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(54) **Title**: PELLETIZED FORM OF A COMPOSITE MATERIAL AND METHOD OF PRODUCING SAME

(57) **Abstract**: A process for the preparation of a pelletized form of a composite material for gas separation applications, the composite material including a solid support material and at least one separate sorption active phase, wherein the process includes the following steps: a. treating the composite material with a gas to alter the physical characteristics of the at least one separate sorption active phase and transform the composite material into a different form to facilitate pelletization of the treated composite material; and, b. compressing or compacting the treated composite material to prepare the pelletized form of the composite material.

PELLETIZED FORM OF A COMPOSITE MATERIAL AND METHOD OF PRODUCING SAME

The present invention relates to a pelletized form of a composite material and a method of producing same. The present invention also relates to the use of a pelletized form of a composite material for gas separation applications.

Background

As an example of a composite material used for gas separation applications, adsorbents have been explored to facilitate CO_2 capture from mixed gas streams such as post combustion flue gas, syngas, natural gas and air to thereby satisfy the world's growing demand for energy whilst reducing the global atmospheric concentration of greenhouse gases in order to slow global warming / climate change. Many recent adsorbent technology developments have focussed in particular on the preparation of such materials as powders. However it has been recognized that pelletized sorbents will be preferable for pressure swing adsorption (PSA) and temperature swing adsorption (TSA) which are typical industrial gas separation processes.

As a specific example, Polyethyleneimine (PEI) loaded with MCM-41 type mesoporous silica has been found to prepare a high capacity "molecular basket" type CO_2 sorbent. PEI was subsequently loaded into mesoporous type silicas with substantially larger pore volumes such as SBA-15 and mesocellular siliceous foam (MCF), to prepare adsorbents with even greater PEI content (and thereby greater CO_2 capacity) both per unit mass and per unit space volume as are therefore more attractive for industrial applications.

Pelletization of MCF-PEI composites has been found to be problematic. Rather than forming pellets when the MCF-PEI composite material was subjected to compression forces, the material was found to extrude and/or become sticky. This was attributed to PEI's being viscous liquids and the MCF-PEI composite material sorbents (at particularly

high PEI loadings) thereby being essentially a solid in liquid dispersion and the presence of "tacky" or "sticky" PEI on the external surfaces of the support material

Therefore it is desirable to provide a pelletized form of composite materials which find use in gas separation applications and a process for preparing same.

Summary

According to one aspect there is provided a process for the preparation of a pelletized form of a composite material for gas separation applications, the composite material including a solid support material and at least one separate sorption active phase, wherein the process includes the following steps:

a. treating the composite material with a gas to alter the physical characteristics of the at least one separate sorption active phase and transform the composite material into a different form to facilitate pelletization of the treated composite material; and,

b. compressing or compacting the treated composite material to prepare the pelletized form of the composite material.

In one form, the process includes the further step c. treating the pelletized form of the composite material to provide at least a partial reversal of the alteration of the physical characteristics of the at least one separate sorption active phase in step a.

According to another aspect there is provided a process for the preparation of a pelletized form of a composite material for gas separation applications, the composite material including a solid support material and at least one separate sorption active phase, the process including the following steps: combining the solid support material with the at least one separate sorption active phase via sonication or vacuum infiltration to form the composite material; and, compressing or compacting the composite material to prepare the pelletized composite material.

In one form the solid support material is selected from a material with: microporosity, mesoporosity or macroporosity or any combinations of the like to support the separate sorption active phase. In one form the solid porous support material is selected from silicas, aluminas, aluminosilicates, zeolites, clays, carbons, carbon nanotubes, metal organic frameworks, organic frameworks, crystalline organic frameworks or functionalised derivatives thereof. In one form the solid support material incorporates functional groups. In a further form the solid support material is selected from one of the following: MCF, SBA-15 or Davisil 60 type mesoporous silicas.

In one form the separate sorption active phase is selected to be supported by the solid porous support material. In one form the separate sorption active phase is the active component utilised for the gas separation applications. In one form altering the physical characteristics of the at least one separate sorption active phase in step a. includes where at least one component of the separate sorption active phase transforms from a liquid to a solid via gas sorption.

In one form the alteration of the physical characteristics of the at least one component of the separate sorption active phase may be reversed via a thermal and/or pressure swing or inert gas purge. In one form the separate sorption active phase is for applications involving the separation of CO_2 from a gas stream.

In one form the composite material is treated with a gas including CO_2 in step a. In a further form the gas including CO_2 includes pure CO_2 or the gas includes at least about 20 wt% CO_2. In one form step a. includes treating the composite material with a gas at a temperature of less than 110°. In a further form step a. includes treating the composite material with a gas at a temperature of between about 40°C and about 70°C. In still a further form step a. includes treating the composite material with a gas for a period of about 30 minutes to about 20 hours. In a further form step a. includes treating the composite material with a gas for a period of about 10 hours to about 18 hours.

In one form step c. includes placing the pelletized composite material under vacuum or contacting the pelletized composite material with a purge gas. In a further form step c. includes placing the pelletized composite material under vacuum for a period of about 30 minutes to about 5 hours at a temperature of about 20°C to about 120°C. It a further form the purge gas is an inert gas selected from nitrogen or argon or a combination of both.

In one form the process as herein described further includes a step of pre drying the composite material which includes placing the composite material under vacuum or contacting the composite material with a purge gas. In one form the step of pre drying the composite material occurs during step a. when the composite material is treated with a gas.

In one form the separate sorption active phase is selected from one or more of the following: primary, secondary or tertiary amines or amidines. In one form the primary secondary or tertiary amines or amidines comprise additional functionality such as to provide steric hindrance or to facilitate hydrogen bonding or otherwise facilitate gas sorption. In one form the separate sorption active phase includes one or more of the following: alkylamines including diethylamine, ethyleneamine, ethylenediamine, diisopropylamine (DIP), diethylenetriamine, tetraethylenepentamine (TEPA) or pentaethylenehexamine; alkanolamines including monoethanolamine (DEA), diethanolamine (DEA), isopropanolamine, diisopropanolamine (DIPA), triethanolamine, N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1-propanediol, 2-hydroxyethylpiperzine and β,β'-hydroxyaminoethylether; amine polymers including polyethyleneimine (PEI), polyallylamine (PAA), and polypropyleneimine; acrylonitrile modified alkanolamines or alkylamines including acrylonitrile modified tetraethyelenpentamine (TEPAN); amine dendrimers including melamine dendrimer, polyaminoamine dendrimer, DAB-Am-4 and DAB-Am-8; sterically hindered amines including 1,4-diazabicyclo-[5,4,0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0] non-5-ene (DBN); polyamidine, polyguanidine, 4-aminophenylamine, paraphenylenediamine and 4-aminoethylaniline; other arylamines, alkylarylamines, amidines, alkazid M, 1,8 p-menthanediamine (MDA), and sarcosine; aminosilicones including 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldsiloxane (GAP-0), 1,3,5-tris(3-

aminopropyl)-1,1,3,5,5-pentamethyltrisiloxane (M'D'M') and tris(3-aminopropyldimethylsiloxy)-3-aminopropylsilane (M'3T'); amino acids, and ionic liquids including dimethylethylenediamine (DMEDAH) formate, (dimethylamino)propylamine (DMAPAH) formate and tris(2aminoethyl)amine (TAEAH) formate and mixtures thereof. In one form the separate sorption active phase includes one or more of the following: PEI, tetraethylenepentamine, polyallylamine, tris(2-aminoethyl)amine (TAEAH) formate, or DAB-Am-4. In one form the separate sorption active phase incorporates additional compounds to provide hydrogen bonding such as alcohols, glycols, ethers including glycerol or polyethyeleneglycol (PEG), to facilitate improved equilibrium gas sorption and/or gas sorption kinetics.

According to another aspect there is provided a pelletized composite material produced by the process as herein described.

According to another aspect there is provided a use of a pelletized composite material as herein described as a sorbent for CO_2 capture.

Brief Description of the Accompanying Figures

The present invention will become better understood from the following detailed description of various non-limiting embodiments thereof, described in connection with the accompanying figures, wherein:

Figure 1 depicts the activation of M80 (4 days N_2 purge 110 °C, then 5 days under evacuation 110 °C, via Micromeritics VacPrep 061);

Figure 2 depicts the carbonation of activated composite MCF-PEI adsorbents;

Figure 3 depicts the thermogravimetric results of CO_2 PPSA (105 °C) for M80-a, M85-a & M90-a (0, 2, 5, 15, 30, 50, 30, 15, 5, 2 & 0 % CO_2 / Ar); and,

Figure 4 depicts the thermogravimetric results of CO_2 PPSA (105 °C) for M80-p, M85-p & M90-p (0, 2, 5, 15, 30, 50, 30, 15, 5, 2 & 0 % CO_2 / Ar).

Detailed Description

The foregoing describes only some embodiments of the present invention, and modifications and/or changes can be made thereto without departing from the scope and spirit of the invention, the embodiments being illustrative and not restrictive.

In the context of this specification, the word "comprising" means "including principally but not necessarily solely" or "having" or "including", and not "consisting only of". Variations of the word "comprising", such as "comprise" and "comprises" have correspondingly varied meanings.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as, an acknowledgement or admission or any form of suggestion that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

As herein described Polyethylenimine (PEI) (or also known as polyaziridine) is a polymer with repeating unit composed of the amine group and two carbon aliphatic CH_2CH_2 spacer. Linear PEIs contain all secondary amines and a terminal primary amine and branched PEIs contain primary, secondary and tertiary amino groups.

As herein described mesocellular siliceous foam (MCF) (or also known as MSF) is a mesoporous silica compound. MCF comprises uniformly sized large spherical cells that are interconnected by uniform windows to create a continuous 3-D pore system.

As herein described pelletizing or pelletization is the process of compressing a material into the shape of a pellet.

In certain embodiments there is provided a process for the transformation of composite material powders into robust pellets whereby the composite material powders before

process of transformation typically extrude, partially extrude or form tacky pellets under compression force. In certain embodiments the process neither involves incorporation of a permanent binder or non-reversible chemical modification of the composite material.

In certain embodiments, the process involves modifying those aspects of the composite material that otherwise render it not readily pelletizable by compression force in such a manner that can be readily reversed after pelletization to produce robust pellets of the composite material.

In certain embodiments this relates to the reversible transformation (chemical or physical) of a separate sorption active component included as part of the composite material into a solid or more solid form to facilitate its pelletization and the subsequent reversal of this transformation process to re-form the composite material which remains in a pelletized form. Often when the separate sorption active phase is incorporated in the composite material during formation, this provides the composite material with physical characteristics such as tackiness, some tackiness, viscous, or even apparently (almost) solid type physical characteristics. Such physical characteristics provide that when the composite material comes under the influence of a compression force during a pelletization process, the composite material will extrude, partially extrude or produce tacky pellets that are unsuitable when a robust pellet may be desired.

In certain embodiments the composite material may be transformed from a solid in liquid dispersion into a solid in solid dispersion.

In certain embodiments the reversible transformation of the composite material may be embodied in a process for the preparation of a pelletized form of a composite material for gas separation applications, the composite material including a solid support material and at least one separate active sorption phase, wherein the process includes a first step a. which involves treating the composite material with a gas to transform the composite material into a different form to facilitate pelletization of the treated composite material. In this step, the gas alters the physical characteristics of the separate sorption active phase to

the extent that the composite material no longer tacky, viscous, semi solid, or solid in liquid dispersion when subjected to a compressive force during pellitization.

In certain embodiments, step a. is then proceeded by step b. which involves taking the treated composite material in which the physical characteristics of the at least one separate sorption active phase have been altered and compressing or compacting the composite material to prepare a pelletized form of the composite material. Once the composite material is in its pelletized form the composite material may undertake a further process step, step c. where the pelletized form of the composite material is treating to provide at least a partial reversal of the alteration of the physical characteristics of the separate sorption active phase.

In one example embodiment, MCF-PEI composite pellets can be prepared by first combining (loading) solid silica powder (MCF) with the viscous liquid polymer (PEI), then treating the MCF-PEI composite with carbon dioxide (CO_2) to transform the viscous polymer component (PEI) into a more solid form (via for example carbamate, bicarbonate and/or carbonate formation), then compressing the MCF-PEI solid / solid composite into pellet form, and then reversing the liquid to solid transformation by the application of heat and/or vacuum, and/or inert gas/vapour purge. It is a further embodiment that the transformation reversal may be first conducted upon use during application of the MCF-PEI which allows for the storage of the MCF-PEI composite in its solid / solid state.

According to certain embodiments it was surprisingly found that by providing an initial carbonation step to MCF-PEI composite material, the composite material undertook a physical change that facilitated the formation of pellets when the composite material is subjected to compression forces. Without wishing to be bound by theory, it was thought that providing an initial carbonation step converted the viscous liquid PEI into a solid which then facilitates the pelletization of the subsequent MCF-PEI composite material. In other words, the liquid amine phase was converted into a solid carbamate phase via CO_2 chemisorption.

According to certain embodiments it was also surprisingly found that combining the solid support material with at least one separate sorption phase via sonication or vacuum infiltration to form the composite material facilitated the pellatization of the composite material. Without wishing to be bound by theory it is thought that the benefits of sonication mixing or vacuum infiltration concern facilitating infiltration and loading of the separate sorption phases to within the internal porosity of the support materials.

According to certain embodiments the process as herein described may further include an optional pre-drying step (eg vacuum or inert purge) to remove sorbed volatiles from the composite materials such as may otherwise likely complicate their pelletization. According to one example embodiment, the optional pre-drying step may even be accomplished by the gas treatment of the composite material in step a. as herein described.

In certain embodiments, the solid support material as herein described may be selected from a material with: microporosity, mesoporosity or macroporosity or any combinations of the like to support the separate sorption active phase. The solid porous support material may be selected from silicas, aluminas, aluminosilicates, zeolites, clays, carbons, carbon nanotubes, metal organic frameworks, organic frameworks, crystalline organic frameworks or functionalised derivatives thereof and the solid support material may incorporate functional groups.

In certain example embodiments, the solid support material is selected from one of the following: MCF, SBA-15 or Davisil 60 type mesoporous silicas.

In certain embodiments, the separate sorption active phase may be selected from one or more of the following: primary, secondary or tertiary amines or amidines. The primary secondary or tertiary amines or amidines may comprise additional functionality such as to provide steric hindrance or to facilitate hydrogen bonding or otherwise facilitate gas sorption.

In certain embodiments, the separate sorption active phase may include one or more of the following: alkylamines including diethylamine, ethyleneamine, ethylenediaemine,

diisopropylamine (DIP), diethylenetriamine, tetraethylenepentamine (TEPA) or pentaethylenehexamine; alkanolamines including monoethanolamine (DEA), diethanolamine (DEA), isopropanolamine, diisopropanolamine (DIPA), triethanolamine, N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1-propanediol, 2-hydroxyethylpiperzine and β,β'-hydroxyaminoethylether; amine polymers including polyethyleneimine (PEI), polyallylamine (PAA), and polypropyleneimine; acrylonitrile modified alkanolamines or alkylamines including acrylonitrile modified tetraethyelenpentamine (TEPAN); amine dendrimers including melamine dendrimer, polyaminoamine dendrimer, DAB-Am-4 and DAB-Am-8; sterically hindered amines including 1,4-diazabicyclo-[5,4,0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0] non-5-ene (DBN); polyamidine, polyguanidine, 4-aminophenylamine, paraphenylenediamine and 4-aminoethylaniline; other arylamines, alkylarylamines, amidines, alkazid M, 1,8 p-menthanediamine (MDA), and sarcosine; aminosilicones including 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldsiloxane (GAP-0), 1,3,5-tris(3-aminopropyl)-1,1,3,5,5-pentamethyltrisiloxane (M'D'M') and tris(3-aminopropyldimethylsiloxy)-3-aminopropylsilane (M'3T'); amino acids, and ionic liquids including dimethylethylenediamine (DMEDAH) formate, (dimethylamino)propylamine (DMAPAH) formate and tris(2aminoethyl)amine (TAEAH) formate and mixtures thereof. The separate sorption active phase may also incorporate additional compounds to provide hydrogen bonding such as alcohols, glycols, ethers including glycerol or polyethyeleneglycol (PEG), to facilitate improved equilibrium gas sorption and/or gas sorption kinetics.

The process and composite material as herein described will become better understood from the following examples of preferred but non-limiting embodiments thereof.

Examples

The MCF was prepared via a neutral template technique using polyethyleneoxide-polypropyleneoxide-polyethyleneoxide block copolymer as template, trimethylbenzene as swelling agent and template removal via calcination; hydrothermal treatment was

conducted within glass reagent bottle contained within a pressure cooker as for 24 h at 105 °C. The calcined product was found to have a BET surface area of ~605 m^2g^{-1} and pore volume of 2.84 $ml.g^{-1}$ (volume retained at p/p0 = 0.90) as calculated from N_2 adsorption and desorption (77 K) isotherms (Micromeritics Tristar 3020).

The MCF was loaded with ~80, 85 & 90 % pore volume equivalents to prepare composite materials comprising 71.2, 72.4 and 73.9 wt % of branched av. 1200 MW PEI (50 wt % in H_2O) via wet impregnation from ethanol solution, the bulk solvents were removed via rotary evaporation under vacuum at 60 °C (2 h) to prepare the MCF-PEI composite crude products M80, M85, & M90 respectively.

Crude product samples were subsequently activated under N_2 purge (4 days at 110 °C) and then 5 days under vacuum (5 days at 110 °C) to assess the thermal stability of the materials.

Crude product samples were also subsequently activated under N_2 purge (24 h at 110 °C) and then in-vacuum (24 h at 110 °C) to prepare the products M80-a, M85-a & M90-a.

Samples of each crude product were also activated under vacuum (24 h at 110 °C) and then carbonated within a CO_2 purge at 20 °C (1 h), 60 °C (1 h), 60 °C (16 h) and 105 °C (1 h) via a Micromeritics VacPrep061 degassing station.

The crude, the activated and the pre-carbonated powder products alike (~0.2 g) were then compressed as prepared between 13 mm dia Specac pellet die via a Specac 15 ton press (~10 min at 8 ton) to prepare pelletized "-p" products. The carbonated pellet products were then re-activated via vacuum (24 h at 110 °C) to prepare their de-carbonated analogues.

General physico-chemical characterization of the materials preparation was supported by gravimetric analysis (Mettler-Toledo analytical balance) and helium pycnometry (Micromeritics Accupyc 1340). The potential of the materials as adsorbents for CO_2

capture from post combustion flue gas was investigated via isothermal CO_2 partial pressure swing adsorption analysis (Setaram TAG24 simultaneous symmetrical thermoanalyser) at 105 °C (under various conditions).

Figure 1 shows the decrease in mass observed for M90 as the crude product was first activated under N_2 purge (4 days) and then under vacuum (5 days) at 110 °C. This figure shows that the crude product lost a substantial fraction of its mass over the first 24 hour period under N_2 purge. Minor further mass loss was observed to occur over the subsequent 24 hour period, consistent with the removal of well retained volatiles, but the product appeared to be dried to essentially a constant mass after 1 day.

Table 1

	Crude	*[a]Aci'd*	*Carbonated (post Activation)*			
Carbonation	-	-	20 °C 1h	60 °C 1h	60 °C 16 h	105°C 1h
Color	white	white	white	white	white	yellow
Tackiness	very sticky	very sticky	very sticky	sticky	dry	dry
Extrusion	all	large	small	none	none	None

[a] Activated.

Some further minor mass loss was subsequently observed to occur upon the application of vacuum, highlighting the potential of this activation technique to more effectively remove both residual solvent and any particularly volatile PEI fraction from this material. It is

noted that the sample was not discoloured (as would be indicative of decomposition) in any way at this time. The preferred vacuum activation method (24 h at 110 °C) for the removal of residual solvent and any readily volatile PEI fraction from the composite materials was adopted based on these results.

Table 1 summarises the observations made for compression of the crude MCF-PEI powder products as prepared, after vacuum activation (24 h at 110 °C) and following subsequent carbonation respectively. These results show that compression of the crude powder products entirely extruded around the pellet die under the applied compression force, consistent with a fine solids in liquid dispersion. The vacuum activated products similarly exhibited substantial extrusion however some of the material was retained between the pellet die as a very sticky compacted layer (pellet). The pre-carbonated powders exhibited less extrusion and tackiness relative to the increasing aggressiveness of the applied carbonation conditions (extent of carbonation).

1h carbonation at 20 °C led to preparation of very sticky pellets and much less product extrusion than with pre-activation alone. Carbonation for 1h at 60 °C was sufficient to prevent product extrusion however still prepared sticky pellets which were not readily removable from the pellet die without loss of integrity. Carbonation for 1h at 105 °C led to the preparation of robust dry pellets however each appeared slightly yellow consistent with minor decomposition which may have been due to urea formation. Prolonged 16h carbonation at 60 °C was found most useful to prepare robust dry pellets without decomposition.

Figure 2 shows the extent of carbonation achieved for each of the activated powders under the various conditions applied. These results not only show that the extent of carbonation was enhanced by the more aggressive carbonation conditions employed, but also that the mass of the materials was found to increase by up to 18.5 wt % (4.2 $mmol.g^{-1}$) under the most aggressive conditions consistent with the uptake of 0.25 molecules of CO_2 per amine N atom present in the product. Furthermore each different powder product was found to

essentially adsorb the same amount of CO_2 under the same carbonation conditions consistent with their similar theoretical PEI loadings.

Table 2 shows the nominal PEI loading of the crude MCF-PEI composite powders as determined by the mass amount of PEI initially mixed with the MCF together with the helium densities measured for the MCF, the activated MCF-PEI powders and the re-activated MCF-PEI pellets. These results show that the helium densities of all of the composites are substantially less than that of the MCF substrate consistent with the greater nominal PEI content of these materials. It is also noted that the MCF-PEI composite powders exhibited greater densities than the analogous pellets, thought due to the greater potential for opportunistic fixation of atmospheric CO_2 to the more accessible sorption sites within the powder products during sample transfer than to those of the analogous pellet products.

Table 2 PEI loading and Helium density data.

Product	[a]*mPEI* (*wt%*)	*dHe* (*ml.g^{-1}*)	[b]*est.PEI* (*wt%*)
MCF	-	2.11	-
M80-a	71.2	1.30	63.6
M85-a	72.4	1.28	67.3
M90-a	73.9	1.28	66.4
[c]M80-p	71.2	1.24	72.5
[c]M85-p	72.4	1.23	73.0
[c]M90-p	73.9	1.21	76.3

[a] Initial mass amount of PEI in the product as initially calculated from the mass amounts of PEI and MCF combined .

[b] PEI loading estimated from the helium density measurements.

[c] Powders carbonated 16 h at 60 °C prior to pelletization & re-activation.

Table 2 also lists the PEI loadings estimated for each composite from the helium density measurements assuming helium density of PEI to be the same as its liquid density (1.07

$g.ml^{-1}$). These results show that the PEI loading estimates for the pellets are in very good agreement with the nominal PEI loadings (gravimetric analysis) consistent with the MCF and PEI being well mixed during synthesis prior to any component loss. The loadings estimated for the powder products essentially vary as expected, however are smaller than expected thought due to the fixation of opportunistic CO_2 as previously noted. These results highlight the potential of simple pycnometry to readily estimate the PEI loading of such composite materials.

Figure 3 shows the thermogravimetric records obtained for CO_2 partial pressure swing adsorption processing of the activated powder products M80-a, M85-a and M90-a via the thermogravimetric analyzer following in-situ 1 h re-activation under Ar purge at 110 °C. These records show that the mass of each activated powder product increased and decreased with the CO_2 partial pressure consistent with CO_2 sorption as expected. It is noted that the powder products exhibited up to 11 wt % (2.5 $mmol.g^{-1}$) CO_2 capacity (0.15 mol CO_2 per mol N) at CO_2 partial pressure of 0.15 (ie. simulated flue gas) as is a conservative estimate of their potential for CO_2 capture from post combustion flue gas via TSA processing. It is also noted that these activated powder products exhibited up to 5 wt % (1.1 $mmol.g^{-1}$) working capacity (0.07 mol CO_2 per mol N) between CO_2 partial pressures 0.15 and 0.05 as is a conservative indication of their potential CO_2 working capacity for CO_2 capture from post combustion flue gas via PSA processing.

Figure 4 shows the thermogravimetric records obtained for CO_2 partial pressure swing adsorption processing of the analogous set of re-activated (de-carbonated) pellet products M80-p, M85-p and M90-p, prepared via pelletization of their respective powder analogues following pre-carbonation for 16 h at 60 °C. These results show that CO_2 sorption for the pelletized products varies with the CO_2 partial pressure similarly to their respective powder products, but with only up to ~9 wt % (~2.0 $mmol.g^{-1}$) working capacity (0.12 mol CO_2 per mol N) for TSA type processing and only up to ~4 wt % (~0.9 $mmol.g^{-1}$) working capacity (0.05 mol CO_2 per N) for PSA type processing. The reduction in these working capacities is in each case attributed to compaction of the sorbent further limiting diffusion of gas (CO_2) to / from the sorption sites.

PEI was loaded into MCF via wet impregnation to prepare MCF-PEI composite powders with 71.2, 72.4 and 73.9 wt % PEI respectively. Compression of the activated powders (vacuum 110 °C) led to extrusion thought due to the product effectively being a solid in liquid dispersion. Carbonation (conversion of amines to carbamates) of the products overcame this problem leading to preparation of robust pelletized sorbent. He pycnometry was found useful to characterize the PEI loadings. The re-activated pellets were found to reversibly adsorb CO_2 from a simulated flue (15 % CO_2 / Ar) with CO_2 working capacities of up to 4 wt % (mol.g^{-1}) for PSA type processing and up to 9 wt % (mol.g^{-1}) for TSA type processing. The pellets were albeit found to exhibit smaller working capacities than the analogous composite powders; nevertheless they were found to be very promising for CO_2 capture from post combustion flue gas via either TSA or PSA processing. Pre-carbonation of the MCF-PEI type adsorbent was found useful to readily prepare pelletized sorbent with potential to selectively capture CO_2 from post combustion flue gas via PSA or TSA.

Table 3 summarises the results for the compression (under ambient conditions) of a further range of solid amine type composite sorbents, as were prepared by loading PEI with MCF over a more extensive range of PEI loadings, by preparing such materials at larger scale, by combining PEI with the alternate support materials SBA-15 and Davisil 60 type mesoporous silicas, and by combining other amines including tetraethylenepentamine, polyallylamine, tris(2-aminoethyl)amine (TAEAH) formate and DAB-Am-4 with mesoporous silica support materials, via wet infiltration from/within ethanol solvent/dispersant within a continuously stirred reactor (stirred 24 h at room temperature) followed by solvent removal via rotary evaporation at 60 °C and subsequent drying within N_2 purge at 60 °C.

The amine was combined with the porous support on the basis of the specified estimated mesopore volume equivalent of the support material, typically prepared from 1 g of silica, two scaled up formulations Mc-100P12 and Mc-PEI-80b, were prepared on the basis of ~80 g of MCF. Table 3 also shows the results from compression of the composite sorbent powder similarly prepared by combining PEI with MCF by wet infiltration via a

continuous stir reactor following initial pre-sonication of the combined solution/dispersion, as was intended to promote better infiltration of the polymer to within the internal porosity of the support material. Each of the products prepared as such was then compressed to form pellets following both degassing, via prolonged (minimum 24 h) vacuum activation at 110 °C (Mc-TP-100 at 25 °C only), and then separately following subsequent treatment with CO_2 gas purge at 60 °C for approximately 16 h. (Mc100P12 at 105 °C for 1 h). Two of the MCF-PEI type products were in addition compressed following "carbonation" in air (16 h at 60 °C) after initial activation. Table 3, in addition, also lists the nominal amine content, the helium density and amine loading as calculated from the helium density of the pellets prepared via the carbonation route upon subsequent decarbonation. These results show the composite sorbent pellets to essentially comprise the amine content as per the initial production of the precursor composite powders.

For the MCF-PEI composites series, as prepared by wet infiltration via a continuous stirred reactor at ~1 g MCF scale, it is noted that compression following activation alone leads to the production of sticky pellets in each case, with typically large amounts of product extrusion accompanying pellet production for powders with higher PEI contents, and smaller amounts of product extrusion accompanying pellet production for powders with lesser amounts of PEI. In contrast, all the same powder products readily compressed to dry robust white pellets when compressed following their carbonation after initial vacuum activation. Thus these results clearly substantiate the benefit of the carbonation to facilitate the production of dry robust pellets of MCF-PEI composites for composites prepared with the larger range of PEI loadings, extending from 60 to 100 % MCF mesopore volume equivalents.

Similar results were observed for the products prepared at the larger scale (~80 g MCF basis). For Mc100P12, the MCF-PEI product prepare with 100% MCF mesopore volume of PEI, a sticky pellet and a large amount of product extrusion is observed for its compression with activation alone, whereas a dry robust pellet is prepared without product extrusion for its compression following its subsequent carbonation. The same result was observed for Mc-PEI-80b excepting that a smaller amount of product extrusion was

observed for compression following activation alone, consistent with its smaller PEI content. These results thus demonstrate the scale-ability of this pellet production technology. 10 g of this same carbonated sorbent powder was also readily compressed to form via a TDP-6T automated single punch tablet press (with 4 mm o.d. standard quadrasect pellet die), thereby further highlighting the scale-ability of the technology.

For PEI products prepared combined via the conventional continuous stirred reactor with SBA-15 and Davisil 60 type mesoporous silicas, compression following activation alone did not appear to exhibit the same complications as per the analogous MCF products. For the SBA-15 case a dry robust pellet was prepared, whereas for the Davisil 60 case, only a brittle sandy pellet, which broke upon removal from the die, could be prepared. However, a dry robust white pellet of each product was readily prepared when the powder products were carbonated following initial activation prior to compression. These results demonstrate that the compression of such composites following activation alone may not become complicated to the same extent, nor in the same manner, for different support types, however, the results demonstrate that the carbonation pre-compression technology is useful to prepare dry robust pellets of the composites in each case.

The products prepared combined via the conventional continuous stirred reactor alone with TEPA, PAA, TAEAH and DAB, compression following activation alone, also did not appear to lead to the same complications as for the PEI products, nor the same complications in each case. For Mc-TP-100, a soft wet/greasy pellet was formed, whereas for Mc-PAA-100 a more robust greasy pellet was formed together with some flaky product extrusion. For Sc-TAEAH-100 and 60-DAB-G1 a dry robust pellet was prepared in each case. Nevertheless, when the products were compressed following carbonation post the initial activation, dry robust pellets were prepared in each case. These results show that although carbonation may not be essential to the production of dry robust pellets for each composite sorbent type, it highlights that the benefit of the compression post carbonation technology to overcome such problems where they do exist, and to facilitate the production of dry robust pellets in each case.

For the PEI composites prepared with MCF and SBA-15 type mesoporous silicas for which sonication mixing was employed prior to mixing via the conventional stir reactor, the results are very similar to those for the analogous products prepared by mixing via the continuous stir reactor alone. Compression of the MCF supported PEI products following activation alone in each case preparing wet/greasy yet sturdy pellets, the product prepared via sonication at 60 °C (Mc-PEI-100-s60) in addition leading to a substantive wet/greasy extrusion. That these results are essentially the same as for that observed when the PEI was combined with the MCF by mixing via the continuous stir reactor alone, does not suggest any particular advantage for the use of sonication. However, for the other cases an apparent beneficial effect was apparent. Compression of the MCF supported PAA composite prepared via the sonication route following activation alone apparently readily prepared a dry robust white pellet. Likewise, so too did compression of the SBA-15 composites loaded with TP (Sc-TP-100-s) and PEI (Sc-PEI-100-s) respectively, following activation alone. Nevertheless, compression following carbonation post activation, where conducted, readily prepared a dry robust pellet in each case, thus highlighting again the benefit of the carbonation pre-compression technology. The results thus suggest the benefit of sonication mixing, which is attributed to this process better facilitating infiltration and loading of the sorbent phases to within the internal porosity of the supports.

Table 3 also shows the results obtained for the compression of the MCF-PEI products Mc-PEI-100 and Mc-PEI-80b after activation alone and after carbonation in air (16 h at 60 °C) following initial activation. The prolonged exposure of these sorbents to a concentrated CO_2 purge stream was previously found to facilitate the production of dry robust pellets, whereas their compression following activation alone was found to lead to the production of sticky pellets accompanied by product extrusion. These additional results show that the compression of these products following "carbonation" via the prolonged exposure to air at 60 °C led to the production of sticky pellets albeit without obvious product extrusion, in each case. These results are attributed to the particularly low concentration of CO_2 in air to facilitate sufficient carbonation. It is noted that although lower process temperatures might improve the extent of carbonation, these would also increase the likely uptake of water,

which it is thought would likely lead to complications for pellet production, and so would require the use of dry air streams.

Table 3:

Sample Id.	Compression as degassed.	Compression as carbonated.	Amount of Amine added (wt %)
Mc-PEI-100	Sticky pellet, some smeary extrusion	Dry robust white pellet.	**68.8**
Mc-PEI-90	Sticky weak white pellet, large extrusion.	Dry robust white pellet.	**73.9**
Mc-PEI-85	Sticky weak white pellet, small extrusion.	Dry robust white pellet.	**72.4**
Mc-PEI-80	Sticky weak white pellet, large extrusion.	Dry robust white pellet.	**71.2**
Mc-PEI-75	Sticky robust white pellet, small extrusion.	Dry robust white pellet.	**69.5**
Mc-PEI-70	Sticky robust white pellet, small extrusion.	Dry robust white pellet.	**68.0**
Mc-PEI-60	Sticky robust white pellet, small extrusion.	Dry robust white pellet.	**64.5**
Mc100P12	Sticky pellet, very large extrusion.	Dry robust light yellow-brown pellet.	**75.2**
Mc-PEI-80b	Sticky robust white pellet, small extrusion.	Dry robust white pellet.	**70.9**
Sc-PEI-100	Robust pellet.	Dry robust yellow pellet.	**48.9**
D60-PEI-100	Brittle sandy pellet, broke upon recovery.	Dry robust white pellet.	**46.4**
Mc-TP-100	Sturdy but soft and wet to touch white pellet.	Dry robust yellow/beige pellet.	**67.2**
Mc-PAA-100	Greasy robust white pellet, some flaky extrusion.	Dry robust white pellet.	**73.6**
Sc-TAEAH-100	Sturdy beige/yellow pellet.	Dry robust beige pellet.	**58.1**
D60-DAB-G1	Dry robust yellow pellet.	Dry robust yellow pellet.	**66.3**
McPEI100-sRT	Robust sticky pellet.	Dry robust pellet.	**68.8**
McPEI100-s60	Sticky wet/greasy pellet, wet/greasy extrusion.	Dry robust pellet.	**68.9**
Sc-PEI-100-s	Dry robust white pellet.	Dry robust beige pellet.	**51.9**
Mc-PAA-100-s	*Dry robust white pellet.	Not prepared	**76.8**
Sc-TP-100-s	*Dry robust off-white pellet.	Not prepared.	**47.3**
Mc-PEI-100	Sticky pellet, some smeary extrusion.	Sticky pellet (Carbonated in Air not CO_2).	**68.8**
Mc-PEI-80b	Sticky pellet, small sticky extrusion.	Sticky pellet, no extrusion (carbonate in Air not CO_2).	**70.9**

Sample Type Nomenclature

Sc – SBA-15 type mesoporous silica (template removed via calcination)

Sx – SBA-15 type mesoporous silica (template removal via ethanol extraction)

Mc – MCF type mesoporous silica (template removed via calcination)

Mx - MCF type mesoporous silica (template removal via ethanol extraction)

D – Davisil type mesoporous silica (40, 60 or 120 anstrom av pore dia).

PEI – polyethyleneimine (provided 50 wt % in H_2O (Sigma-Aldrich).

PAA – polyallylamine (liquid (www.chemicalbook.com), typically supplied as H_2O solution (20 wt % Sigma-Aldrich) or salt powder)

TP – tetraethylenepentamine (Sigma-Aldrich T11509 - viscous liquid, Mw=189.3 g/mol)

DAB-Am-4: Polypropylenimine tetramine dendrimer, generation 1 (viscous liquid, Mw 316.53 g/mol)
TAEAH - tris(2-aminoethyl)amine (TAEAH) formate (viscous brown/yellow liquid).

Many modifications will be apparent to those skilled in the art without departing from the scope of the present invention.

The Claims:

1. A process for the preparation of a pelletized form of a composite material for gas separation applications, the composite material including a solid support material and at least one separate sorption active phase, wherein the process includes the following steps:

    a. treating the composite material with a gas to alter the physical characteristics of the at least one separate sorption active phase and transform the composite material into a different form to facilitate pelletization of the treated composite material; and,

    b. compressing or compacting the treated composite material to prepare the pelletized form of the composite material.

2. A process according to claim 1 including a further step c. treating the pelletized form of the composite material to provide at least a partial reversal of the alteration of the physical characteristics of the at least one separate sorption active phase in step a.

3. A process for the preparation of a pelletized form of a composite material for gas separation applications, the composite material including a solid support material and at least one separate sorption active phase, the process including the following steps: combining the solid support material with the at least one separate sorption active phase via sonication or vacuum infiltration to form the composite material; and, compressing or compacting the composite material to prepare the pelletized composite material.

4. A process according to any one of the preceding claims wherein the solid support material is selected from a material with: microporosity, mesoporosity or macroporosity or any combinations of the like to support the separate sorption active phase.

5. A process according to any one of the preceding claims wherein the solid porous support material is selected from silicas, aluminas, aluminosilicates, zeolites, clays, carbons, carbon nanotubes, metal organic frameworks, organic frameworks, crystalline organic frameworks or functionalised derivatives thereof.

6. A process according to any one of the preceding claims wherein the solid support material incorporates functional groups.

7. A process according to any one of the preceding claims wherein the solid support material is selected from one of the following: MCF, SBA-15 or Davisil 60 type mesoporous silicas.

8. A process according to any one of the preceding claims wherein the separate sorption active phase is selected to be supported by the solid porous support material.

9. A process according to any one of the preceding claims wherein the separate sorption active phase is the active component utilised for the gas separation applications.

10. A process according to any one of claims 1, 2 and 4 to 9 wherein altering the physical characteristics of the at least one separate sorption active phase in step a. includes where at least one component of the separate sorption active phase transforms from a liquid to a solid via gas sorption.

11. A process according to according to any one of claims 1, 2 and 4 to 10 wherein the alteration of the physical characteristics of the at least one component of the separate sorption active phase may be reversed via a thermal and/or pressure swing or inert gas purge.

12. A process according to any one of the preceding claims wherein the separate sorption active phase is for applications involving the separation of CO_2 from a gas stream.

13. A process according to any one of claims 1, 2 and 4 to 12 wherein the composite material is treated with a gas including CO_2 in step a.

14. A process according to claim 13 wherein the gas including CO_2 includes pure CO_2 or the gas includes at least about 20 wt% CO_2.

15. A process according to any one of claims 1, 2 and 4 to 14 wherein step a. includes treating the composite material with a gas at a temperature of less than 110°.

16. A process according to any one of claims 1, 2 and 4 to 15 wherein step a. includes treating the composite material with a gas at a temperature of between about 40°C and about 70°C.

17. A process according to any one of claims 1, 2 and 4 to 16 wherein step a. includes treating the composite material with a gas for a period of about 30 minutes to about 20 hours.

18. A process according to any one of claims 1, 2 and 4 to 17 wherein step a. includes treating the composite material with a gas for a period of about 10 hours to about 18 hours.

19. A process according to any one of claims 2 and 4 to 18 wherein step c. includes placing the pelletized composite material under vacuum or contacting the pelletized composite material with a purge gas.

20. A process according to claim 19 wherein step c. includes placing the pelletized composite material under vacuum for a period of about 30 minutes to about 5 hours at a temperature of about 20°C to about 120°C.

21. A process according to claim 19 wherein the purge gas is an inert gas selected from nitrogen or argon or a combination of both.

22. A process according to any one of the preceding claims further including a step of pre drying the composite material which includes placing the composite material under vacuum or contacting the composite material with a purge gas.

23. A process according to claim 22 wherein the step of pre drying the composite material occurs during step a. when the composite material is treated with a gas.

24. A process according to any one of the preceding claims wherein the separate sorption active phase is selected from one or more of the following: primary, secondary or tertiary amines or amidines.

25. A process according to claim 24 wherein the primary secondary or tertiary amines or amidines comprise additional functionality such as to provide steric hindrance or to facilitate hydrogen bonding or otherwise facilitate gas sorption.

26. A process according to any one of the preceding claims wherein the separate sorption active phase includes one or more of the following: alkylamines including diethylamine, ethyleneamine, ethylenediamine, diisopropylamine (DIP), diethylenetriamine, tetraethylenepentamine (TEPA) or pentaethylenehexamine; alkanolamines including monoethanolamine (DEA), diethanolamine (DEA), isopropanolamine, diisopropanolamine (DIPA), triethanolamine, N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1-propanediol, 2-hydroxyethylpiperzine and β,β'-hydroxyaminoethylether; amine polymers including polyethyleneimine (PEI), polyallylamine (PAA), and

polypropyleneimine; acrylonitrile modified alkanolamines or alkylamines including acrylonitrile modified tetraethyelenpentamine (TEPAN); amine dendrimers including melamine dendrimer, polyaminoamine dendrimer, DAB-Am-4 and DAB-Am-8; sterically hindered amines including 1,4-diazabicyclo-[5,4,0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0] non-5-ene (DBN); polyamidine, polyguanidine, 4-aminophenylamine, paraphenylenediamine and 4-aminoethylaniline; other arylamines, alkylarylamines, amidines, alkazid M, 1,8 p-menthanediamine (MDA), and sarcosine; aminosilicones including 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldsiloxane (GAP-0), 1,3,5-tris(3-aminopropyl)-1,1,3,5,5-pentamethyltrisiloxane (M'D'M') and tris(3-aminopropyldimethylsiloxy)-3-aminopropylsilane (M'3T'); amino acids, and ionic liquids including dimethylethylenediamine (DMEDAH) formate, (dimethylamino)propylamine (DMAPAH) formate and tris(2aminoethyl)amine (TAEAH) formate and mixtures thereof.

27. A process according to any one of the preceding claims wherein the separate sorption active phase includes one or more of the following: PEI, tetraethylenepentamine, polyallylamine, tris(2-aminoethyl)amine (TAEAH) formate, or DAB-Am-4.

28. A process according to any one of the preceding claims wherein the separate sorption active phase incorporates additional compounds to provide hydrogen bonding such as alcohols, glycols, ethers including glycerol or polyethyeleneglycol (PEG), to facilitate improved equilibrium gas sorption and/or gas sorption kinetics.

29. A pelletized composite material produced by the process according to any one of claims 1 to 28.

30. Use of a pelletized composite material according to claim 29 as a sorbent for CO_2 capture.

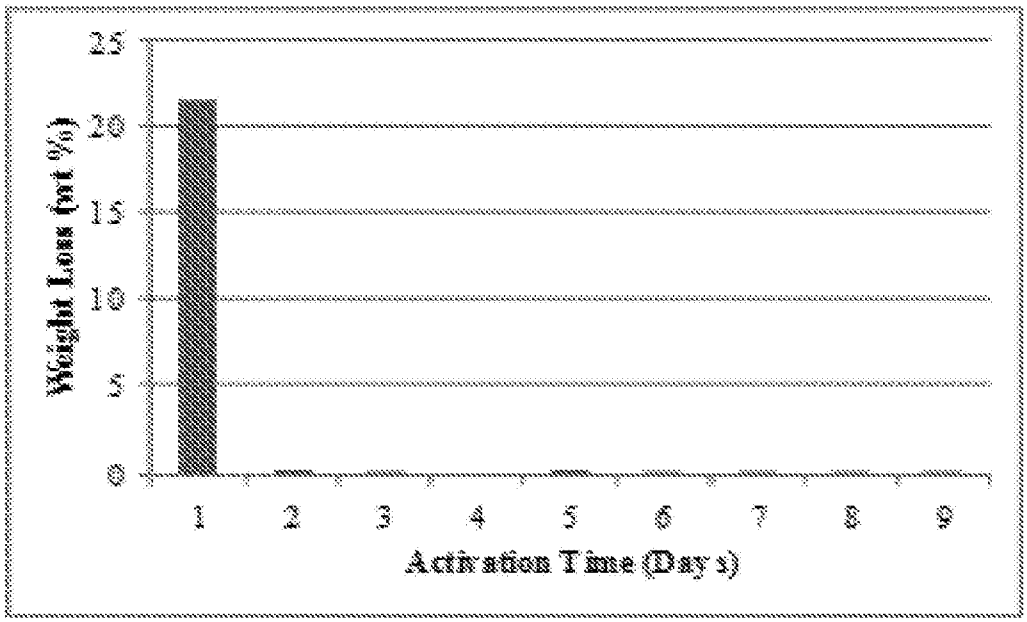


Figure 1

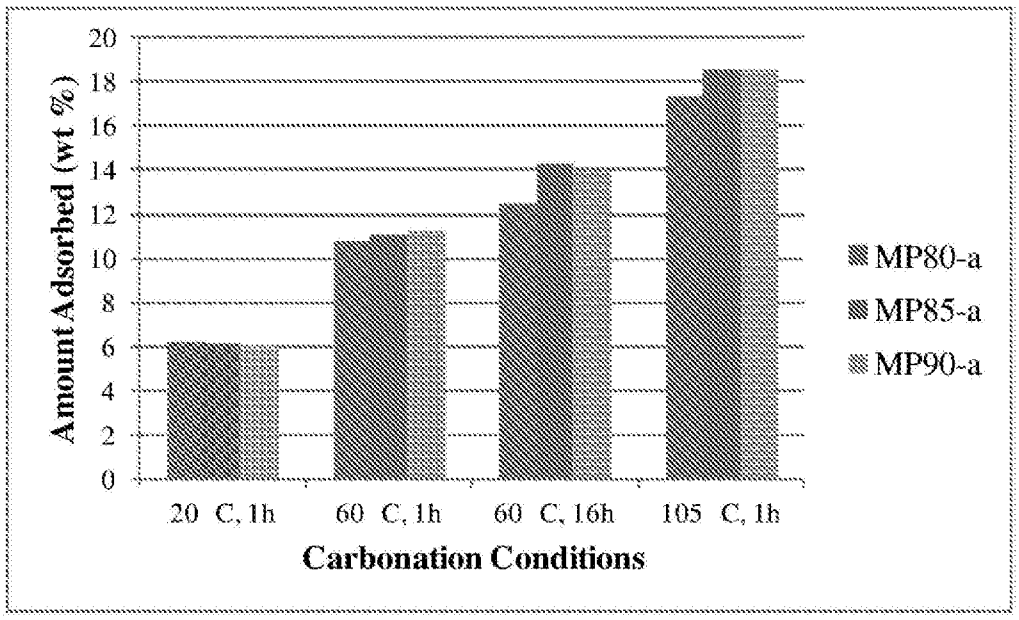


Figure 2

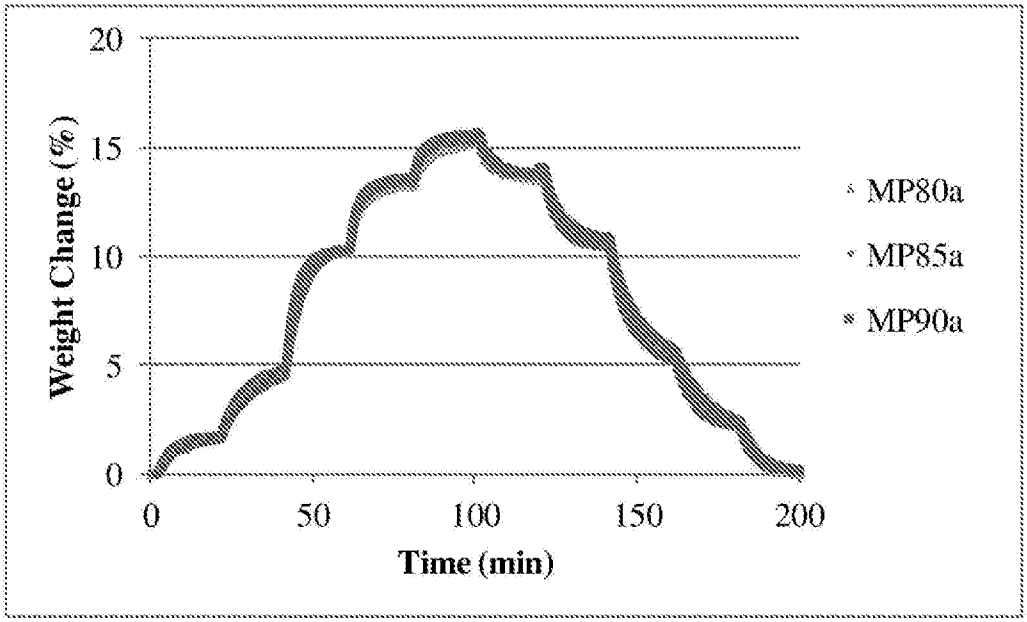


Figure 3

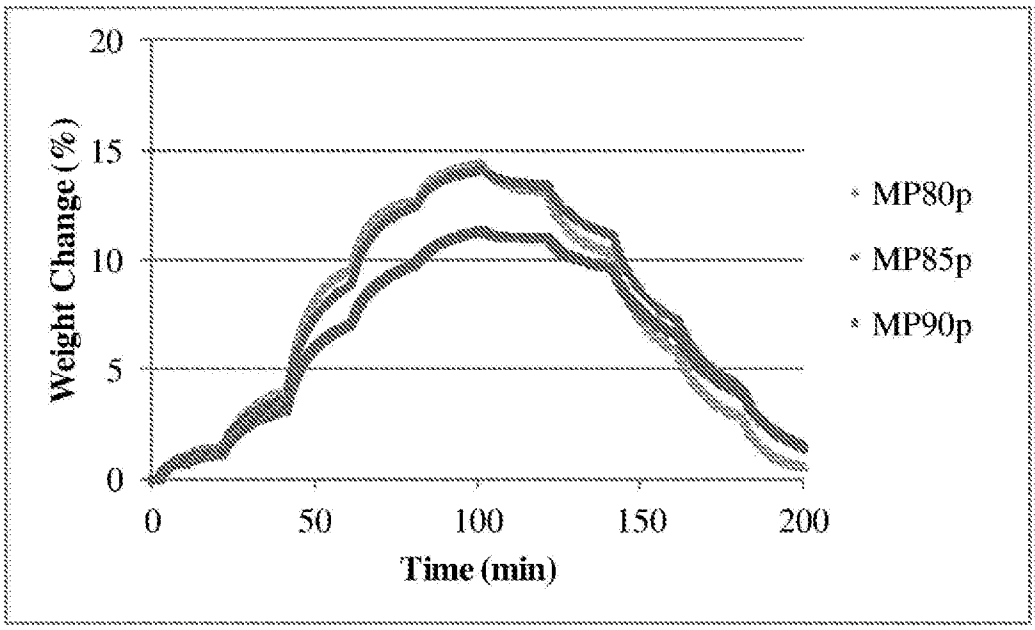


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050376

A. CLASSIFICATION OF SUBJECT MATTER

B01J 20/28 (2006.01) B01D 53/02 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPOQUE X-FULL: Databases: TXTAU1, TXTCA1, TXTEP1, TXTGB1, TXTSG1, TXTUS0, TXTUS1, TXTUS2, TXTUS3, TXTUS4, TXTUS5, TXTWO1, WPI, EPODOC, keywords: sorbent, adsorbent, pellet, compress, compact, carbon dioxide, gas, modify, transform, alter, change, convert, characteristics, phase, form, sonication, vacuum infiltration, support, substrate, base, silica, zeolite, clay, etc.. Espacenet and Google Patent searches: Applicant name: monash, Inventor name: knowles, chaffee, IPC marks: B01D, B01J, KW: adsorbent, absorbent, sorbent, pellet, granule, compress, extrude, compact, gas, carbonation, modify, alter, convert, tacky, polyethyleneimine, PEI, sonication, vacuum infiltration, CO2, support, matrix, etc..

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 January 2015	23 January 2015
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Hong Yu AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262837946

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2014/050376**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	WO 2013/003948 A1 (HER MAJESTY THE QUEEN IN RIGHT OF CANADA AS REPRESENTED BY THE MINISTER OF NATURAL RESOURCES) 10 January 2013	
X	Abstract, claims	29-30
A	Abstract, claims	1-28
	WO 2012/158911 A2 (ENVERID SYSTEMS INC.) 22 November 2012	
X	Abstract, claims	29-30
A	Abstract, claims	1-28
	US 4061593 A (SUMMERS) 06 December 1977	
X	Abstract, column 3, examples	29
A	Abstract, column 3, examples	1-28, 30
	JP 63-104647 A (TODAKA AKIMOTO ET AL.) 10 May 1988, Patent Abstracts of Japan	
X	Abstract	29
A	Abstract	1-28, 30
	JP 63-030310 A (SUMITOMO METAL IND LTD) 09 February 1988, Patent Abstracts of Japan	
X	Abstract	29
A	Abstract	1-28, 30

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050376

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:

because they relate to subject matter not required to be searched by this Authority, namely:

the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including

2. ☐ Claims Nos.:

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos:

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box

Continuation of: **Box III**
This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-2, 4-30(in part) are directed to a process for preparing pelletized form of a composite material for gas separation. The feature of treating a composite material with a gas to alter the physical characteristics of a separate sorption active phase of said composite material and transforming same into a different form to facilitate pelletization of the treated composite material by compressing or compacting is specific to this group of claims.

- Claims 3, 4-30(in part) are directed to a process for preparing pelletized form of a composite material for gas separation. The feature of combining a solid support material with a separate sorption active phase via sonication or vacuum infiltration to form a composite material, before compressing/compacting same into pelletized form is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only features common to all of the claimed inventions include a composite material having a separate sorption active phase, and pelletized composite material from compressing/compacting. However it is considered that these features are generic in this particular art.

Therefore these common features cannot be a special technical feature. Hence there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

The International Searching Authority believes that a search and examination for the second invention will not involve more than negligible additional search and examination effort over that for the first invention and so no additional search fee is required in order to search and examine that invention.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2014/050376**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
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End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.