

# Pelletized silica and amine composites for CO<sub>2</sub> capture via adsorption

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## ABSTRACT

A broad range of mesoporous silica – amine composite powders were prepared, and readily shaped into robust forms, as are preferred for industrial applications, in accord with recently patented binderless shaping technologies. Such materials are of key interest to facilitate CO<sub>2</sub> capture, such as to help mitigate global warming. Shaping of the powders was otherwise found to be problematic due to product extrusion and/or texture. Select shaped products prepared in accord with the patent technologies were then subjected to CO<sub>2</sub> partial pressure swing adsorption (PPSA) processing. These products were found to exhibit up to ~5 wt % and ~11 wt % CO<sub>2</sub> working capacity, as estimated for the post combustion capture (PCC) of CO<sub>2</sub> from simulated flue gases via pressure swing adsorption (PSA) and thermal swing adsorption (TSA) processing respectively. The patent technologies were thus found to provide a promising opportunity to facilitate the preparation of robust sorbent options for CO<sub>2</sub> capture applications.

**Keywords:** pellet, amine, adsorption, carbon capture, CO<sub>2</sub>

## 1 INTRODUCTION

Solid amine type sorbents are being developed to provide highly selective, water tolerant and high capacity sorbent options to facilitate CO<sub>2</sub> capture from mixed gas streams such as post combustion flue gas, natural gas and air [1]. These developments are motivated by strategic interests to establish carbon capture technologies to reduce global atmospheric greenhouse gases, and so to reduce global warming, whilst facilitating growing world energy demands [1]. Adsorption driven separation process technologies are of particular interest to provide cheaper options than traditional absorption driven technologies [2]. Such developments have typically focussed on the preparation and characterisation of powdered type sorbents, however, shaped (pelletized) sorbents are typically preferable for industrial gas separation processes [1],[3],[4].

“Molecular basket” [5] type solid amine sorbents such as those prepared via the combination of polyethyleneimine (PEI) with mesoporous silicas such as MCM-41 [5], SBA-15 [1], and mesocellular siliceous foam (MCF) [6],[7], are of particular interest for the simplicity of their preparation, and large potential CO<sub>2</sub> working capacity. PEI loaded MCF composite powders in particular were found to adsorb up to ~10 wt % CO<sub>2</sub> from both anhydrous and wet simulated post

combustion flue gases (105 °C) [7]. However, shaping of such composites incorporating 80, 85 & 90 % MCF pore volume equivalents of 1200 MW branched PEI was initially found to be problematic, due to product extrusion under compression force, and stickiness [8],[9].

The patented binderless shaping technology Process A was then developed, providing a means to overcome these problems, to prepare robust dry sorbent pellets with promising potential for CO<sub>2</sub> capture applications [8],[9]. The following demonstrates the broader relevance of this technology to likewise facilitate the shaping of other molecular basket type amine sorbents, which incorporate various PEI loadings, different mesoporous supports and different amines, as is also now patented [10].

MCF and SBA-15 type mesoporous silicas were prepared, and Davisil 60 silica sourced, as supports. N<sub>2</sub> physisorption at 77 K was conducted for each to facilitate estimation of their mesopore volume, and subsequent amine loading on a per unit mesopore volume basis.

MCF-PEI composites were prepared via wet impregnation of MCF with 1200 MW PEI at 60, 70, 75 and 100 % MCF mesopore volume equivalents, to compare with those previously prepared at 80, 85 and 90 % MCF mesopore volume equivalents, to further investigate the effect of amine loading. The same PEI was separately loaded into SBA-15 and Davisil 60 mesoporous silicas at 100 % mesopore volume equivalents to investigate the effect of different support materials.

Composite sorbents were also separately prepared by loading 1<sup>st</sup> generation polypropyleneimine tetramine dendrimer DAB-Am-4 (DAB) [N,N,N',N'-Tetrakis(3-aminopropyl)-1,4-butanediamine], polyallylamine (PAA) and tetraethylenepentamine (TEPA) into MCF type mesoporous silica, and tris(2-aminoethyl)amine (TAEAH) formate into SBA-15 type mesoporous silica, at 100 % mesopore volume equivalents respectively, to investigate the effects of different amines.

PEI composite powder products were also prepared by a modified process “B” to investigate its potential to also better facilitate their shaping.

A 200 g batch of a MCF-PEI composite sorbent incorporating 80 % MCF mesopore volume equivalents of branched 1200 MW PEI was also prepared, to facilitate testing the fitness for purpose of such sorbents under more realistic process conditions.

The composite sorbent powders were then separately compressed, following initial pre-activation (drying), and in accord with the patented Process A. Visual observation of

the shaping process was conducted in each case, and the form of the pellets (sticky/dry, weak/robust), and the significance of product extrusion, or not, noted. Both the amine and silica precursors were accurately pre-weighed prior to their combination, to facilitate estimation of the nominal composition of their adducts. Product characterisation was also furthered via He pycnometry.

Select sorbent powders were purged with anhydrous CO<sub>2</sub> at 60 °C for ~16 h, and then cooled within the same atmosphere to facilitate a preliminary assessment of their relative CO<sub>2</sub> capacities. CO<sub>2</sub> partial pressure swing adsorption processing of select sorbents was subsequently conducted in-situ within a thermogravimetric analyser (anhydrous and humidified conditions) to facilitate the assessment of their potential for PCC applications.

## 2 EXPERIMENTAL

### 2.1 Chemicals

Pluronic “P123” (EO<sub>20</sub>-PO<sub>70</sub>-PO<sub>20</sub> – Aldrich), 1,3,5-trimethylbenzene (TMB - Fluka 99%), ammonium fluoride (Aldrich, 98 %), HCl (BDH, 32%), tetraethylorthosilicate (TEOS - Aldrich 98 %), ethanol absolute (EtOH – Merck), methanol (MeOH – BDH Analar), PEI branched (Sigma-Aldrich, 1200 Mw, 50 wt % in H<sub>2</sub>O), TEPA (Aldrich, tech.) PAA (Polysciences, av 15,000 Mw, ~15 wt % in H<sub>2</sub>O), DAB (Sigma-Aldrich, #460699) and Davisil grade 634 silica gel (D60 – Aldrich), or equivalents, were used as supplied. Tris(2-aminoethyl)amine (TAEAH) formate was used as supplied by Prof Douglas MacFarlane and Dr Vijay Ranganathan (Monash University, Clayton, Vic., Aust).

### 2.2 Preparation of MCF and SBA-15 silicas

MCF was prepared via neutral templating techniques using P123 as template, TMB as swelling agent and TEOS as silica source. **MCFa** was prepared by a method based on that reported by Han et al 2007 [11]. **MCFb** was prepared by a method adapted from that reported by Schmidt-Winkel et al 2000 [12]. Hydrothermal treatments were conducted within a glass reagent bottle, within a pressure cooker, at 105 °C as previously described [1]; the templates were then removed via calcination at 550 °C.

SBA-15 type mesoporous silicas **SBAa**, **SBAb** and **SBAc** were also prepared via a neutral templating technique, using P123 as template and TEOS as silica source, as per methods adapted from that reported by Zhao et al [13]; template removal was via calcination at 550 °C.

### 2.3 Preparation of Composite Sorbents

The range of MCF-PEI composites were in general prepared via infiltration of the amine from ethanol solution into ~1 g of the respective pre-dried mesoporous silica, while magnetically stirred for 24 h at ~40 °C under parafilm seal. The bulk solvents were subsequently

removed via rotary evaporation under vacuum (up to 60 °C). **MCFa-PEI80**, **MCFa-PEI85** and **MCFa-PEI90** were thus prepared by combining MCFa with 80, 85 and 90 % MCFa mesopore volume equivalents of PEI as previously reported [8],[9]. **MCFa-PEI60**, **MCFa-PEI70** and **MCFa-PEI75** were likewise prepared by combining MCFa with 60, 70 and 75 MCFa mesopore volume equivalents of PEI respectively. **MCFb-PEI100**, **MCFb-DAB100**, **MCFb-PAA100**, **MCFb-TEPA100** were similarly prepared by combining MCFb with a 100 % MCFb mesopore volume equivalents of PEI, DAB (synthesis in MeOH), PAA and TEPA respectively.

**D60-PEI100**, **SBAa-PEI100** and **SBAb-TAEAH100**, were similarly prepared by combining D60, SBAa and SBAb with PEI and TAEAH respectively.

**MCFa-PEI80b** was similarly prepared by combining ~70 g MCFa with PEI as previously reported [10].

**MCFb-PEI100-B1**, **MCFb-PEI100-B2** and **SBAc-PEI100-B** were prepared by combining MCFb and SBAc with PEI via the more recently patented modified infiltration process (Process B) at room temperature, 60 °C and 60 °C respectively [10].

Each of these composite sorbents was then activated by degassing via vacuum at 110 °C, excepting TEPA and TAEAH products which were activated under vacuum at 25 and 60 °C respectively, prior to further processing.

The products were then compressed as activated alone, and/or in accord with the patented Process A, to form pellet (shaped) products via a Specac 15 ton manual hydraulic press. Additionally, MCFa-PEI80b was shaped via a Shanghai Chengxiang Machinery Co. TDP-6T Automated Single Punch Tablet Press (SPTP) fitted with a 4 mm standard concave quadrisection die set, to investigate the potential of the patented process technology to facilitate the shaping of such products on a larger scale.

### 2.4 Characterisation of Materials

N<sub>2</sub> physisorption at 77 K was measured via a Micromeritics Tristar 3020 gas sorption analyser, and for some samples, via a Coulter Omnisorp 360 CX gas sorption analyser. The mesopore volume of products was estimated from the amount of N<sub>2</sub> remaining adsorbed at p/p<sub>0</sub> ~0.90, from desorption isotherms. MCFa, MCFb, SBAa, SBAb, SBAc and D60 exhibited volumes of 2.83, 2.06, 1.04, 1.12, 0.93 and 0.80 ml/g respectively.

He densities were measured by a Micromeritics Accupyc 1340 pycnometer.

The CO<sub>2</sub> sorption capacity of composite powder products was measured via a Mettler Toledo AB204s balance, by weighing them both before and after first purging them with CO<sub>2</sub> for 16 h at 60 °C, and then cooling them to room temperature within the CO<sub>2</sub> purge.

Thermogravimetric analysis of the CO<sub>2</sub> partial pressure swing adsorption processing of select sorbents was conducted via a custom modified [1] Setaram TAG24-16 Simultaneous Symmetrical Thermoanalyser.

### 3 RESULTS AND DISCUSSION

Table 1 lists the nominal amine content (wt%) and the helium density of each of the activated composite powder products. The nominal amine contents are consistent with the target loadings. The helium densities show general agreement with the nominal amine contents, assuming the density of each amine to be ~1.0 g/ml and the helium density of each silica to be ~2.2 g/ml, and so likewise support the preparation of the products as intended.

Additionally, Table 1 shows the amount of CO<sub>2</sub> adsorbed by the activated powder products following their prolonged exposure to a CO<sub>2</sub> purge at 60 °C. These results show that each of the products exhibited substantial CO<sub>2</sub> capacity under these conditions, excepting the PAA products, highlighting their potential for CO<sub>2</sub> capture applications. PAA type sorbents are known to more readily adsorb CO<sub>2</sub> at higher process temperatures [14].

Observations made for the shaping of these powders as compressed following activation alone, and as processed in accord with the patent Process A, via the manual hydraulic press, are also shown in Table 1. These results show that shaping via compression following activation alone of each of the PEI composite powders prepared via the standard wet infiltration process, with different PEI loadings and different silica supports, was in each case found to be complicated by the production of a sticky or greasy and/or weak pellet, and/or product extrusion. However, shaping of the same powder products via Process A was found to lead to dry robust pellets in each case, thus demonstrating the broader relevance of this patented shaping technology.

Similarly each of the other composite powders prepared via the standard wet infiltration process incorporating the different amines, excepting that for the SBAb-TAEAH100, were similarly complicated when shaped via compression as activated alone. Nevertheless, each of these sorbents was readily prepared into a dry robust pellet when prepared in accord with the patented Process A. Thus these results further highlight the broader relevance of this technology.

Table 1 also shows the observations made for compression of the powder products prepared via the modified infiltration Process B. These results show that each of these products formed dry robust pellets when shaped in accord with Process A, and that compression via activation alone of the MCF-PEI sorbents was complicated by product stickiness and extrusion. Nevertheless, these results show that the SBAC-PEI100-B product formed a dry robust pellet via compression following activation alone, demonstrating the potential of this Process B technology.

Table 1 also lists the helium density measure recorded for each of the products shaped via Process A. These pellet products are thus found to exhibit essentially the same helium density as their powder analogs, indicative of their like composition. Thus it is concluded that the shaping Process A does not lead to any substantial net change in the chemical composition of the sorbent.

Product Id.	AC	HD powd	CO <sub>2</sub> powd	Char'n of shaping (*refer to key)		HD pellet
	wt%	g/ml	wt%	Act'd	Proc A	g/ml
MCFa-PEI60	64.5	1.26	16.7	SRE	DRN	1.27
MCFa-PEI70	68.0	1.23	16.9	SRE	DRN	1.25
MCFa-PEI75	69.5	1.23	14.3	SRE	DRN	1.23
MCFa-PEI80	71.2	1.30	12.5	SWE	DRN	1.24
MCFa-PEI85	72.4	1.28	14.3	SRE	DRN	1.23
MCFa-PEI90	73.9	1.28	14.0	SRE	DRN	1.21
MCFb-PEI100	68.8	1.23	16.1	SRE	DRN	1.23
MCFb-DAB100	88.8	1.22	17.6	DRN	DRN	1.26
MCFb-PAA100	67.6	1.29	2.2	GRE	DRN	1.30
MCFb-TEPA100	67.2	1.19	23.2	GWN	DRN	1.38
SBAb-TAEAH100	58.1	1.37	12.0	DRN	DRN	1.42
SBAA-PEI100	48.9	1.50	-	SRN	DRN	1.49
D60-PEI100	46.4	1.42	6.85	DWN	DRN	1.42
MCFa-PEI80b	70.9	1.21	13.8	SRE	DRN	1.24
MCFb-PEI100-B1	68.8	1.25	16.4	SRE	DRN	1.24
MCFb-PEI100-B2	68.9	1.24	15.3	SRE	DRN	1.24
SBAC-PEI100-B	51.9	1.40	-	DRN	DRN	1.41

Table 1: Basic product and shaping characterisation: nominal amine content (AC), helium density (HD) and CO<sub>2</sub> capacity of powder products, observations for shaping as Activated (Act'd) alone or via Process A (\*Dry, Sticky or Greasy - Robust or Weak – with notable product Extrusion or Not), & the helium density (HD) of pellets (Process A).

Figure 1 shows the gravimetric record obtained for the CO<sub>2</sub> partial pressure swing processing of MCFa-PEI60, MCFa-PEI70 and MCFa-PEI75 pellets as were shaped in accord with Process A via the manual hydraulic press. These records show these products to exhibit substantial CO<sub>2</sub> sorption capacities, as appear useful for the PCC of CO<sub>2</sub> from typical flue gases via pressure swing adsorption (PSA) and/or thermal swing adsorption (TSA) processing, and that the capacities of these products increase with their PEI loading, up to ~5 wt % (1.1 mmol.g<sup>-1</sup>) and ~9 wt % (2.0 mmol.g<sup>-1</sup>) for PSA and TSA processing respectively. However, it is noted that this MCFa-PEI75 pellet was found to exhibit slightly larger PSA capacity to analogous products prepared with higher PEI loadings [8],[9], despite slightly less TSA working capacity, suggesting a limit to the benefit of such higher loading.

MCFa-PEI80b powder was also readily shaped into dry robust pellets in accord with Process A via the SPTP as separately used in both manual and automated modes. Figure 2 shows the gravimetric records obtained for the isothermal (90, 105 and 115 °C) CO<sub>2</sub> partial pressure swing adsorption processing (within a humidified (~15 % H<sub>2</sub>O) gas stream) of such a shaped MCFa-PEI80b product, including its initial 60 minutes pre-exposure to humidified (15 % H<sub>2</sub>O) Ar, following initial activation in dry Ar. These records show that this product adsorbed negligible water under these conditions, however sorbed substantial CO<sub>2</sub> in response to CO<sub>2</sub> pressure. The CO<sub>2</sub> sorption capacity of the sorbent appears to decrease with temperature, however sorption kinetics improved with

temperature such that it would seem that this sorbent is best suited to facilitate CO<sub>2</sub> capture via PSA within the range 105 – 115 °C. The sorbent exhibits similar PSA and TSA capacities to the MCFa-PEI75 pellet product shown in Figure 1. Thus these results demonstrate the potential of the patent technology to facilitate a more realistic path for the shaping of such sorbents, and the promising potential of these products for the PCC of CO<sub>2</sub> application in particular.

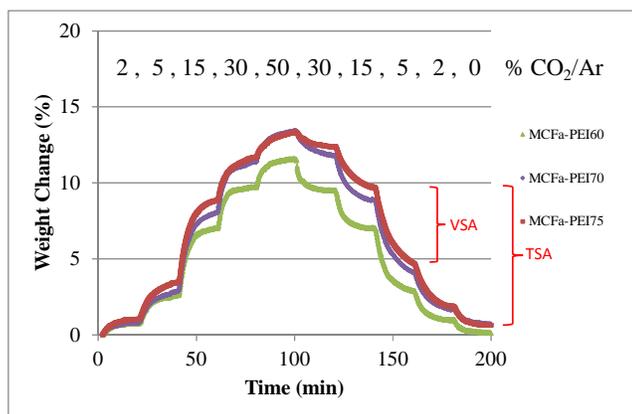


Figure 1: Gravimetric records for anhydrous isothermal (105 °C) PPSA processing of products shaped in accord with Process A via the Specac press.

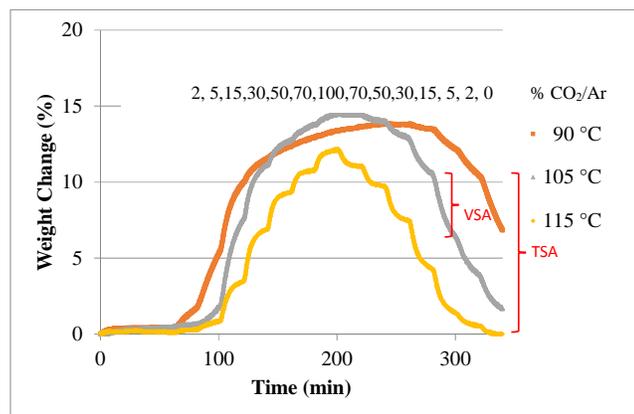


Figure 2: Gravimetric records for isothermal PPSA processing of MCFa-PEI80b (as shaped via Process A with the SPTP (manual mode)) within humidified (50 °C) CO<sub>2</sub>/Ar atmospheres.

## 4 CONCLUSION

The patented processes A & B were found useful to facilitate the shaping of a broad range of powdered mesoporous silica–amine composite adsorbents into robust pellet forms such as were found to be of promising potential to facilitate CO<sub>2</sub> capture. Further improvements are envisaged for optimisation of traditional process parameters (e.g. compaction pressure and temperature).

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