

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

G.P. Knowles\* and A.L. Chaffee\*\*

<sup>a</sup>Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), School of Chemistry, P.O. Box 23, Monash University 3800 Victoria, Australia, greg.knowles@monash.edu

<sup>\*\*</sup>Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), School of Chemistry, P.O. Box 23, Monash University 3800 Victoria, Australia, alan.chaffee@monash.edu

## ABSTRACT

Polyethyleneimine (PEI) loaded mesocellular siliceous foam (MCF) composite powders were compressed via a novel process to prepare the sorbents in pelletized form, as preferred for CO<sub>2</sub> capture processes, without additional binder. Direct compression of the MCF-PEI composite powders to prepare pelletized sorbent was found to be complicated by product extrusion and tackiness. A novel method to overcome this problem was developed in this work. This resulted in pellets that exhibit similar CO<sub>2</sub> capacities to the analogous powdered sorbents, with only slightly reduced sorption capacities and kinetics. The pellets exhibited up to 9 wt % and 4 wt % CO<sub>2</sub> process adsorption capacity for simulated CO<sub>2</sub> capture from flue gas (~15 % CO<sub>2</sub>) via temperature swing adsorption (TSA) and pressure swing adsorption (PSA) respectively. Thus, the MCF-PEI pellets prepared by this new approach are of particular interest for application to the post combustion capture (PCC) of CO<sub>2</sub> from flue gas streams.

**Keywords:** polyethyleneimine, pellet, adsorption, carbon capture, post combustion.

## 1 INTRODUCTION

Amine adsorbents are of interest to facilitate CO<sub>2</sub> capture from mixed gas streams such as post combustion flue gas, syngas, natural gas and air. This interest is motivated by the desire to reduce global atmospheric CO<sub>2</sub> (greenhouse gas) emissions so as to slow global warming / climate change, whilst still fulfilling humanity's growing demands for energy. Recent adsorbent technology developments have focussed on the preparation of powdered forms of such materials; however, it is recognized that pelletized forms of such materials will be preferred for use in conjunction with industrial gas separation process technologies such as pressure swing adsorption (PSA), and temperature swing adsorption (TSA) [1].

Polyethyleneimine (PEI) / polyol composite adsorbents were initially prepared using a variety of high surface area and highly porous supports to capture CO<sub>2</sub> from closed cabin environments [2]. It was subsequently suggested that amine type adsorbents could be useful to capture the CO<sub>2</sub> emitted from fossil fuel power generators towards halting

global warming [3]. For this purpose, PEI was combined with MCM-41 mesoporous silica to prepare a high capacity "molecular basket" type CO<sub>2</sub> sorbent [4]. Porous supports with substantially larger pore volumes, such as SBA-15 [5] and mesocellular siliceous foam [6] (MCF), were later used to prepare adsorbents with even greater PEI content (and thereby greater CO<sub>2</sub> capacity), both per unit mass and per unit space volume [7, 8], so as to be more attractive for industrial applications.

The application of compression forces to such MCF-PEI composites, to transform them into pellet forms, was more recently found to be complicated by product extrusion and tackiness. Thus the application of compression force alone was found to be unsatisfactory to reliably prepare robust MCF-PEI pellets. A novel alternate approach was thus developed to overcome these problems and, thereby, facilitate the preparation of viable MCF-PEI pellets [9]. The following procedures were undertaken to demonstrate the ability of this alternate approach to prepare a viable pelletized sorbent option for the PCC of CO<sub>2</sub>.

MCF powder was prepared and then loaded with 80, 85 & 90 % pore volume equivalents of branched PEI via wet infiltration from ethanol. The crude composite MCF-PEI products thus prepared were then activated under N<sub>2</sub> purge and / or vacuum, and their thermal stability assessed. Each product was also subsequently processed in accord with the novel alternate approach. Crude, activated and novelly processed products were then subjected to compression force to form pellets. General physico-chemical characterization of the materials was supported by gravimetric analyses and helium pycnometry. The potential of the materials as adsorbents to capture CO<sub>2</sub> was investigated by thermogravimetric analysis, using a previously established protocol involving isothermal CO<sub>2</sub> partial pressure swing adsorption (PPSA) at 105 °C [7].

## 2 EXPERIMENTAL

### 2.1 Preparation of Materials

MCF was prepared in accord with the neutral template technique [10] using polyethyleneoxide-polypropyleneoxide-polyethyleneoxide block copolymer (Aldrich #435455) as template, trimethylbenzene (Sigma-Aldrich #M7200) as swelling agent, tetraethylorthosilicate "TEOS" (#131903) as silica source and template removal

via calcination as previously described [7]. The hydrothermal treatment was conducted within a glass reagent bottle contained within a pressure cooker as previously described [7] for 24 h at 105 °C. The calcined product was found to have a BET surface area of ~620 m<sup>2</sup>.g<sup>-1</sup> and a pore volume of ~2.83 ml.g<sup>-1</sup> (volume retained at p/p<sub>0</sub> = 0.90) as calculated from N<sub>2</sub> adsorption and desorption (77 K) isotherms (Micromeritics Tristar 3020).

The MCF prepared was separately loaded with 71.2, 72.4 and 73.9 wt % (~80, 85 & 90 % pore volume equivalents) of branched av. 1200 MW PEI (Sigma-Aldrich #482595, supplied as a solution, 50 wt % in H<sub>2</sub>O) by infiltration from ethanol solution. The bulk solvents were removed via rotary evaporation under vacuum at 60 °C (2 h) to prepare the crude products M80, M85 & M90 respectively. Crude product powders were subsequently activated via a Micromeritics VacPrep 061 degasser. The crude product powders were activated under N<sub>2</sub> purge (4 days at 110 °C) and then under vacuum (5 days at 110 °C) to assess their thermal stability; products were cooled to room temp and removed under an atmosphere of N<sub>2</sub> daily and then re-weighed, to monitor their mass throughout this process. Crude product powders were also separately activated under N<sub>2</sub> purge (24 h at 110 °C) and then in-vacuum (24 h at 110 °C) to prepare the activated products M80-a, M85-a & M90-a. Crude products were also separately first activated under vacuum (24 h at 110 °C) and then processed in accord with the invention [9].

Crude products M80, M85 & M90, activated products M80-a, M85-a and M90-a and the products processed in accord with the novel procedure were then separately compressed between 13 mm diameter Specac pellet dies via a Specac 15 ton press (~10 min at 8 ton) to prepare pelletized products. Key MCF-PEI pellets prepared in accord with the invention [9] are designated as M80-p, M85-p & M90-p respectively.

## 2.2 Characterization of Materials

Gravimetric analyses were conducted via a Mettler Toledo AB204-S analytical balance. Helium pycnometry was conducted via a Micromeritics Accupyc 1340 pycnometer using a 3.5 ml cell insert calibrated with a 2.422429 cm<sup>3</sup> standard volume. N<sub>2</sub> adsorption / desorption was measured via a Micromeritics Tristar 3020 gas sorption analyzer; BET SA was determined from the adsorption isotherm data over the partial pressure point (p/p<sub>0</sub>) range 0.05 – 0.15, pore volume was estimated from the volume of gas adsorbed on the desorption isotherm at p/p<sub>0</sub> = 0.90. CO<sub>2</sub> partial pressure swing adsorption (PPSA) was measured in-situ within a Setaram TAG24-16 simultaneous symmetrical thermoanalyzer; gas supplies were regulated to the instrument via Bronkhurst model F-201DV-RAD-11-K mass flow controllers as previously described [7]. Samples were initially re-activated in-situ under Ar purge (35 ml.min<sup>-1</sup>) for 1 hour prior to PPSA processing. The sample furnace was progressively supplied with 0, 2, 5, 15, 30, 50,

30, 15, 5, 2 & 0 % CO<sub>2</sub> in Ar (35 ml.min<sup>-1</sup>) over 20 minute steps to effect CO<sub>2</sub> PPSA at 105 °C. The samples were subsequently re-activated in-situ under Ar at 110 °C prior to removal and re-weighing.

## 3 RESULTS & DISCUSSION

Figure 1 shows the decrease in mass observed for the crude product M80 as it was first activated under N<sub>2</sub> purge (4 days) and then under vacuum (5 days) at 110 °C. This figure shows that this crude product lost a substantial fraction of its mass under the first 24 hours of N<sub>2</sub> purge, consistent with the removal of residual synthesis solvent. It shows that the product exhibited only minor further mass loss over the subsequent 24 hour period, consistent with the removal of well retained volatiles.

Minor additional mass loss was however subsequently observed coinciding with the application of vacuum, highlighting the potential of this activation technique to more effectively remove both residual solvent and any minor fraction of particularly volatile PEI from the powder product. It is also noted that the product remained white (did not become discolored as indicative of decomposition) over the entire 9 day activation period. Based on these results, heating under vacuum at 110 °C for 24 hours was adopted as the preferred method for product activation.

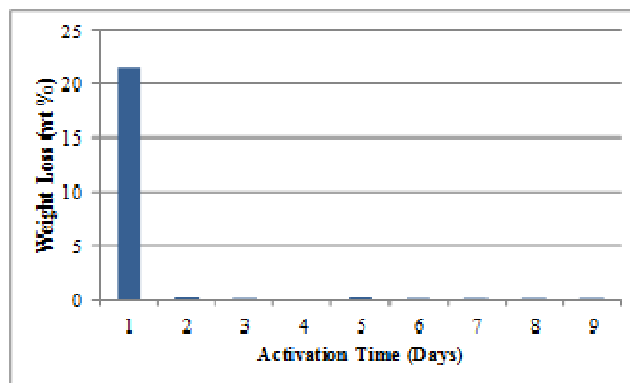


Figure 1: Activation of M80 (4 days x N<sub>2</sub> purge at 110 °C, then 5 days x evacuation at 110 °C).

Table 1 summarises the observations made for the compression of the crude MCF-PEI powder products as prepared, after vacuum activation (24 hours at 110 °C) and following subsequent processing in accord with the invention. These results show that each of the crude powder products essentially fully extruded around the pellet dies under the compression force. The vacuum activated products similarly exhibited substantial extrusion, but some of each of these products was retained between the pellet die as a very sticky compacted layer (pellet). Each of the products processed in accord with the invention [9], however, exhibited less extrusion and less tackiness, and under more favorable process conditions led to the

formation of dry robust pellets without any product extrusion.

	Crude	*Act'd	A	B	C	D
Color	white	white	white	white	white	yellow
Tackiness	very	very	very	tacky	dry	dry
Extrusion	all	large	No	no	no	no

Table 1: Characterization data obtained for the compression of MCF-PEI powders (M80, M85 & M90) as crudely prepared, after 24 h vacuum activation at 110 °C (\*Act'd), and after processing in accord with the invention by variations A, B, C & D.

Process condition “A” still led to the preparation of very sticky pellets but with essentially no product extrusion. Process condition “B” likewise prevented product extrusion but still prepared sticky pellets which were not readily removable from the pellet die without loss of pellet integrity. Process conditions “D” led to the preparation of robust dry pellets, but they appeared lightly discolored (yellow) consistent with minor decomposition. Process condition “C”, however, was found most useful to prepare robust dry pellets without discoloration.

Table 2 shows the nominal PEI loading of the crude MCF-PEI composite powders as determined by the mass of PEI mixed with the MCF, together with the helium densities measured for the MCF, the activated MCF-PEI powders (M80-a, M85-a & M90-a) and the pellets (M80-p, M85-p & M90-p) ultimately obtained from them via processing in accord with the invention. These results show that the helium densities of all of the composites are substantially less than that of the MCF substrate, consistent with their nominal PEI loading. The activated MCF-PEI composite powders (M80-a, M85-a & M90-a) are also noted to exhibit greater densities than the analogous pellets (M80-p, M85-p & M90-p) prepared from them. This is thought to be due to the powder products, with more readily accessible sorption sites, absorbing more CO<sub>2</sub> during transfer to the pycnometer than the analogous pellet products.

Table 2 also lists the PEI loading estimated for each of the composite products from their helium density measurement, assuming the helium density of PEI to be 1.08 g.ml<sup>-1</sup> (the density of the PEI supply solution). These results show that the PEI loading estimates for the pellets are in good agreement with their nominal PEI loadings (gravimetric analysis), consistent with the MCF and PEI components being well mixed during composite preparation prior to any component loss. The loadings estimated for the powder products vary essentially as expected, although they are a little smaller than anticipated. This is thought to be due to opportunistic adsorption of CO<sub>2</sub> during sample transfers, as previously noted. Furthermore, these results highlight the potential of simple pycnometry to readily facilitate estimation of the PEI loading of the composite materials.

Product	PEI Added (wt%)	Helium Density (g.ml <sup>-1</sup> )	Est. PEI Load (wt%)
MCF	0.0	2.11	0.0
M80-a	71.2	1.30	64.8
M85-a	72.4	1.28	68.6
M90-a	73.9	1.28	67.6
<sup>c</sup> M80-p	71.2	1.24	73.9
<sup>c</sup> M85-p	72.4	1.23	74.4
<sup>c</sup> M90-p	73.9	1.21	77.8

Table 2: Nominal PEI loading (amount of PEI added), helium density and PEI loading estimated from helium density measurements for products prepared.

Figure 2 shows the thermogravimetric records obtained from CO<sub>2</sub> PPSA processing of the activated powder products M80-a, M85-a & M90-a after initial in-situ re-activation under Ar. These records show that the mass of each activated powder product increased and decreased with the CO<sub>2</sub> partial pressure consistent with CO<sub>2</sub> sorption as expected. It can be seen that these powder products exhibit up to 11 wt % (2.5 mmol.g<sup>-1</sup>) CO<sub>2</sub> capacity (0.15 mol CO<sub>2</sub> per mol N) at CO<sub>2</sub> partial pressure of 0.15 (i.e. simulated flue gas). This amount is thus a realistic estimate of their potential for CO<sub>2</sub> capture from post combustion flue gas via TSA processing. It is also noted in particular that these activated powders exhibit up to 5 wt % (1.1 mmol.g<sup>-1</sup>) CO<sub>2</sub> capacity (0.07 mol CO<sub>2</sub> per mol N) between CO<sub>2</sub> partial pressures 0.15 and 0.05. This provides an estimate of their CO<sub>2</sub> adsorption potential in a single cycle of PSA process for CO<sub>2</sub> capture [7].

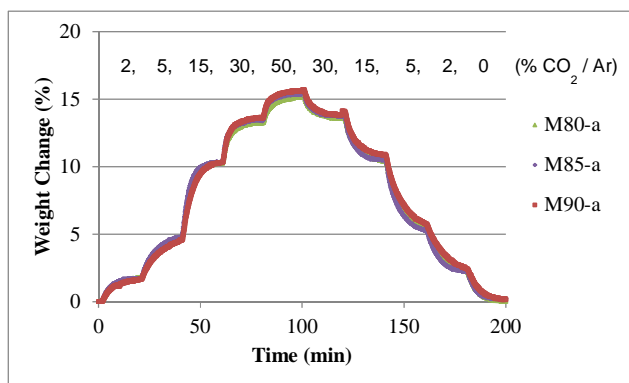


Figure 2: Gravimetric records obtained for TGA of CO<sub>2</sub> PPSA processing of powder products at 105 °C.

Figure 3 shows the thermogravimetric records obtained for the CO<sub>2</sub> PPSA processing of the analogous set of MCF-PEI pellets M80-p, M85-p and M90-p, which were prepared in accord with the invention [9]. These results show that CO<sub>2</sub> sorption for these pellet products varies with the CO<sub>2</sub> partial pressure in a manner similar to their respective powder precursor products, but with only up to ~9 wt % (~2.0 mmol.g<sup>-1</sup>) adsorption capacity (0.12 mol CO<sub>2</sub> per mol N) for TSA type processing, and up ~4 wt % (0.9 mmol.g<sup>-1</sup>)

working capacity (0.05 mol CO<sub>2</sub> per N) for PSA type processing. The small reduction in these working capacities is, in each case, attributed to compaction of the sorbent limiting the diffusion of gas (CO<sub>2</sub>) to / from the sorption sites to a small extent.

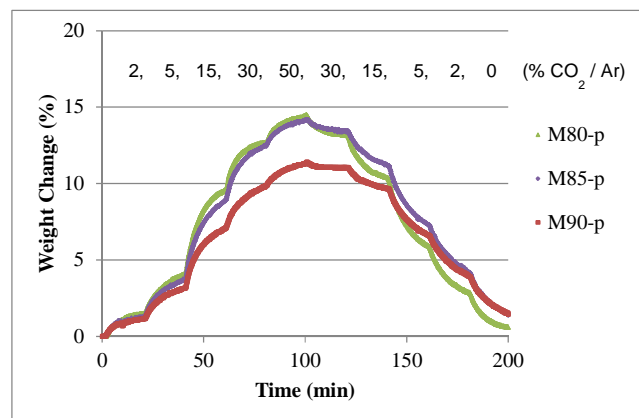


Figure 3: Gravimetric records for the TGA of CO<sub>2</sub> PPSA processing of pellet products at 105 °C.

#### 4 CONCLUSIONS

MCF-PEI composite powders were prepared by combining MCF and PEI via a wet infiltration process, incorporating 71.2, 72.4 and 73.9 wt % PEI (constituting 80, 85 & 90 % MCF pore volume equivalents of PEI) respectively. Compression of these powder products to prepare pellet products, both as initially prepared and after activation under vacuum (110 °C), was complicated by product extrusion and tackiness. A novel treatment procedure was identified that enabled the preparation of robust pellets from the same powder products. He pycrometry was shown to be useful to characterize the PEI loadings of the products prepared.

The pellets prepared in accord with the invention were found to reversibly adsorb CO<sub>2</sub> from a simulated flue gas (15 % CO<sub>2</sub> / Ar) with CO<sub>2</sub> working capacities of up to 9 wt % (2 mmol.g<sup>-1</sup>) for TSA type processing and 4 wt % (0.9 mmol.g<sup>-1</sup>) for PSA type processing. The pellets were thus found to exhibit only slightly reduced working capacities than the analogous powder products (up to 11 wt % and 5 wt % for TSA and PSA processing respectively), and so, were found to be very promising for CO<sub>2</sub> capture from post combustion flue gas via either TSA or PSA processing. The novel pelletization process invention was thus found useful to readily prepare pelletized MCF-PEI products with the potential to selectively capture CO<sub>2</sub> from post combustion flue gas via PSA or TSA.

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