in cementitious and simulated environments. In this work package, a demonstrated strategy to achieve optimisation with the carriers investigated is thoroughly exemplified, paving the way for further development of CO2 carriers as per the scope of this project.

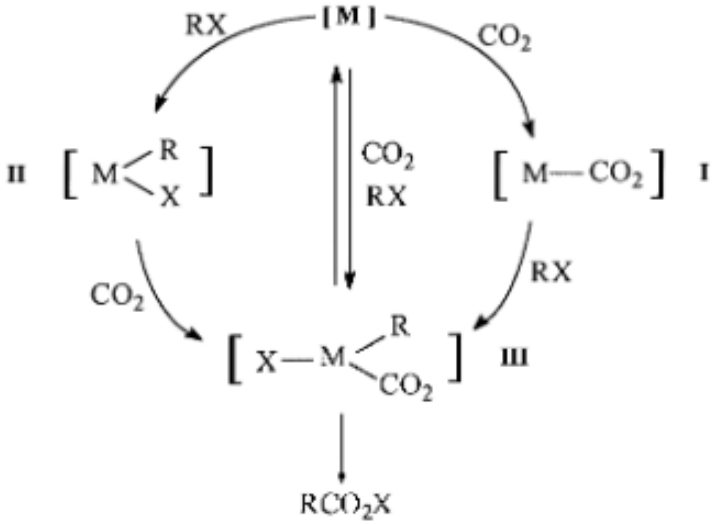
Work Package 2.2 – Investigate dopants to minimise desorption of CO2 (objective: control/slow-release rate)

Doping (introduction of heteroatoms to a material matrix) was investigated as a complementary strategy towards the optimisation of CO2 release rates. By doping the materials used, we can alter the desorption chemistries and change the rates of desorption based on the doping strategy. BET as a methodology was not of particular importance as the goals here are not to modify surface areas or pore-morphologies of the associated carriers.

The doping of the amine grafted carrier systems was identified as an important potential route to further developing strategies to improve and evaluate potential carriers for use in complex CO2 capture and delivery mechanisms. Doping through the incorporation of metal ions within the structure of the amine-functionalised surfaces was investigated due to fulfilment of several global parameters: non-toxicity, cement compatibility and low-cost.

CO2 as a molecule is intensively stable and typically requires a significant degree of 'activation' to interact with other chemical species (Figure 23).1 In comparison with organic species, the availability for redox-cycling, changes in spin-multiplicity and back-pi-bonding make metal ions extremely ideal for the capture of CO2 in such systems. In the case of amine-grafted silicas, metal ions aid the CO2 capture process- shortening reaction times, increasing capacities due to the activation of CO2 and the facilitation of CO2 chemisorption. This could have a significant benefit on the energetic requirements of the CO2 sorbent system upon absorption.

Figure 23: Example of CO2 activation[1]



In addition, the CO2 interaction of certain metal ions lend themselves to providing another route to the CO2 release of materials through the formation of metastable, insoluble metal carbonates. These species can provide an alternative route for CO2 to release to instead of being released to air, or to cement where relevant. As a result, both in-air, and in simulated environments (to be performed in subsequent work-packages), metal-doping of amine-grafted silicas was an appropriate and valuable investigative step in the development of carrier materials with slowed CO2 release rates. A plethora of metal ions are known to elicit activation of CO2, such as: Pt,[2] Rh,[1] Cu,[1] [3] Ni,[1] Zn[4] and Au[5]. The exact nature of the metal-ion's coordination to CO2 is vastly dependent on the metal properties and environment. However,

[1] X. Yin and J. R. Moss, Recent developments in the activation of carbon dioxide by metal complexes, 1999, vol. 181
[2] E. S. Gutterød, A. Lazzarini, T. Fjermestad, G. Kaur, M. Manzoli, S. Bordiga, S. Svelle, K. P. Lillerud, E. Skúlason, S. Øien-Ødegaard, A. Nova and U. Olsbye, J Am Chem Soc, 2020, 142, 999–1009
[3] J. Zhao, S. Xue, J. Barber, Y. Zhou, J. Meng and X. Ke, J. Mater. Chem. A, 2020, 8, 4700–4734
[4] J. Tapiador, P. Leo, A. Rodríguez-Diéguez, D. Choquesillo-Lazarte, G. Calleja and G. Orcajo, Catal Today, 2022, 390–391, 230–236
[5] S. Chen and A. Chen, The Journal of Physical Chemistry C, 2019, 123, 23898–23906

from the initial list demonstrated here, only two metal candidates fulfil the requirements of low cost and toxicity: Cu and Zn. Based on this, the initial investigation conducted during this work-package was focused on the introductions of these metal ions to an amine-grafted silica system.

Metal ion doping of amine grafted materials was conducted though utilizing the chelating properties of the Amine 3.5amine 3.5@Si system, whereby the bidentate diamine species can act as a ligand to coordinate to both Cu and Zn systems.

Both metals were employed as their divalent ions, Cu2+ and Zn2+ respectively, where are known to favour 4-coordinate systems dominated by a square-planar and tetrahedral geometry. However, given the d10 electron configuration of the Zn2+ system, it has no strong preference for coordination geometry and exhibits a more-flexible coordination system. Both metal ions are known to produce insoluble carbonates: CuCO3 and ZnCO3 respectively, which, when formed in conditions such as at the surface of amine-grafted materials could exhibit greatly slowed CO2 release to the environment.

In both cases metal ion doping was conducted at high- and low- doping levels to examine the effect on the surface chemistry and CO2 sorption properties.

Metal-doped amine functionalised silicas

Synthesis of metal-doped amine functionalised silica

Cu2+ and Zn2+ doped variants of Amine 3.5@Si were prepared by stirring Amine 3.5@Si in aqueous solutions of CuCl2 and ZnCl2 (starting materials shown in Figure 24).

Figure 24: CuCl2 (left), ZnCl2 (middle), Amine 3.5@Si (right)

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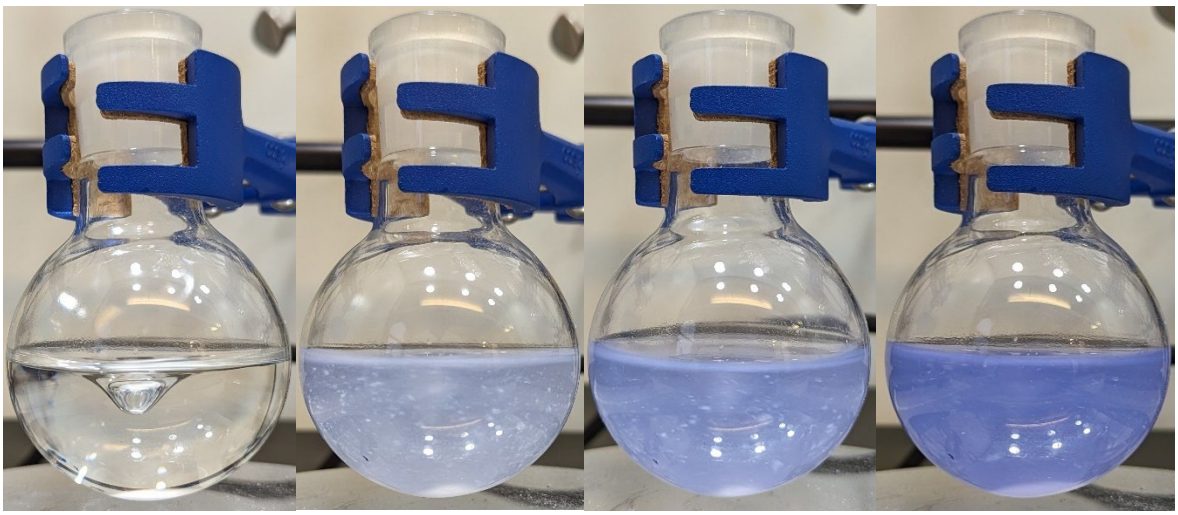
Synthesis of Amine 3.5@Si-Cu1mM

A 1 mM solution of CuCl2 was prepared by adding deionised water (50 mL) and CuCl2 (0.007g) to a round bottomed flask, and stirring the mixture. To this solution, Amine 3.5@Si (0.10 g) was added, and the reaction mixture was stirred at room temperature for 2 hours. Over the course of the reaction, the clear starting solution changed colour, progressively

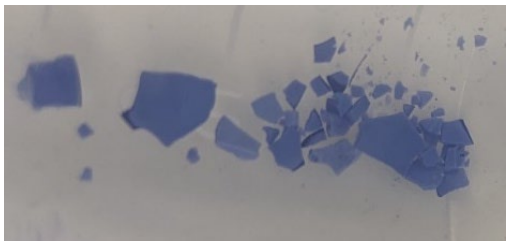
appearing a darker shade of purple. The appearance of the reaction solution over time is shown in Figure 25.

Figure25: Evolution of reaction mixture during synthesis of Amine 3.5amine 3.5@Si-Cu1mM



The reaction mixture was decanted into a centrifuge tube, where the solid product was isolated by centrifugation (6000 rpm, 30 minutes). The wet solid was subsequently dried at 70°C under vacuum to afford a lilac solid product (Amine 3.5amine 3.5@Si-Cu1mM, Figure 26).

Figure 7: Amine 3.5@Si-Cu1mM



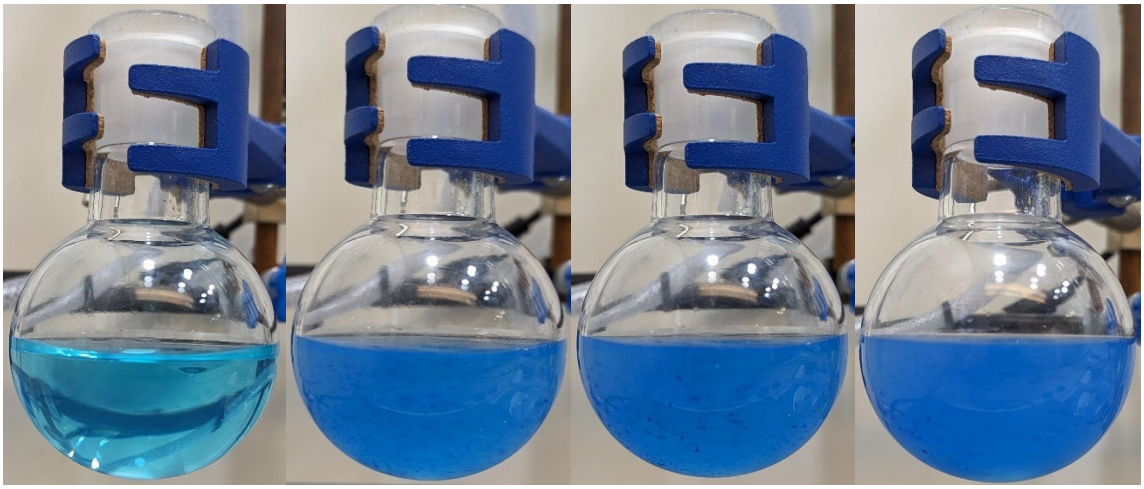
While the concentration of the starting CuCl2 solution is too weak to show a distinct colour, over time the reaction solution turns lilac in colour (Figure 24). This is a result of grafted amine groups of Amine 3.5@Si leaching into the reaction solution, and forming co-ordination complexes with Cu2+ ions, which absorb specific wavelengths of light to appear coloured. The lilac appearance of the product solid (Figure 36) shows that Cu2+ doped amine groups are still grafted to the surface of the Amine 3.5@Si support, as immobilised ammino-copper complexes give the product its distinct colour compared to the white colour of the parent Amine 3.5@Si support material.

Synthesis of Amine 3.5@Si-Cu100mM

A 100 mM solution of CuCl2 was prepared by adding deionised water (50 mL) and CuCl2 (0.672 g) to a round bottomed flask, and stirring the mixture. To this solution, Amine 3.5@Si (0.10 g) was added, and the reaction mixture was stirred at room temperature for 2 hours. Over the course of the reaction, the light blue starting solution progressively became a darker

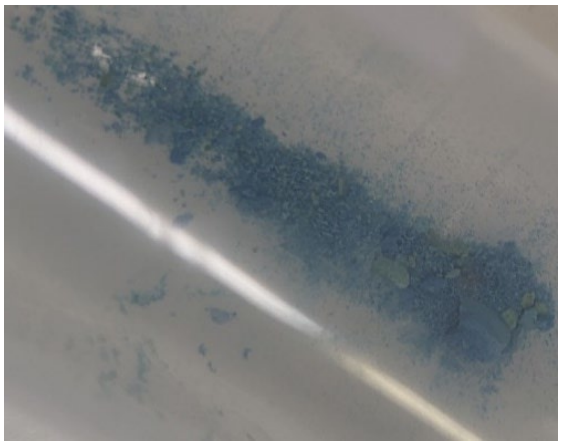
blue colour, and the colour of the pre reaction Amine 3.5@Si appeared to change from white to blue. The appearance of the reaction mixture over time is shown in Figure 27.

Figure 8: Evolution of reaction mixture during synthesis of Amine 3.5@Si-Cu100mM



The reaction mixture was decanted into a centrifuge tube, where the solid product was isolated by centrifugation (6000 rpm, 30 minutes). The wet solid was subsequently dried at 70°C under vacuum to afford a blue solid product (Amine 3.5@Si-Cu100mM, Figure 28)

Figure 9: Amine 3.5@Si-Cu100mM

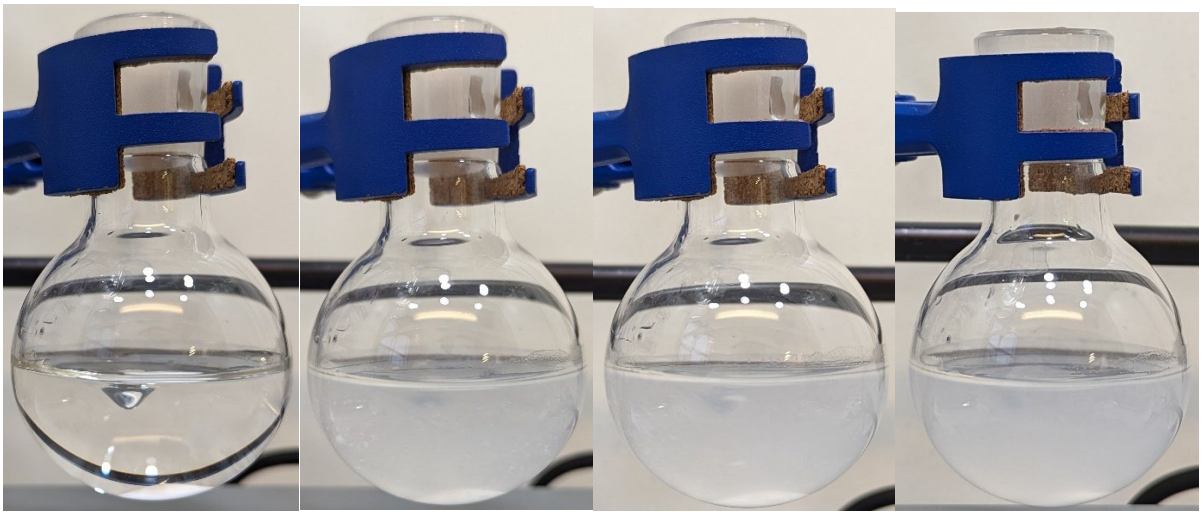


On introduction to water, the brown CuCl2 starting material (Figure 34) forms the corresponding hexahydrate complex, leading to the observed colour change from brown starting solid to blue solution (Figure 37). Grafted amine groups on Amine 3.5@Si coordinate with Cu2+ ions in solution, producing immobilised complexes that absorb characteristic wavelengths of light, resulting in the blue colour of Amine 3.5@Cu100nM product, compared to the white appearance of the parent Amine 3.5@Si. This is evidence that the parent amine-grafted silica sorbent was successfully doped with Cu2+ ions.

Synthesis of Amine 3.5@Si-Zn1mM

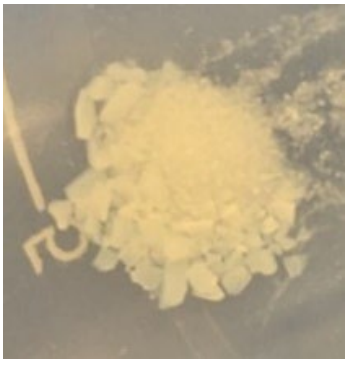
A 1 mM solution of ZnCl2 was prepared by adding deionised water (50 mL) and ZrCl2 (0.008 g) to a round bottomed flask, and stirring the mixture. To this solution, Amine 3.5@Si (0.10 g) was added, and the reaction mixture was stirred at room temperature for 2 hours. No significant colour change was observed during the course of the reaction (Figure 29).

Figure 10: Evolution of reaction mixture during synthesis of Amine 3.5@Si-Zn1mM



The reaction mixture was decanted into a centrifuge tube, where the solid product was isolated by centrifugation (6000 rpm, 30 minutes). The wet solid was subsequently dried at 70°C under vacuum to afford a white solid product (Amine 3.5@Si-Zn1mM, Figure 30).

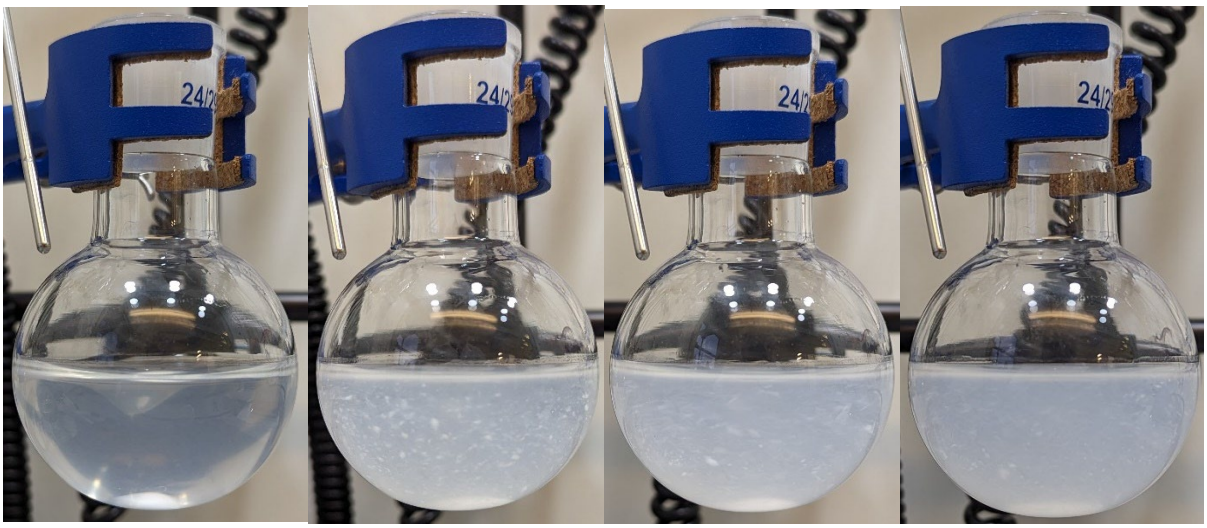
Figure 30: Amine 3.5@Si-Zn1mM



Synthesis of Amine 3.5@Si-Zn100mM

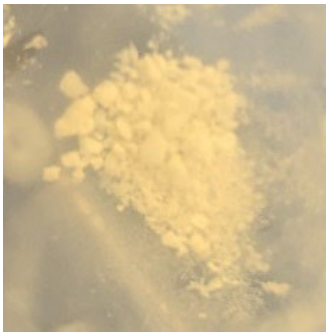
A 100 mM solution of ZnCl2 was prepared by adding deionised water (50 mL) and ZrCl2 (0.685g) to a round bottomed flask, and stirring the mixture. To this solution, Amine 3.5@Si (0.10 g) was added, and the reaction mixture was stirred at room temperature for 2 hours. No significant colour change was observed during the course of the reaction (Figure 31).

Figure 11: Evolution of reaction mixture during synthesis of Amine 3.5@Si-Zn100mM



The reaction mixture was decanted into a centrifuge tube, where the solid product was isolated by centrifugation (6000 rpm, 30 minutes). The wet solid was subsequently dried at 70°C under vacuum to afford a white solid product (Amine 3.5@Si-Zn100mM, Figure 32)

Figure 12: Amine 3.5@Si-Zn100mM



Thermal decomposition TGA characterisation

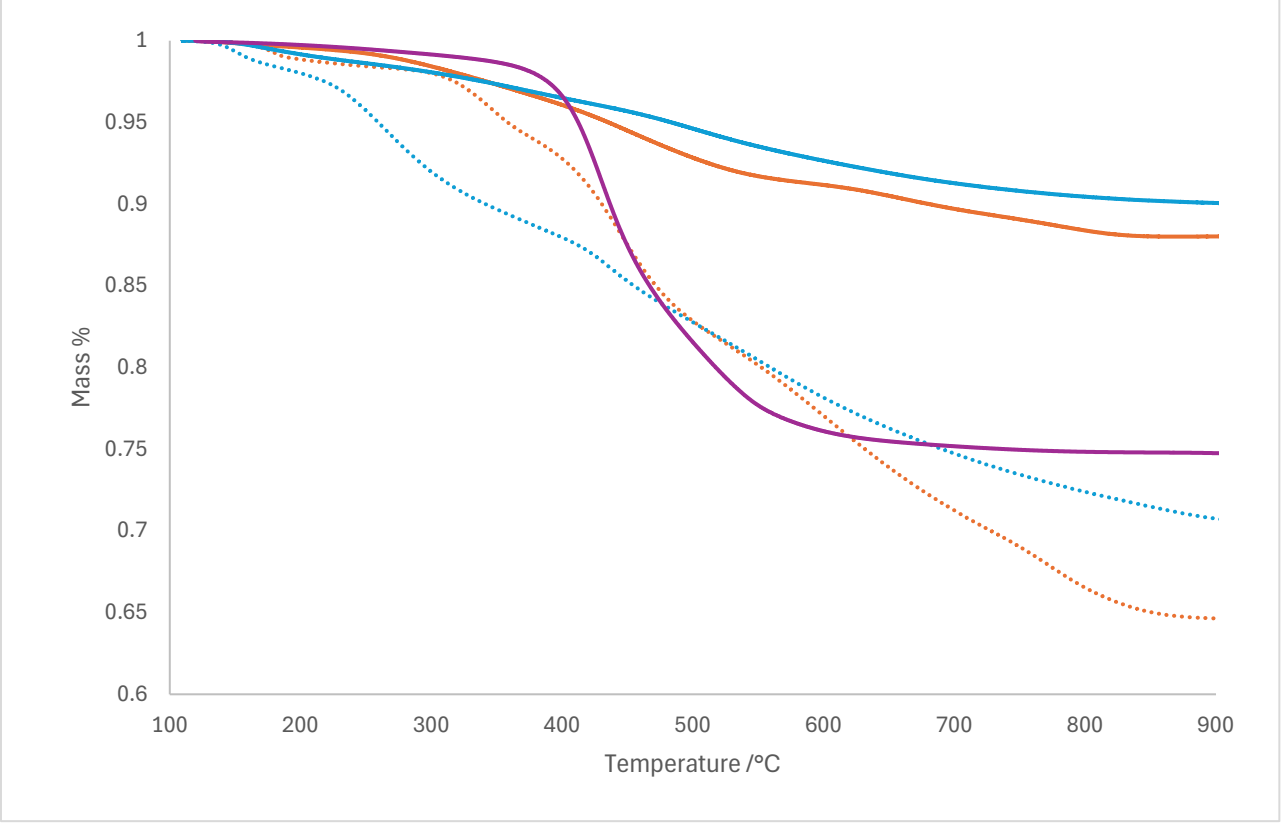
The produced metal doped amine functionalised silicas were characterised by TGA decomposition to evaluate changes in surface-loading of material during the functionalisation reaction, as well as FTIR to evaluate changes in the chemical surface composition.

TGA evaluation of surface loading (Figure 33), demonstrated a significant departure from the characteristics of the parent amine-grafted silicas: low metal ion-doping demonstrated a reduction in mass loss over the 400-800°C region (Table 13). Given the expected variability in surface chemistry it was not possible to calculate an exact mmol/g loading of amine-metal ion complexes, thus they are presented as weight percentages. The parent Amine 3.5@Si is present as described in section 3 of this report as comparison.

Table 13: Surface loading calculated from mass loss between 400 and 800°C from TGA results

Sample	Loading / wt%
Amine 3.5@Si	24.96
Amine 3.5@Si-Cu1mM	9.55
Amine 3.5@Si-Cu100mM	27.62
Amine 3.5@Si-Zn1mM	11.62
Amine 3.5@Si-Zn100mM	33.68

Figure 13: TGA thermal decomposition results for doped silicas. Purple: Amine 3.5@Si (for reference), orange solid line: Amine 3.5@Si-Zn1mM, blue solid line: Amine 3.5@Si-Cu1mM, orange dotted line: Amine 3.5@Si-Cu100mM, blue dotted line: Amine 3.5@Si-Zn100mM



For the low-doping conditions, a significant decrease in the loading of surface species was observed. This suggests that the metal loading conditions investigated significantly impacted the degree of surface located amine. For the high-doping conditions, a significant increase in

surface loading was observed. This suggests that the surface loading and surface properties of the materials is significantly impacted by the doping methodology, initially suggesting that at low-doping conditions this led to the removal of surface loaded material. The metal ion choice seemed to exhibit a significant impact: with Zn resulting in comparatively higher surface loadings in both cases, likely due to the facilitation of oxidation associated with utilizing Cu2+.

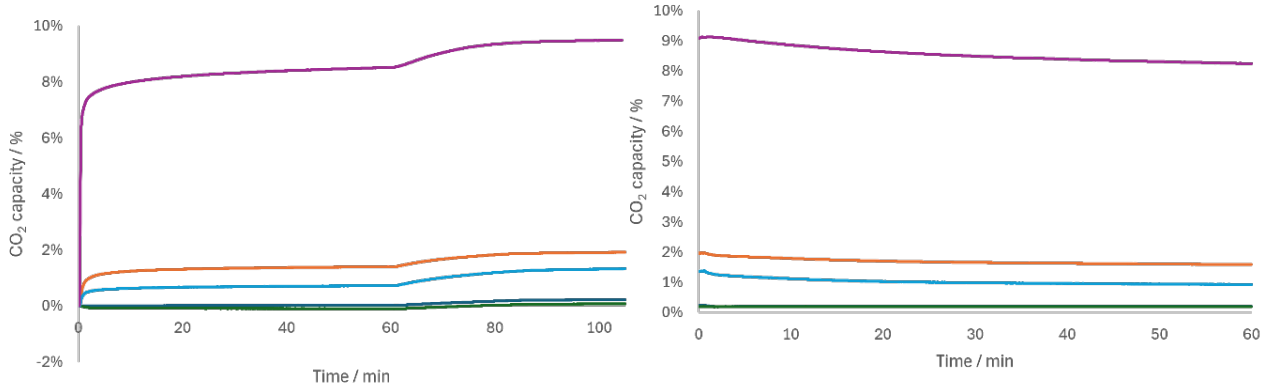
CO2 sorption profiles of metal-doped amine functionalised silicas

CO2 adsorption (Figure 44) and CO2 desorption (Figure 34) were investigated according to a two-temperature sorption investigation at atmospheric pressure, to investigate CO2 chemisorption (75°C) and CO2 physisorption (25°C), summarised by Table 14. Both low- and high-doping conditions demonstrated significantly altered CO2 sorption properties following metal doping. The 'low' doped materials exhibited reduced CO2 adsorption compared to the parent Amine 3.5@Si amine grafted species, both in chemi- and physisorption. High doping conditions appeared to demonstrate the almost complete abrogation of CO2 chemisorption, with practically no observable chemisorption.

Table 14: CO2 capacities of doped silicas

Sample	CO2 capacity (Chemisorb)
Amine 3.5@Si	9.50 (8.75)
Amine 3.5@Si-Cu1mM	1.36 (0.77)
Amine 3.5@Si-Cu100mM	0.17 (0)
Amine 3.5@Si-Zn1mM	1.96(1.45)
Amine 3.5@Si-Zn100mM	0.20 (0.03)

Figure 14: (left) CO2 sorption for doped silicas by TGA (25°C, 1 h, CO2 99.995%). (right) desorption of CO2 under nitrogen using TGA (25°C, 2 h, N2). Purple: Amine 3.5@Si (for reference), orange: Amine 3.5@Si-Zn1mM, blue: Amine 3.5@Si-Cu1mM, Green: Amine 3.5@Si-Cu100mM, turquoise: Amine 3.5@Si-Zn100mM



However, despite the significant impact on CO2 adsorption, the low-doping conditions exhibited significantly improved CO2 desorption rates (i.e. reduced) as evidenced by the reduction in gradient of the CO2 release curves. Particularly, the Amine 3.5@Si-Zn1mM desorption was observed at a particularly slow rate, retaining almost all of the chemi- and physiosorbed CO2. Extrapolations were not performed due to the extremely poor capacity performance of the carriers, meaning that no matter what the desorption times were, they would not represent suitable materials.

These results suggest that whilst metal-ion doping of the amine-grafted carrier negatively impacted the CO2 adsorption capacity, likely as a result of the cleavage of surface amine during the CO2 sorption experiment, CO2 desorption rates are significantly improved. These results suggest the future development of alternating the sources of metal ion impregnation, improving the resistance of the grafting conditions to the metal doping experiment are potential routes to the further development of these materials as carriers. Nevertheless, unless adsorption capacities can be significantly improved, the doping in this manner is unlikely to be a viable option.

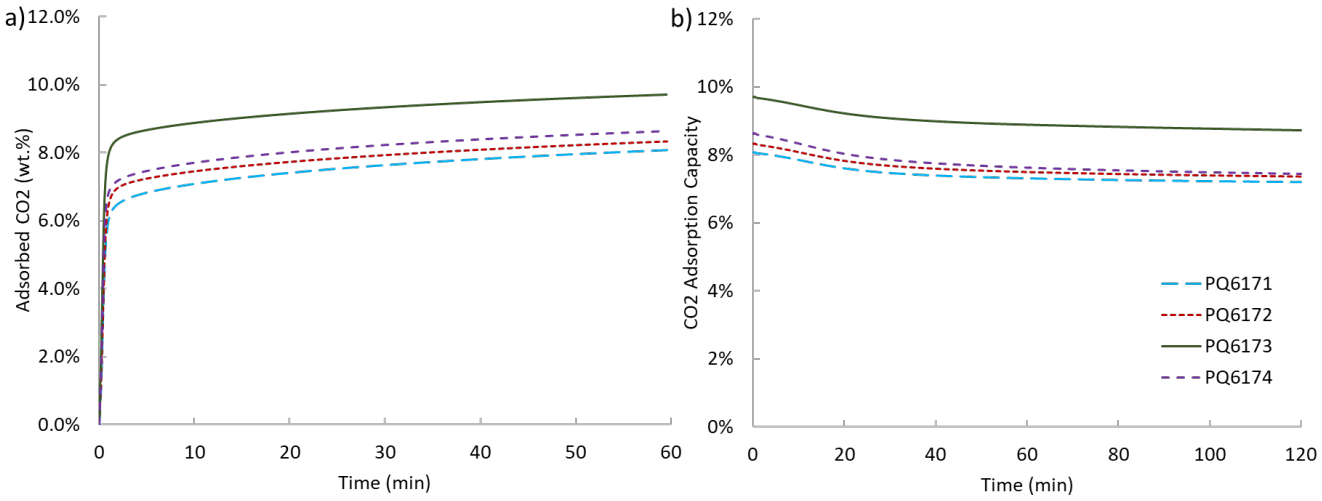
Doping of amine impregnated silica sorbent materials

Given the success of amine impregnated silica sorbents reported in WP1, such as silica 1AMINE 2 50% and MBAMINE 150%, further investigations were performed through the chemical doping of the silica sorbent itself. Given the main component of amine impregnated materials responsible for CO2 sorption is the central nitrogen atom driving chemisorption through ammonium carbonate or ammonium carbamate formation, a key route to improving CO2 sorption properties of amine impregnated materials was to employ already nitrogen/amine loaded materials. Such materials were available from PQ corporation, whereby sequentially

increased nitrogen quantity can be observed. PQ6171-PQ6174 containing increased intrinsic amine content were first examined according to their CO2 sorption properties (Figure 35). Contrary to the raw materials used in WP1 (MB and Silica 5), unmodified PQ silicas exhibit significant CO2 sorption properties. Interestingly, where PQ6174 exhibits the largest amine content, it's CO2 adsorption capacity was shown to be significantly reduced when compared to that of PQ6173. In fact, the CO2 desorption rate can be observed to be marginally increased for the PQ6174 sample, further demonstrating a non-linear relationship between amine content and CO2 capacity. Nevertheless, the unmodified PQ silicas exhibited a significant degree of CO2 retention after 1 hour, with an apparent very flat curve for the CO2 loss after 120 minutes exhibiting their potential to decrease CO2 desorption rates by providing further resorption opportunities for already desorbed CO2.

As PQ6173 exhibited the highest intrinsic CO2 adsorption capacity (9.1 wt%) and retention after 120 minutes, it was chosen for further impregnation experiments with both AMINE 2 and AMINE 1800.

Figure 15: (left) CO2 loading for PQ silica materials by TGA (25°C, 1 h, CO2 99.995%). (right) desorption of CO2 under nitrogen using TGA (25°C, 2 h, N2)



AMINE 1 modification was performed evaluating 20, 30, 40, and 50 wt% loadings of AMINE 1. This showed an increase in adsorption capacity at 50 wt% loading up to 11.33 wt% CO2. A gradual desorption time over an extended period was observed. Interestingly, with lower loadings (20 and 30 wt%), a decrease in CO2 sorption capacity and rapid desorption was found. It remains unclear as to the root cause of this- however based on learnings by the company it is likely that we have significantly impacted surface area but not increased the available amine content sufficiently to compensate for this. For higher loadings, the CO2 sorption properties increased from 9.1 wt% to a maximal loading of 11.5 wt% under atmospheric pressure with PQ AMINE 150% (Figure 35). This is reflected in CO2 desorption rates; whereby over 120 minutes less than 5% of adsorbed CO2 had been released, a significant improvement over that observed for the parent PQ6173 material.

Loading of PQ6174 with AMINE 2 at 40-60 wt% gave significantly higher loading capacities, up to 14 wt% at atmospheric pressure for PQ-AMINE 2 50 wt%, again retaining more than 95% of adsorbed CO2 following 1 hour of desorption under N2. The rate of desorption after 60 minutes at 25°C was exhibited to be negligible, suggesting extremely slow CO2 desorption. Interestingly, once loaded over 50 wt%, a drop off in CO2 capacity was observed, but with absolutely no observable desorption after 60 minutes. This suggests the blocking of available surface area for CO2 sorption, but with the extremely dense packing of amine within the material, almost no CO2 loss is possible under N2 gas flow, likely due to further resorption within the dense amine network.

Table 15 :CO2 capture properties of amine doped silicas

Carrier	CO2 capacity / mMolg-1	CO2 capacity / wt%	CO2 retention (48 hr/480 hr)
PQ AMINE 1 20% MW800	1.38	6.08	36.2 % / 22.4 %
PQ AMINE 1 30% MW800	1.86	8.18	50.1 % / 47.0%
PQ AMINE 1 40% MW800	2.44	10.75	78.0% / 70.1 %
PQ AMINE 1 50% MW800	2.64	11.62	84.3 % / 75.0 %
PQ AMINE 2 40%	2.93	12.93	76.0 % / 70.2 %
PQ AMINE 2 50%	3.01	13.25	84.3 % / 75.0 %
PQ AMINE 2 60%	1.89	8.32	-

Results summary

During these investigations in doping, already developed carrier materials with both metal ions and intrinsic nitrogen contents of silica substrates we have proved able to significantly slow the CO2 desorption rates of our carrier materials. Metal ion doping incurred a significant cost of CO2 adsorption capacity, however with Zn doping at low-levels resulted in the almost total retention of CO2. Doping of the amine-impregnated systems yielded carriers with improved CO2 capacities with respect to the un-doped materials, further exhibiting improved CO2 sorption. Future work with both doped systems will depend on their suitability and compatibility in cementitious environments, already outlined in the plans for future work-packages.

Work Package 2.3 – Investigate encapsulation of carrier materials (objective: stabilise interactions with concrete)

CO2 sorbent materials are most commonly developed for direct air capture (DAC) development, utilising pressure- or temperature swing adsorption (PSA/TSA) processes where the only role of the sorbent is to capture high quantities of CO2 then release rapidly ‘on cue’ so the CO2 can be stored via other processes. Typically, sorbents are targeted for high capacity and cyclability, with a focus on reducing degradation. These technologies have been adapted somewhat by C4C with an envisaged application as single-use CO2 carriers for transferring and permanently sequestering CO2 within cement: a technology with vastly different requirements in terms of the fate of CO2 in the sorbent once captured. C4C requires stable CO2 sorption over the course of cement curing and as single use sorbent and thus they key desired characteristic of DAC CO2 sorbents, cyclability, is not a requirement. In fact, in our case, avoiding the rapid release of CO2 is a key requirement for our carriers.

As such, encapsulation is a particularly available and clear route forward in maintaining tighter regulation over CO2 release in air, and eventually in cementitious materials. This will allow the carrier to be used for particular concrete applications where curing time requires further control. This will open a new market for the C4C carriers. Encapsulation, for the purposes of this project, is the coating/modification of sorbent materials with material shells which can slow the release of CO2 to the appropriate environment.

Encapsulation methodologies/materials are wide ranging, and for this stage of development were evaluated on the following bases:

- Accessibility and cost

Given the focus on producing large-quantities of single use materials, as with the sorbents themselves, encapsulants must be available from cheap and readily available sources. The

methodologies for encapsulation need to be similarly compatible with eventual large scale production.

- Biodegradability/low-toxicity

As C4C is committed to providing an environmental benefit in the form of CO2 sequestration, encapsulant materials must exhibit minimal long-term persistence in the environment. Of course, as they are to be incorporated within cement structures, the degradation of the carriers can occur over a more extended timescale than other applications, however the use of 'forever-chemicals' must be avoided at all cost. This is especially important when considering the fact that a large quantity of encapsulation methodologies utilise polymers and plastics. Where available and technically feasible, biodegradability of encapsulants is a top priority.

- Compatibility with CO2 sorption

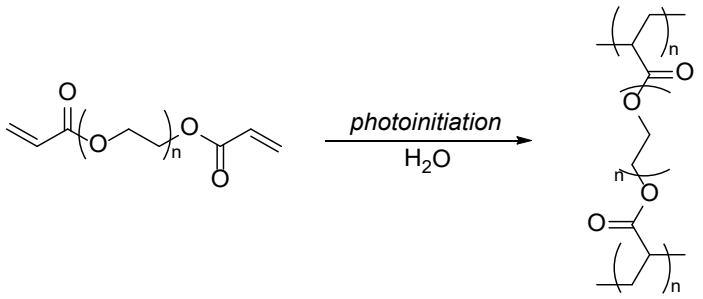
When encapsulating a sorbent material, the candidate materials must still be able to adsorb CO2 to a comparable degree to the unmodified carriers. Coating a sorbent with a totally CO2 impermeable membrane would result in the impossibility of CO2 capture, negating the resulting materials usage in line with the goals of this project. This issue can be addressed as part of the engineering aspect on the CO2 loading process: the permeability of CO2 through a given membrane is proportional to the partial pressure of CO2 at either side of that membrane, thus by employing high-pressure CO2 loading it is possible to maintain CO2 capture ability and slowing desorption at ambient pressures utilised in concrete.

Photocurable hydrogels, polymer networks formed from water-soluble monomers, are ideal initial candidates owing to their compatibility with aqueous carrier dispersions. However, given their reasonably hydrophilic nature, they typically adsorb water and swell, suggesting that they would not produce a completely impermeable shell to water. Given the aim of encapsulation, however, is not to completely arrest CO2 desorption but to slow the rate, this does not preclude their use.

POLYCAPPolycap (is a relatively simple and cost-effective hydrogel polymer, with a variety of different PEG chain lengths available (from Mn = 250 - 10000 available from Merck), which has been detailed to produce polymer networks rapidly with the assistance of light. Photolytic radical initiation by the photosensitizer drives the polymerisation of sequential acrylate chains (Figure 36).[6] [7]

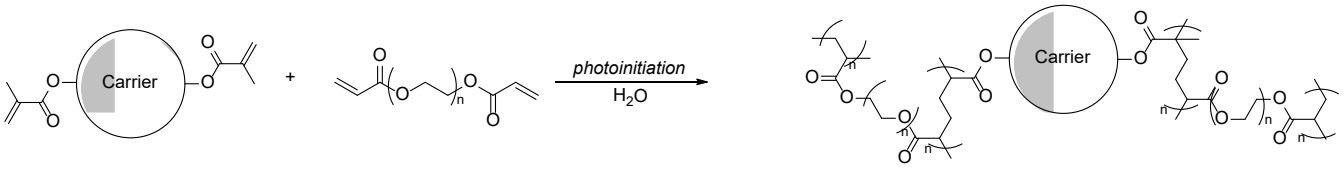
[6] N. B. Palaganas, J. D. Mangadlao, A. C. C. De Leon, J. O. Palaganas, K. D. Pangilinan, Y. J. Lee and R. C. Advincula, ACS Appl Mater Interfaces, 2017, 9, 34314–34324
[7] A. Bagheri and J. Jin, ACS Appl Polym Mater, 2019, 1, 593–611

Figure 36: Polymerisation of the POLYCAP monomer



Templating of -POLYCAP to silica-based carrier materials can be achieved through surface-incorporation of a methacrylate functionality (Figure 36, produced either by grafting or through sol-gel Silica particle synthesis). As the POLYCAP monomer is highly water soluble, it can be directly added to an aqueous carrier dispersion, with or without pre-loading with CO2 as appropriate. The polymeric material is then no-longer water soluble and directly bound to the carrier material- forming an encapsulating layer at the carrier surface.

Figure 36: Surface template polymerisation of POLYCAP



Poly POLYCAP hydrogels are permeable towards carbon dioxide, displaying selectivity for CO2 over O2 and N2, likely due to their high dipole moment across the amide bonds preferring interaction with gas molecules with high quadrupole moments.

From a cost and sustainability perspective, POLYCAP is readily available at moderate cost (100 mL from Merck ~ £50), relatively non-toxic as a monomer almost completely non-toxic as the polymeric material. POLYCAP is biodegradable, breaking down on the timescale of 2-28 days in normal conditions (suggesting compatibility with the desired CO2 release rate in concrete) likely somewhat faster in the highly alkaline environment of concrete by ester hydrolysis. POLYCAP as a monomer is water soluble and can be introduced along with commercially available photo-initiator systems to an aqueous carrier dispersion. Poly POLYCAP hydrogels are permeable towards carbon dioxide, displaying selectivity of CO2 over O2 and N2, likely due to their high dipole moment across the amide bonds preferring interaction with gas molecules with high quadrupole moments.

A photocuring reactor was designed and built by C4C using stainless steel 304 with a cooling jacket to provide a controlled environment for photopolymerization reactions. The stainless steel 304 is chosen for its corrosion resistance and inertness, which is important to prevent reactions with the photoinitiators and monomers used in the photocuring process (as a future proofing precaution). The cooling jacket will be used to control the temperature of the reaction

mixture, as temperature may affect the rate and extent of photopolymerization. This will be a future optimisation process.

The photocuring reactor was made up of the following components:

- Reaction vessel where the photopolymerization reaction takes place. It was made of stainless steel.
- The light source providing the energy required for the photopolymerization reaction. It was sourced specifically from Germany.
- The mixer distributing the mixture evenly throughout the reactor. This ensures that the photopolymerization reaction proceeds uniformly.
- The cooling jacket circulates a coolant around the reaction vessel to control the temperature of the reaction mixture. This is important to prevent overheating, due to the exothermic nature of the reaction as well as heat from the light source.

Synthesis of POLYCAP encapsulated silicas

Initially, AMINE 6) and AMINE 3.1 would be grafted to the surface of Silica 1, to produce a material with the amine functionalisation required for the chemisorption of CO2 through ammonium-carbamate pair formation, combined with methacrylate functionality encapsulation via poly POLYCAP formation. AMINE 3.1/AMINE 6@Si would then be reacted with polyethylene glycol diacrylate in a photochemical reaction to functionalise the carrier material with poly POLYCAP and achieving encapsulation. AMINE 3.1/AMINE 6@Si would be mixed with POLYCAP, a photo-initiator and a lipophilic surfactant to form a dispersion in DCM, and then slowly added to an aqueous solution of hydrophilic surfactant to form an emulsion. The emulsion would then be illuminated with high intensity UV-light to form the poly-POLYCAP encapsulated carrier material.

Synthesis of methacrylate/AMINE 3.1 functionalised silicas

As a general preparation, Silica 1 was dispersed in toluene (400 mL) and water (1 mL) by stirring at room temperature for 12 hours. To this suspension, AMINE 3.1 and AMINE 6 were added, and the reaction mixture was stirred at 100°C for 24 hours. The resulting suspension was filtered, and the solid product was washed thoroughly with toluene and isopropanol. The product was dried under air for 1 hour at 75°C. Samples are identified as x:y_A-M@Si, where the ratio of AMINE 3.1 to AMINE 6 added to the reaction mixture is shown by x:y. The material production matrix shown in Table 15 shows the analogues of methacrylate/AMINE 3.1 functionalised silica that were prepared by C4C.

Table 16: Production matrix for x:y_A-M@Si analogues

Condition	Mass silica / g	[AMINE 3.1] / mmol	[MPMTS] / mmol	Quantity of toluene	Quantity of water
9:1_A-M@Si	1	18	2	400 mL	1 mL
95:5_A-M@Si	1	19	1	400 mL	1 mL
99:1_A-M@Si	1	19.8	0.2	400 mL	1 mL
AMINE 3.1@Si	1	20	0	400 mL	1 mL

Encapsulation of methacrylate/AMINE 3.1 functionalised silicas

Encapsulation of methacrylate/AMINE 3.1 functionalised silicas was conducted according to the general procedure below.

A-M@Si, polyethylene glycol diacrylate (POLYCAP), (POLYCAP 2) (from a 10% stock solution in DCM) and (photo-initiator) were stirred vigorously. This mixture was slowly added to a solution of sodium dodecyl sulfate (SDS) in water under rapid mechanical stirring to create an emulsion. The mechanical stirrer was replaced with magnetic stirring, and the mixture was stirred for a further 5 minutes. In a dark room, using a photo reaction, the emulsion was irradiated at full power with UV radiation for 20 minutes. The mixture was then filtered, thoroughly washed with deionised water and the solid product was dried in a vacuum oven (200 mBar) at 75°C. The material production matrix shown in Table 16 shows the reagent loadings added to produce encapsulated 9:1_A-M@Si, 95.5:1_A-M@Si and 99:1_A-M@Si.

Table 17: Production matrix for poly POLYCAP encapsulated A-M@Si carriers

Condition	A-M@Si / g	POLYCAP 250 / g	POLY CAP 2 in DCM / g	Photo-initiator / g	Water / mL	SDS / mg
Encap 9:1_A-M@Si	0.538	10.289	1.031	0.5	450	50
Encap 95:5_A-M@Si	0.505	10.707	1.052	0.5	450	50
Encap 99:1_A-M@Si	0.501	10.523	1	0.529	450	50

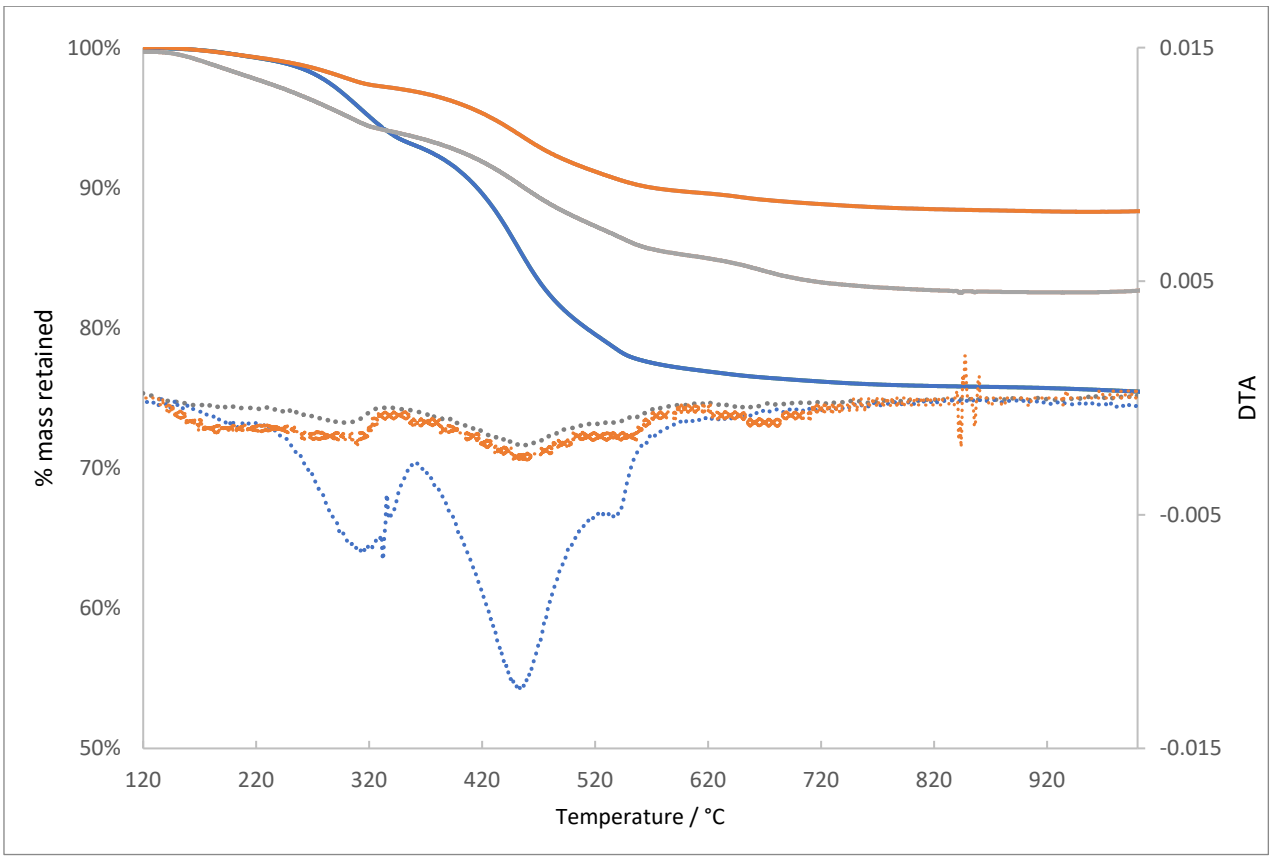
Material characterisation

Initially, to determine the quantities of the A-M@Si analogues that were prepared with different ratios of AMINE 3.1:AMINE 6 were analysed by thermal decomposition TGA to determine whether amine and acrylate were both attached to the silica surface. Examining DTA traces obtained from the decomposition curves of these materials was of interest to determine whether two distinct mass losses were occurring, that could be attributed to the thermal decomposition of both AMINE 3.1 and AMINE 6 from Silica 1. Thermal decomposition TGA of the encapsulated A-M@Si materials would allow for determination of the extent of surface-grafted polymer formation, by observing the increase in wt% loss during heating compared to the analogous non-encapsulated material. High pressure CO2 adsorption analysis would then be performed on the encapsulated and non-encapsulated A-M@Si CO2 carriers, to rationalise whether encapsulation was significantly detrimental to CO2 adsorption capacity.

Thermal decomposition of AMINE 6/AMINE 3.1 functionalised silicas

TGA and DTA traces for the non-encapsulated 9:1_A-M@Si, 95.5:1_A-M@Si and 99:1_A-M@Si carriers are shown in Figure 37.

Figure 37: Surface modified Silica 1 degradation profiles- 9:1 A-M@Si (Blue), 95:5 A-M@Si (orange) and 99:1 A-M@Si (grey). TGA results (solid line) and differentiated decomposition curves (dotted lines).

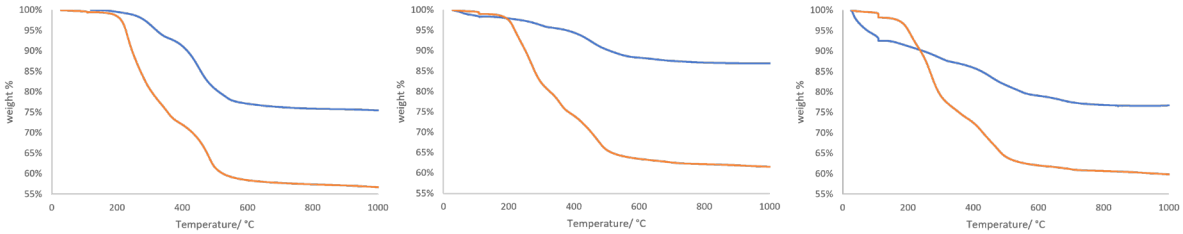


As previously shown in the 'Work Package 1 – Screen candidate CO2 sorbent (carrier) materials' report, the peak in the DTA curves at 440°C for the three A-M@Si materials is characteristic of the thermal decomposition of surface-grafted AMINE 3.1, however, an additional decomposition peak at 310°C is present. This is indicative of the presence of an additional surface grafted moiety, which is representative of grafted AMINE 6 on the silica surface, indicating that both the desired amine and methacrylate functionality were present on the silica, and that encapsulation by poly POLYCAP was feasible. There was no clear trend between AMINE 6 loading and surface concentration, likely due to methodological inconsistencies during early-stage development. However, AMINE 3.1 and AMINE 6 functionalisation was demonstrated, and these carrier materials were utilised for encapsulation.

Thermal decomposition of encapsulated AMINE 6/Amine 3.4 functionalised silicas

Poly POLYCAP encapsulated A-M@Si materials were analysed by TGA for thermal decomposition, to rationalise the extent of polymer formation on the grafted methacrylate sites. The complete thermal degradation of POLYCAP has been reported below 410°C, hence by comparing A-M@Si degradation and encapsulated A-M@Si degradation between 200-800°C (Figure 38), surface polymer loading could be calculated as increased mass loss from the encapsulated material.

Figure 38: POLYCAP Encapsulated surface functionalised Silica 1 samples (orange) in comparison with non-encapsulated species (blue). 9:1 A-M@Si (left), 95:5 A-M@Si (middle) and 99:1 A-M@Si(right).



As observed in figure 10, each of encapsulated A-M@Si materials exhibits a significant increase in thermal degradation mass loss when compared to their non-encapsulated analogue. These differences have been quantified and utilised to determine the quantity of polymer grafted to each of the encapsulated 9:1_A-M@Si, 95.5:1_A-M@Si and 99:1_A-M@Si carriers (Table 17).

Table 18: Thermal decomposition (wt%) of A-M@Si and non-encapsulated A-M@Si carriers, and polymer loadings on encapsulated materials

Condition	%w (mass loss)	Polymer Loading
9:1_A-M@Si	23.8%	-
9:1_A-M@Si post encapsulation	41.7%	18%
95:5_A-M@Si	11.1%	-
95:5_A-M@Si post encapsulation	36.3%	25%
99:1_A-M@Si	15.9%	-
99:1_A-M@Si post encapsulation	36.3%	20%

Interestingly, no trend was observed when considering the ratio of AMINE 3.1:AMINE 6 added to the synthesis of the A-M@Si carriers versus the loading of polymer on the encapsulated materials. As the carrier prepared with the highest loading of AMINE 6, 9:1_A-M:Si was predicted to show the highest polymer loading due to the theoretical greater number of methacrylate sites available for polymerisation by POLYCAP. However, this encapsulated

material showed the lowest polymer loading of the three carriers that were tested. The highest polymer loading was on the encapsulated 95.5_A-M@Si (25 %), highlighting a lack of dependency of surface methacrylate concentration on polymer loading.

CO2 Adsorption of pre- and post-encapsulated AMINE 6/AMINE 3.1 functionalised silicas

As polymer encapsulation of the A-M@Si analogues had been determined by TGA, high pressure CO2 adsorption analysis was performed on the three A-M@Si carriers and their encapsulated variants to determine whether encapsulation had a detrimental effect on CO2 adsorption capacity (Table 18).

Table 19: CO2 Adsorption capacities of pristine and encapsulated A-M@Si carriers

Condition	CO2 Adsorption Capacity / wt%
9:1_A-M@Si	4.5
Encap 9:1_A-M@Si	1.4 (68.9 % reduction)
95:5_A-M@Si	8.0
Encap 95:5_A-M@Si	0.0 (100 % reduction)
99:1_A-M@Si	13.8
Encap 99:1_A-M@Si	1.6 (88.4 % reduction)

For the non-encapsulated A-M@Si carriers, a trend of increased loadings of AMINE 3.1 in the synthesis producing carriers with higher CO2 adsorption capacities is observed. However, when the A-M@Si carriers are encapsulated with poly POLYCAP, CO2 adsorption capacities are significantly impacted. Encapsulated 9:1_A-M@Si experiences a 68.9% reduction in CO2 adsorption capacity compared to the non-encapsulated variant, while encapsulated 99:1_A-M@Si and 95.5:1_A-M@Si exhibiting 88.4 % and 100 % reductions in CO2 adsorption capacities respectively compared their corresponding non-encapsulated carriers. The CO2 adsorption capacities of the encapsulated A-M@Si carriers described Table 18 are too low for use by C4C, hence further process optimisation was conducted.

Encapsulation optimisation

It was theorised that the poor CO2 adsorption characteristics of the previously analysed encapsulated A-M@Si carriers was a result of the encapsulation layer being too thick, preventing CO2 access to the silica surface for adsorption by grafted AMINE 3.1. Hence further investigation into the synthesis of encapsulated A-M@Si was to be focussed on reducing POLYCAP loading in the encapsulating reaction. A-M@Si encapsulation by thinner polymeric layers was targeted, to allow high pressure CO2 adsorption, while slowing desorption rates.

Encapsulated carrier synthesis

The encapsulated A-M@Si carriers prepared in 5.1.2 all utilised a 20:1 POLYCAP:A-M@Si ratio, hence similar syntheses were carried out with lower ratios of POLYCAP:A-M@Si. Using 99:1_A-M@Si as the carrier material, encapsulated analogues were prepared with POLYCAP:A-M@Si ratios of 10:1 and 2:1, to determine whether in previous studies, the polymer encapsulation layer was too thick for effective CO2 adsorption by encapsulated A-M@Si. The material production matrix for these materials is shown in Table 19 (prepared according to the same procedure described in 5.1.2).

Table 20: Production matrix for encapsulated 99:1_A-M@Si carriers with varied POLYCAP loadings

Condition	A-M@Si / g	POLYCAP 250 / g	POLYCAP 2 in DCM / g	Photo-initiator / g	1% SDS in water / mL
Encap 99:1_A-M@Si (10:1)	2	20	2	0.5	1000
Encap 99:1_A-M@Si (2:1)	2	3.6	2	0.5	1000

Material characterisation- CO2 sorption

High pressure CO2 adsorption analysis was conducted on both encapsulated 99:1_A-M@Si (10:1) and encapsulated 99:1_A-M@Si (2:1). Samples were loaded with 10 bar CO2 overnight at a temperature of 75°C, and the mass change of the encapsulated carriers before and after CO2 adsorption would be measured to determine adsorption capacities (Table 20).

Table 21: CO2 adsorption capacities of poly POLYCAP encapsulated 99:1_A-M@Si (10:1) and poly POLYCAP encapsulated 99:1_A-M@Si (2:1)

Condition	CO2 Adsorption Capacity / wt%
Encap 99:1_A-M@Si (10:1)	0
Encap 99:1_A-M@Si (2:1)	0

The encapsulated A-M@Si carriers designed to have thinner polymeric layers were both inactive for the adsorption of CO2. The failure of the encapsulated carrier prepared with a 2:1 ratio of POLYCAP to A-M@Si to adsorb any CO2 was surprising, and indicated that POLYCAP or surface grafted poly POLYCAP may be blocking AMINE 3.1 derived CO2 adsorbent sites. The results presented in Table 20 showed that amine-grafted silica CO2 carriers were incompatible with poly POLYCAP encapsulation, and that this specific encapsulation route was not viable for C4C towards the production of slow-desorbing CO2 carrier materials for cement.

Material characterisation

While effective strategies have been developed for formation of a layer of poly POLYCAP on silica, better control of CO2 adsorption and release from encapsulated materials is required for applications in cement. This could be achieved by tuning the coating thickness to achieve a thinner uniform coating. In addition, other polymers with suitable permeability to CO2 and water can be investigated.

Neither the degree of grafting nor the quantity of POLYCAP used in the reaction were found to give reliable control of the amount of poly POLYCAP formed on the surface. Modification of the existing encapsulation method to target a thinner polymer shell could be achieved by better control of emulsion formation and droplet size. A thinner oil layer in the solid-oil-water emulsion formed during the reaction would give a smaller volume in which poly POLYCAP can form, and this could be expected to produce a thinner layer of polymer. Methods for controlled emulsification include the use of high speed homogenisers, microfluidics or membrane emulsification.[8] These techniques can give access to stable emulsions with good control of droplet size. The sizes and size distributions of droplets within emulsions can be measured using techniques such as light scattering. Gaining better control and understanding of the emulsification process will allow closer control of the thickness and quality of the polymer coating.

[8] C. A. Scholes, S. Kanehashi, G. W. Stevens and S. E. Kentish, Sep Purif Technol, 2015, 147, 203–209

Results summary

In this deliverable, we successfully developed an encapsulation methodology for amine-grafted silica (A-M@Si) using poly POLYCAP, demonstrating the feasibility of the methodology. This achievement involved designing and building a custom reactor tailored for the encapsulation process, ensuring precise control over the encapsulation conditions.

The encapsulation process resulted in the formation of a layer of poly POLYCAP around the A-M@Si particles, effectively shielding them from environments with the aim to reduce the release rate of CO2. This protective layer serves as a barrier against chemical reactions, moisture, and elevated temperatures, ensuring the reduction in the diffusivity and reaction of CO2-captured on the A-M@Si surface.

Based on the results it was concluded that the thickness of the poly POLYCAP layer could be further optimised to maximise CO2 adsorption/desorption performance. A slightly thicker layer hinders CO2 adhesion to the A-M@Si surface, reducing their ability to capture CO2.

To achieve a balance between protection, dispersibility, and CO2 adsorption, the plans is to investigate alternative encapsulant types and adjust the encapsulation process. This optimisation effort will focus on developing a thinner and more effective polymer layer that maintains the protective and dispersing properties while minimizing its impact on CO2 access.

Hence, it is concluded that the investigation was successfully conducted in line with the deliverable objectives. This is one of the methodologies of CO2 release reduction for specific environments and does not affect the overall delivery of the project. Multiple methodologies and optimisation mechanisms have been investigated to de-risk a highly complex technological development process.

In the poly POLYCAP work described here, branched polymer chains are formed in situ by reaction between POLYCAP monomers and methacrylate groups grafted to onto the silica surface. Grafting of polymers on solid materials can be achieved by “grafting from” methods in which a polymerisation reaction is initiated by a group bound to the polymer surface, or by “grafting to” in which whole polymer chains with one or more reactive groups form bonds to functional groups on the solid surface.[9] Grafting techniques can give controllable introduction of polymer chains localised at the surface, and high density is often achievable.[10] For “grafting to” methods, any polymer of interest can be used provided a reactive group such as a carboxylic acid can be incorporated, along with a complementary group on the particle surface. In “grafting from” strategies, rapid, controlled polymerisations including radical techniques such as ATRP or RAFT can be used. “Grafting from” can often give higher grafting densities because it lacks the steric hindrance of already grafted chains.

[9] M. Mafi, A. Kushmaro, C. Greenblatt, S. Agarwal and A. Greiner, Macromol Biosci, 2021, 21, 2000419
[10] J. Kolář, P. Kovačík, T. Choděrová, Z. Grof and F. Štěpánek, Powder Technol, 2021, 386, 505–518

Direct deposition of polymer onto the surface of particles without forming covalent bonds may also be a viable option. Dispersing solid particles in a solution of polymer followed by removal of the solvent by spray drying could produce a film of polymer on the particle surface. Adjusting the dispersion composition as well as parameters such as temperature and liquid and gas flow rates would allow optimisation of the polymer thickness and porosity. Coating of particles can also be achieved in a fluidised bed by injecting an atomised stream of the encapsulant material either in solution, suspension or molten.[11] [12] This deposits on the particles to form a coating, and the thickness can be controlled with careful control of parameters.

Alternative encapsulant materials should be investigated, including synthetic polymers as well as bioderived materials. Encapsulants of interest will display moderate to high CO2 permeability, combined with low water solubility and low water permeability. Suitable polymers may be hydrolysable in a basic aqueous environment but the rate must not be so high that the contents are released sooner than the target timescale. As such, biodegradable polyesters such as polylactide or polycaprolactone are of interest. Alternatively, instead of breaking down in cement, polymers could allow CO2 release via diffusion through the polymer shell.

Water soluble polymers such as polyvinyl alcohol might be suitable if their solubility can be reduced by crosslinking with e.g. a dialdehyde.[13]

If reduction of water penetration into the silica core is a priority, fluoropolymers could be used which have higher permeability to CO2 than to water.[14] [15] However, these have associated environmental concerns as described earlier due to their persistence and toxicity and are therefore unlikely to be suitable.

Polymer encapsulation can be applied not only to amine grafted silicas but to many other solid carriers, provided a reactive group can be grafted to the surface. This allows for the future-proofing of encapsulation strategies, achievable with any surface modifiable substrate.

Conclusions and further work

In this work-package, the detailed development and optimisation of carriers has been conducted to yield large improvements in carrier capacities. Among the 3 candidate carriers, we are able to directly control CO2 capacities and release rates through formulations. Carrier development results are detailed extensively in the relevant sections of the report, with highlights being:

[11] S. Minko, in Polymer Surfaces and Interfaces, ed. M. Stamm, Springer Berlin Heidelberg, Berlin, Heidelberg, 2008, pp. 215–234
[12] A. J. Chancellor, B. T. Seymour and B. Zhao, Anal Chem, 2019, 91, 6391–6402
[13] L. Giorno, G. De Luca, A. Figoli, E. Piacentini and E. Drioli, in Membrane Operations, eds. E. Drioli and L. Giorno, Wiley, 1st edn., 2009, pp. 463–497
[14] Neela, V. & von Solms, N. Permeability, J Polym Res, 2014, 21, 401
[15] Wicks, J. et al. Adv Mater, 2021, 33, e2003855

- Scaled up CO2 carriers based on amine-impregnated silica produced at >50 g, exhibiting CO2 capacities of 14 wt% at ambient pressure, and over 20 wt% following CO2 adsorption at 10 bar with desorption rates in line with the 48-480 hour target.
- Polymer 1-AMINE 3 based carriers impregnated with AMINE 2 exhibiting over 20 wt% and moderate CO2 retention properties with desorption rates in-line with the 48-480 hour target.
- Amine grafted silica carriers exhibiting CO2 capacities in excess of 13 wt% and extremely well-defined and controllable CO2 chemisorption capability and regulated release rates with desorption rates in-line with the 48-480 hour target.

In every case, WP2 details the further optimisation of carrier performance through formulation and demonstrates an iterative and flexible approach whereby formulations can be tweaked to achieve desired properties in a rapid fashion. Doping of the carrier materials was also developed, demonstrating a clear ability to control/slow the release of CO2 through modulating the routes of CO2 interactions and desorption. N-doping of silica materials increased capacities and CO2 retention, whilst metal doping affected capacity negatively, however, they did demonstrate an extremely slow CO2 desorption.

Encapsulation technologies have been developed and demonstrated in concept, with clear routes forward to further develop these materials for the already developed carriers. The encapsulation concept was demonstrated to be effective, although the choice of polymer is to be further developed.

These results clear the path for the development of carriers within simulated concrete environments (WP3), where upon the knowledge gained from the optimisation and encapsulation processes developed will be able to directly inform the interactions with the novel carriers developed by C4C and the altered environment. To achieve process optimisations in simulated environments, the knowledge and ability to characterise in depth the exact nature of CO2 chemisorption allows for the intelligent design of further formulations based on how we would expect these species to behave.[8] [9] [10] [11] [12] [13]

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