Gap Analysis for Solid Sorbents for Post Combustion CO_2 Capture

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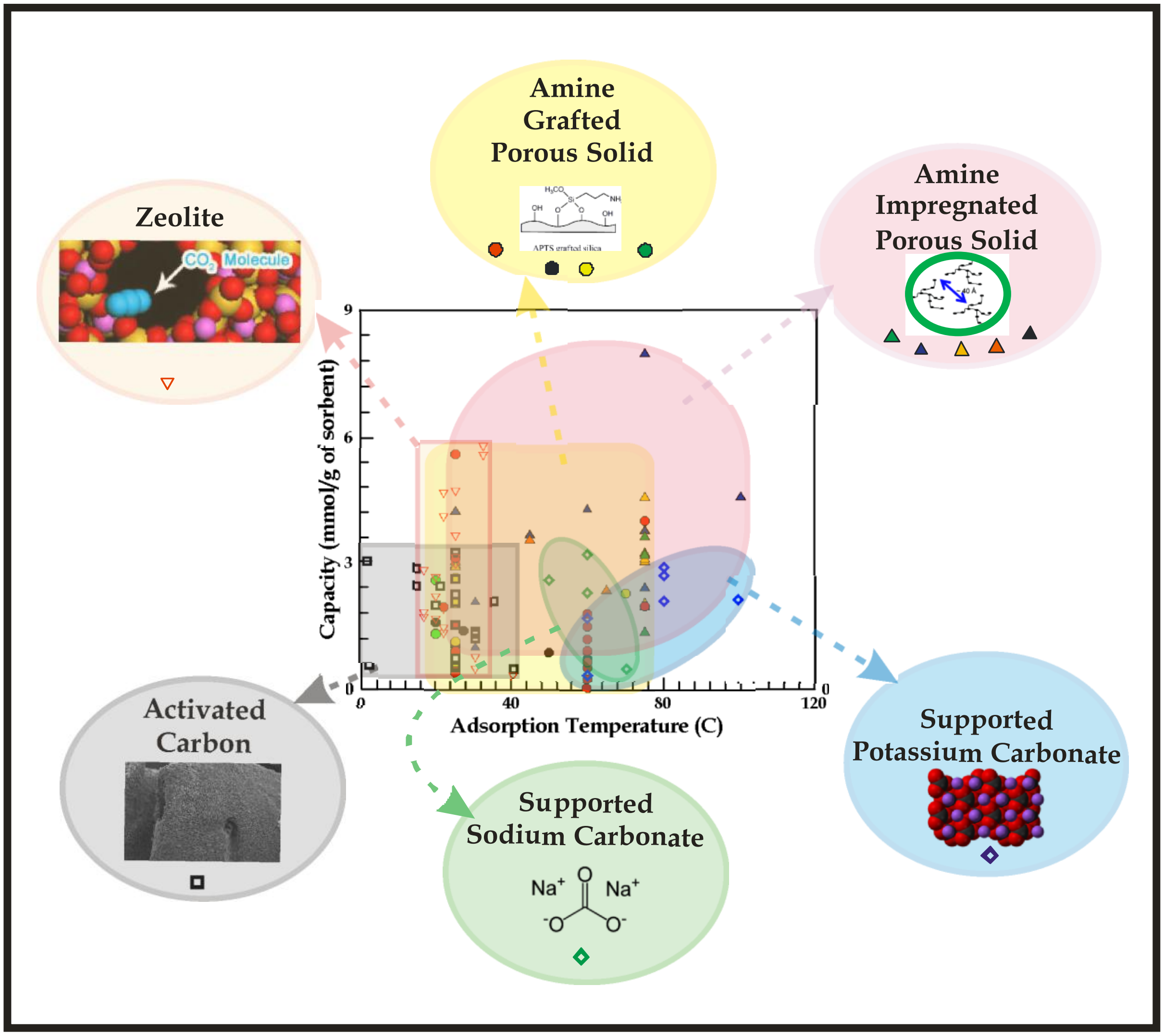
Solid Sorbents Mapping for Post-Combustion CO_2 Capture



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1. Introduction

International Energy Agency (IEA) developed energy scenario suggest that carbon capture and storage (CCS) from power plants might contribute by 2050 to around 10% of the energy-related CO_2 emission reduction required to stabilize global warming [1]. Canada has more than 725Mt of CO_2 annual emissions, where more than 40% of emissions come from stationary sources burning coal or oil or gas in air for generation of power or heat. Federal and provincial governments are aiming for significant reductions in forecast greenhouse gas emissions by 2050 with emissions from the energy production sector (and particularly power generation) being one of the key areas for such reductions. CCS has been identified as a technology with the greatest potential to drive large emission reductions.

The main focus of CCS today is fossil fuel based power plants. The block diagram in ***Figure 1*** illustrates the post-combustion CCS process. In a conventional power plant, fuel is burned with air in a boiler to produce steam that drives a turbine/generator to produce electricity. CCS includes four primary steps: CO_2 capture, compression, transport, and storage. To economically sequester CO_2, it must be in a relatively pure, high-pressure form which necessitates cost-effective capture and compression of the CO_2 emitted by the fossil-fuel based power plant.

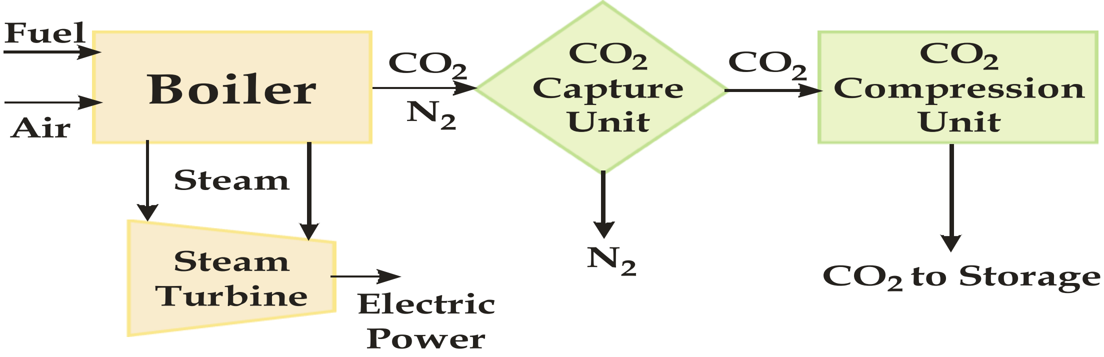


Figure 1 Power plant block diagram with post-combustion CO_2 capture.

Depending on the type of plant, broadly three general approaches are envisaged for CO_2 capture from fossil-fuel based power plants: precombustion, postcombustion, and oxy-combustion/or CLC (chemical looping combustion) [2,3]. Precombustion capture is applicable to integrated gasification combined cycle (IGCC) plants, while oxy-combustion and post-combustion could be applied to conventional coal or gas-fired power plants. However, in their present development stage these approaches are still not ready for implementation due to three primary reasons:

- these technologies have not been demonstrated in large scale;
- the required parasitic loads to supply both power and steam to the CO_2 capture plant would reduce power generation capacity by approximately one-third;
- if successfully scaled-up, they would not be cost effective at their present phase of process development [4].

Amine based CO_2 scrubbing using aqueous solutions of amine, such as monoethanolamine (MEA), is a mature technology that was developed over 70 years ago. Amine scrubbing has been widely practiced for CO_2 capture from gas streams in natural gas, refinery off-gases and synthesis gas processing [5-7]. The gas streams in these processes are usually at a high pressure. The major challenges for CO_2 capture from fossil fueled based thermal power plants are the large volumetric flow rates of flue gas at essentially atmospheric pressure, with large quantity of CO_2 at low partial pressures and a gas temperature range of about 100-150°C. Typical compositions flue gases are provided in ***Table 1***. The presence of ash particles, SO_x, NO_x and significant oxygen partial pressure in the flue gas are additional issues for implementation of amine absorption process for CO_2 capture from power plant flue gas streams.

Table 1 Typical Gas Quality in Applications to CO_2 Capture

Process	CO_2 (vol%)	Impurities
Natural gas turbine exhaust	3-5	Low SO_x and NO_x levels, O_2: 12-15%
Coal/Oil Fired Boiler	11-15	High SO_x and NO_x levels, O_2: 2-5%
IGCC syngas turbine exhaust	4.5-6	Low SO_x and NO_x
Blast furnace gas (after combustion)	25-30	SO_x and NO_x present
Cement kiln off-gas	15-35	Could have many impurities

The state-of-the-art amine process uses 20-30 mass % aqueous monoethanolamine (MEA) for regenerative absorption of CO_2. However, this process is highly energy intensive due to the high regeneration energy requirement. In addition, thermal and oxidative degradation of the solvents result in large solvent make-up, besides producing products that are corrosive. A techno-economic and environmental assessment study suggests an 80% increase in the cost of electricity when CO_2 capture with 30 wt % aqueous MEA absorption process is implemented with coal fired power plant [8]. The CO_2 capture and compression account for 80% of the total cost, while the balance of the cost (20%) is due to transportation and sequestration. This high cost of CO_2 capture is the main barrier of implemention of the MEA process for CO_2 capture from the flue gas of fossil fuel based power plants [9].

Thus, improved, cost effective processes for CO_2 capture from flue gas streams of power plants is essential today in order to mitigate the global warming problems. Among the many process technology options used for CO_2 capture from flue gases, there is a growing interest today in using adsorption processes as a promising alternative separation technique. Adsorption processes using novel solid sorbents capable of reversibly capturing CO_2 from flue gas streams. Solid sorbents have many potential advantages compared to other separation techniques for CO_2 capture, such as ease of handling, greater capacity, reduced energy for regeneration, etc. Adsorption on porous solid media using pressure and/or temperature swing approaches is an emerging alternative that seeks to reduce the costs associated to the capture step.

According to operating temperature regime, the solid sorbents can be classified in three major categories as shown in the ***Figure 2.*** In this classification, sorbents with operating temperature >400°C is considered high temperature sorbents. High temperature sorbents are Temperature Swing Adsorption (TSA) based. Typical operating temperature range of Lithium-based sorbents is 400°-700°C and calcium oxide is 500°-900°C. Intermediate temperature sorbents are mainly hydrotalcite and MgO with an operating regime 200°-400°C. The working principle for intermediate and high temperature sorbents are chemisorption based. The low temperature regime working principle is either chemisorption or physorption.

For post-combustion CO_2 capture, the sorbents with operating temperature below <200°C, i.e., only low temperature are useful. Last few years several research groups worldwide have initiated work on development of new low temperature (<200°C) solid sorbents for CO_2 capture from flue gas with superior performance and desired economics. The impurities in flue gases such as oxides of nitrogen and sulfur often reduce the performance of the sorbents. Ample proof of the fact can be found in open literature. Characterization and understanding the behavior of the sorbents in actual flue gas conditions is of importance. This study reviews and analysis recent progress in solid sorbents to determine their potential for CO_2 capture from flue gas.

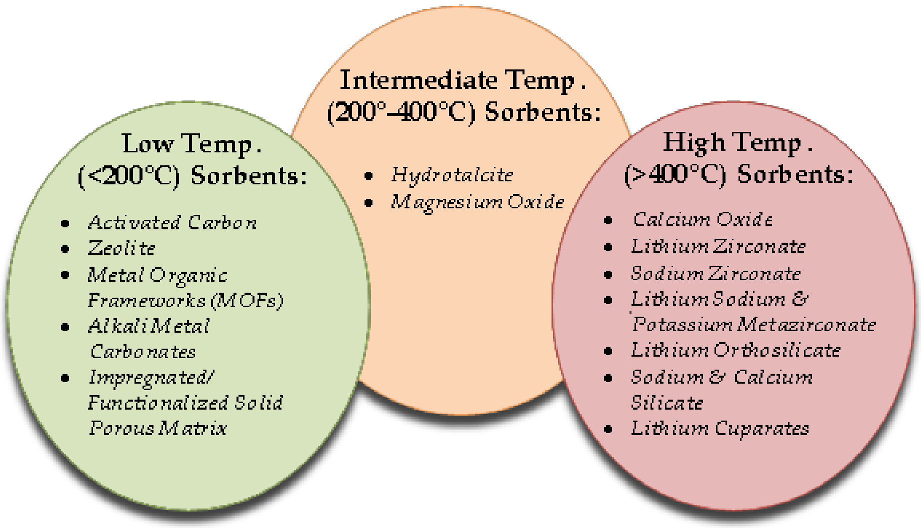


Figure 2 Solid sorbents classification on the basis of operating temperature.

1.1 Desired Characteristics of Solid Sorbent

Criteria that sorbent materials must satisfy, for CO_2 capture from flue gas to be both economical and operational are [10-13]:

- **Adsorption capacity for CO_2:** This is one of the most important parameters since the capital cost of the capture system depends on it. It fixes the amount of adsorbent required and the volume of the adsorber vessels. High adsorption capacity for CO_2 reduces both sorbent quantity and process equipment size. In order for solid sorbents to be competitive with existing MEA (30 wt% base case) scrubbing system, CO_2 capture capacity should be greater than 2.0 $mmol.g^{-1}$ sorbent (hereafter shorten to $mmol.g^{-1}$). However, other important parameters such as, adsorption/desorption kinetics, regeneration energy should also be considered during the selection of solid sorbents for postcombustion CO_2 capture.

- **CO_2 selectivity:** Flue gas streams from fossil-fuel fired power plants contain N_2 and O_2. Potential sorbents should exhibit high CO_2 selectivity over these bulk gas components. It is also important that solid sorbents also show high capacity for CO_2 in the presence of the significant amount of water vapor present in flue gas.

- **Reaction kinetics:** The kinetics of adsorption and desorption controls the cycle time of the adsorption system. Fast kinetics yields a sharp CO_2 breakthrough curve. Kinetics determines the amount of sorbent required and the foot print of the sorption system.

- **Microstructure and morphological stability:** The regenerable sorbents must demonstrate microstructural and morphological stability in multi-cycling operation. The engineered (tailored) sorbent microstructure features are critical for maintaining high reaction kinetics and high adsorption capacity i.e., sorbent conversion efficiency.

- **Mechanical Robustness:** Sorbents must have sufficient mechanical stability to withstand disintegration in operating conditions, such as high volumetric flow rate of flue gas, vibration and temperature swings. The mechanical degradation could also happen by abrasion or crushing. An adequate mechanical robustness of sorbent is therefore critical to minimize sorbent makeup rate, avoid generation of hazardous fine particles and to keep CO_2 capture process cost-effective.

- **Chemical Stability/Tolerance to Impurities:** Solid sorbents, in particular amine functionalized sorbents, should be stable in the oxidizing environment of flue gas and resistant to common flue gas contaminants. It is likely that contaminants such as SO_x and NO_x and heavy metals will also require removal from flue gas as they unfavorably affect CO_2 adsorption capacity of the sorbent materials.

- **Regeneration Energy of Sorbents:** Heat of adsorption, a measure of the energy required for regeneration should be substantially low to have a low energy penalty for implementation of CO_2 adsorption systems. Heats of adsorption are generally in the range of -25 to -50 $kJ.mol^{-1}$ and -60 to -90 $kJ.mol^{-1}$ for physisorption and chemisorptions cases, respectively. Ease of regeneration of the CO_2 sorbent will also help to lower the cost of capture.

- **Cost of Sorbents:** Cost is perhaps the most subtle characteristic. Working life span, adsorption capacity and kinetics will play a critical role to determine acceptable cost structure of the solid sorbents and associated systems.

The above-mentioned attributes are the desired characteristics of an ideal adsorbent for CO_2 capture. Rarely will a single adsorbate be optimal in all these attributes. However, useful adsorbents will be those that effectively and economically capture CO_2 from flue gas streams.

2. Physical Sorbents

CO_2 from flue gas may be removed with a variety of solid physisorbents materials including porous carbonaceous materials, zeolites, alumina, silica gels, and metal organic frameworks (MOFs). For physisorption, such as adsorption of CO_2 by zeolite or activated carbon, the mechanism for CO_2 capture can be visualized as

$$CO_2 + \text{surface} \Leftrightarrow (CO_2)\bullet(\text{surface})$$

where, selective adsorption of CO_2 in comparison with N_2 is caused by van der Walls attraction between the CO_2 molecule and adsorbent surface as well as by pole-ion and pole-pole interactions between the quadrupole of CO_2 and the ionic and polar sites of the solid adsorbent surface [14].

This section summarizes the recent progress in CO_2 capture using solid physisorbents, namely activated carbon, carbon nanotubes, carbon molecular sieves, zeolites and MOFs.

2.1 Activated carbon based solid sorbents

Inorganic carbon is available in various forms, such as porous activated carbons (AC), carbon molecular sieves (CMS) and carbon nanotubes (CNT). ACs are widely used as adsorbent in various industrial applications, e.g., gas purification, water treatment etc. due to the low cost of raw materials and wide availability [14-16]. It can be produced by various physical and chemical activation processes from different precursors, such as lingo-cellulosic materials and coals of different rank. It is possible to prepare ACs with high active surface area, porosity (meso or micro) and adsorption capacity. Sorption behavior of CO_2 on commercial and synthesized ACs derived from different natural organic materials as well as carbon molecular sieves have been widely studied experimentally and theoretically by various research groups at low to very high pressure [17-38]. The adsorption capacities of carbon based adsorbents are summarized in ***Table 2.***

Applications of pressure swing adsorption (PSA) process are being reported to remove CO_2 from gas streams using ACs [15-18,20,32-33]. However, low recovery rate is one of the shortcomings reported with this process. Yang and co workers [18] studied the feasibility of PSA process first time to separate and concentrate CO_2 from flue gas using BPL ACs and carbon molecular sieves as sorbent. Pure component adsorption capacity for CO_2 at 298K was about 2.1 $mmol.g^{-1}$ for AC. They achieved a CO_2 recovery of about 68.4% from a flue of 17% CO_2+ 4%O_2 + 79%N_2 using ACs at 298K, while the amount of CO_2 contaminant in the adsorption product was around 6.3%. They also concluded that the equilibrium separation of CO_2 from flue gas using ACs is better than the kinetics separation by CMS. In another work this group reported that in case of equilibrium separation, zeolite 13X is better than the ACs [19] comparing the performance of AC and zeolites 13X at different temperature and for two feed compositions (16% and 26 % CO_2 in N_2). For zeolite 13 X isothermal equilibrium capacity was ca. 4.5 $mmol.g^{-1}$ at 15°C and a pressure of about 1bar. The heat of adsorption, ΔH_{ad} of activated carbon (ΔH_{ad}=30 $kJ.mol^{-1}$) was lower than that of zeolites (ΔH_{ad}=36 $kJ.mol^{-1}$) due to its weaker interaction with CO_2 compared to ACs. Na et al [28] also demonstrated PSA process using commercial activated carbon to separate CO_2 from flue gas of a power plant. They also measured the adsorption isotherm of CO_2 at the temperature of 15-55°C and pressure of 0-2 atm. The CO_2 adsorption capacities decreased significantly e.g., from ca. 3.2 to ca. 1.6 $mmol.g^{-1}$ when temperature was increased from 288 to 328 K at 1 atm. The maximum recovery of 34% with a purity of 99.8% was obtained from PSA process from a flue gas composed of 17% CO_2+ 4%O_2 + 79%N_2.

Table 2 CO_2 Adsorption Capacity of Carbonaceous Solid Sorbents

Sorbent	T(K)	p_{CO2} (atm)	Capacity (mmol.g^{-1})	Process	Ref.
AC	298	1	2.07	PSA	18
AC	288	1	2.45	PSA	20
AC	298	0.2	0.75		23
AC	298	1	3.23		28
AC	298	1	2.61	PSA	32
AC	298	0.1	0.57	GC-TCD	31
AC[d]	298	1	2.25		38
AC[e]	298	1	1.53		38
AC-A35/4	293	1	2.00	Flow desorption	24
AC-F30/470	288	1	2.86	Volumetric analysis	46
AC-F30/470	297.3	0.15			21
AC-RB	303	1	1.22		33
AC Norit RB1	294.2	1	2.456	Gravimetric analysis	27
AC Norit RB1	313.1	0.15	0.50	TPD	19
AC-Norit R1 Extra	298	0.15	0.538		25
Bamboo derived AC	275	2	3.00	Volumetric analysis	30
Bamboo derived AC	275	2	0.54[a]	Volumetric analysis	30
Anthracite based Ac[b]	303	1	1.38	TGA	37
Anthracite based Ac[c]	303	1	1.33	TGA	37
SWNT	308	1	2.07		51
Graphene	195	1	0.80		52
CMS	303	1	2.43		54

a. Wet bamboo activated carbon with water loading in the range of 1.35 to 2.36. Water loading refers to the weight ratio of water to dry carbon.
b. Activated at 850°C for 3h.
c. Activated at 850°C for 2h.
d. Activated carbon without chemically acid treated.
e. Activated carbon with chemically acid treated.

Do et al. [23] in 1998 presented theoretical and experimental results on CO_2 adsorption isotherm at three different temperatures and at a pressure up to 20kPa on Ajax activated carbon. The reported adsorption capacity was ca. 0.75, 0.36 and 0.11 mmol.g^{-1} at 298, 323 and 373K, respectively. They also observed that CO_2 adsorption capacity decreases significantly with increase in temperature. This was also corroborated by Berlier et al. (***Figure 3***) [21]. Siriwardane et al. [32] compared the volumetric adsorption isotherm of CO_2 on G-32H activated carbon and molecular sieves 13X and 14A at 25°C up to a pressure of about 20 atm. They found that at lower pressures (<2 atm) CO_2 uptake of activated carbon was lower than that of molecular sieve 13X, but at higher pressures (>2 atm) activated carbon exhibited significantly higher uptake than molecular sieves. They established that the surface affinity for CO_2 of molecular sieve

13X was relatively better than that of activated carbon and CO_2 adsorption capacity of three sorbents was not adversely affected by the adsorption of other gases such as N_2, H_2. From their competitive adsorption rate studies for gas mixtures at 25°C, they concluded that the rate of adsorption of CO_2 on activated carbon at 1 atm was lower than that for molecular sieve 13X but it was possible to obtain excellent separation of CO_2 from a gas mixture containing 14.8% CO_2 and 85.2% N_2 with both types of sorbents. Maroro-Valer and his group [34-37] produced AC from various carbon sources such as anthracite coal and unburned carbon in fly-ash. The highest surface area reported was with 1071 $m^2.g^{-1}$ from anthracite coal with two hours of activation at 890°C and the highest CO_2 adsorption capacity obtained was 1.49 $mmol.g^{-1}$ using thermogravimetric analysis (TGA) and pure CO_2. Wang et al. [30] conducted a comparative study of CO_2 sorption on ACs prepared from bamboo chips and coconut shell in presence of water and concluded that water showed detrimental effect on CO_2 sorption at low pressure. However, at higher pressure it showed a significant rise in capacity with increasing pressure and water content of gas stream. This was explained based on the possibility of condensation of CO_2 and hydrate formation inside the pores.

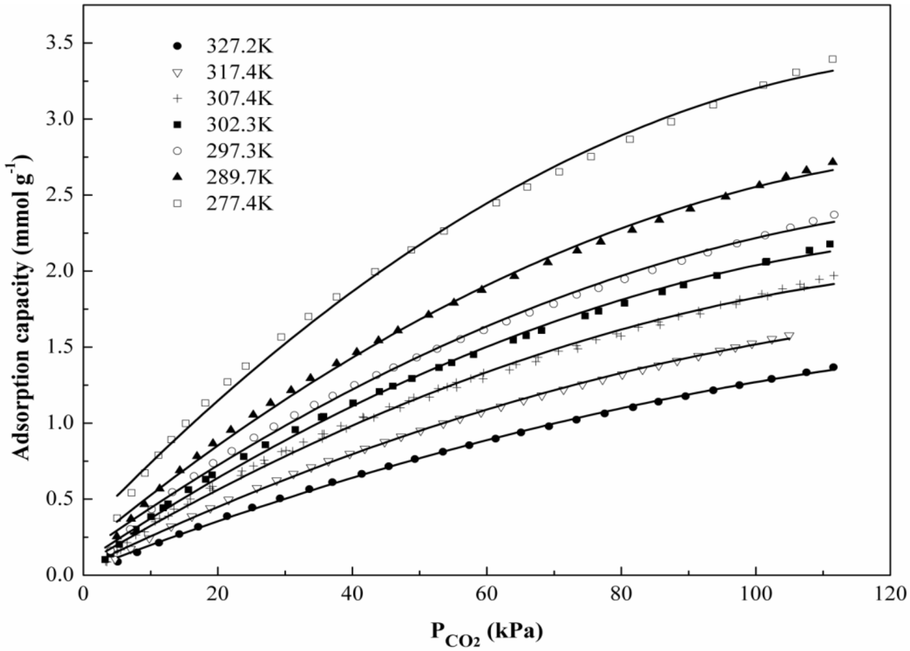


Figure 3 Isotherm for adsorption of CO_2 on activated carbon [21].

Recently, Radosz et al. [38] proposed a low cost low pressure carbon filter process to capture CO_2 from flue gas. Carbon-rich materials, such as AC or charcoal were selected for this study. All carbonaceous materials studied in this work exhibited a rapid sorption rate and short sorption cycle. The Carbon filter process proposed in this work could recover at least 90% of the flue-gas CO_2 of 90% purity.

In summary, activated carbons are low cost with fast adsorption kinetics and require low regeneration energy. However, the predominance of the porous media of ACs still fails to offset the drawbacks of physical adsorption process - selectivity. At low partial pressure of CO_2, ACs exhibits lower adsorption capacity and selectivity than zeolites due to their unfavorable adsorption isotherms [20] The existence of water may negatively affect the capacity of AC as water gets adsorbed competitively [30]. Additionally, other components or contaminants in flue gas have a detrimental impact on the CO_2 adsorption capacity.

2.2 Carbon molecular sieves

Carbon molecular sieves (CMS), a special class of microporous carbon materials whose unique textural characteristics permit kinetic separation of gas mixtures, i.e., separation as a result of differences in the diffusion rates of the species involved, are also studied for CO_2 capture. For a CMS to be useful for gas separation, it must possess a narrow pore size distribution (PSD) consisting of pore mouths of molecular sizes and a relatively high micropore volume, features which confer them selectivity and capacity, respectively [53]. A porous monolithic carbon fiber composite molecular sieve (CFCMS) based on isotropic pitch derived carbon fibers was developed. These are characterized by Burchell et al. [54] CO_2 isotherm measured volumetrically and gravimetrically showed CO_2 uptake of >2.27 mmol.g^{-1} at 30°C and atmospheric pressure. CO_2 uptake reduces at elevated temperature, increases with increasing pressure. However, analysis of equilibrium and kinetics of batch adsorption of CO_2 with a CMS (a commercial CMS from Takeda chemical company termed 5A) indicated no molecular sieving action but instead micropore diffusion was shown to be rate limiting in the process of adsorption dynamics [55]. Recently, Alcañiz-Monge et al. [56] studied CO_2 separation by CMS-monoliths prepared from nitrated coal tar pitch and reported that developed microporous carbon monoliths showed faster CO_2 kinetics than commercially available Takeda 3A CMS.

2.3 Carbon nanotubes based solid sorbents

The use of new generation materials, such as CNT and graphene has also become an **active area of research** for separation of gas mixtures over the last several years. Considerable experimental and theoretical research efforts are being devoted to investigate adsorption of CO_2 and N_2 and their mixtures on CNT (see ***Table 2***) [31,40,51,57-67]. By choosing the appropriate pore size and shape and optimum conditions, CNT can act as suitable candidate for CO_2 separation and sequestration [62,66]. Cinke et al. [51] reported adsorption of CO_2 on purified single-walled carbon nanotubes (SWCNT) in the temperature range of 0–200° C (***Figure 4***). SWCNT exhibited a BET surface area of 1587 m^2. g^{-1}, total pore volume of 1.55 cm^3.g^{-1} and micropore volume is 0.28 cm^3. g^{-1}. The CO_2 adsorption capacity of SWCNTs was twice that of AC. However, Lu and his group [31,40] observed that equilibrium CO_2 adsorption capacity of raw CNT was relatively lower than that of granular AC at 25°C. Skoulidas et al. [61] studied detailed simulations to examine the adsorption and transport diffusion of CO_2 and N_2 in single-walled carbon nanotubes at room temperature as a function of nanotube diameter. They reported that transport diffusivities for CO_2 in nanotubes with diameters ranging from ~1 to ~5 nm are roughly independent of pressure. The observed diffusion mechanism is not Knudsen like diffusion. Based on Monte Carlo simulations, Huang et al. [62] showed that CO_2 adsorption in the range of 4 mmol g^{-1} to 9 mmol g^{-1} is an increasing function of the diameter of CNT and CNT demonstrated a higher selectivity toward CO_2 than other sorbents, such as ACs, zeolites 13X, and metal-organic frameworks reported in the literature. Razavi et al. [66] also supported that CNT exhibits higher selectivity of CO_2 over nitrogen compared to other carbon-based materials for separation of CO_2/N_2 mixture. Lithoxoos et al. [67] obtained type I (Langmuir) behavior of the adsorption isotherm for CO_2 for SWCNTs.

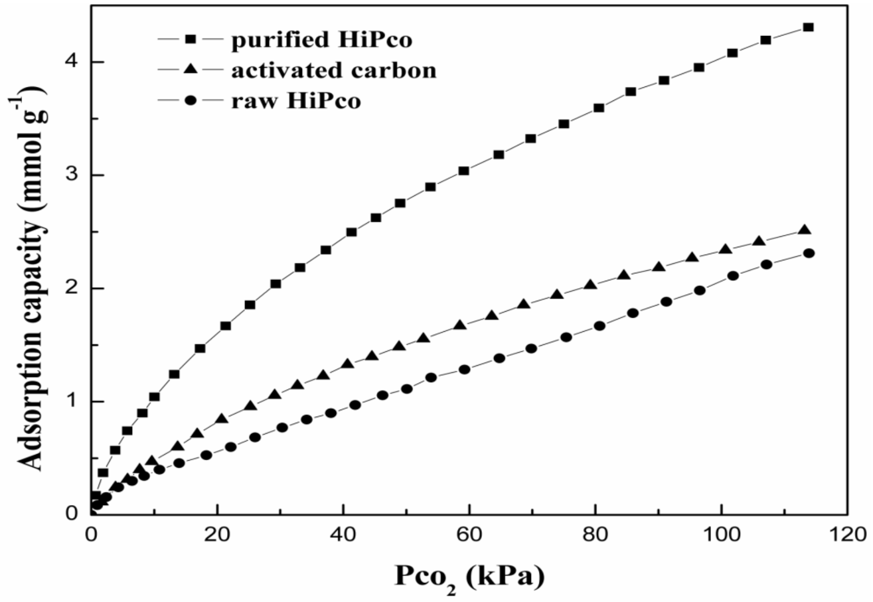


Figure 4 Comparison of CO_2 adsorption capacities of HiPco SWNTs and activated carbon at 35°C [51].

2.4 Zeolite sorbents

Microporous crystalline framework materials such as synthetic as well as natural zeolites are widely used in the field of gas separation and purification. Conventional zeolites are based on silicate frameworks in which substitution of some of the Si with Al (or other metals) leads to a negative charge on the framework, with cations (usually Na or other alkaline or alkaline earth metals) within the pore structure. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. Due to their defined crystalline structures, these sorbents have uniform pore sizes in the interval of 0.5 to 1.2 nm [68], a property that allows them to separate molecules by means of the molecular sieving effect. Separation of gases in zeolites can also take place through the mechanism of selective adsorption of those molecules that have relatively large energetic dipole and quadrupole. The adsorbates that have high quadrupole moment, such CO_2 (-14.29×10^{-40} C.m^2) [69] interact strongly with the electric field created by the structural cations of zeolites and this favors their adsorption. Separation of gases by the zeolitic adsorbents depends on various factors: structure and composition of the framework, cationic form, zeolitic purity, size and shape of the molecules, and molecular polarity. Zeolitic materials have shown promising results for separation of CO_2 from gas streams. There are several published literature concerning CO_2 adsorption over different types of zeolites such zeolite A, X, Y, and other natural zeolites like chabazites, clintopiles, ferrierite, and mordenites etc [17,32,47,48,70-98]. ***Table 3*** summarizes the various zeolites that have been explored to date for application of CO_2 separation from gas mixtures. Earlier, a study of adsorption of CO_2 on various natural zeolites, namely mordenite, ferrierite, clinoptilolite and chabazite and synthetic zeolites, namely 4A, 5A and 13X showed chabazite and 13X, among the natural and synthetic zeolites, respectively to be a better adsorbents for CO_2 separation from N_2 [74]. The work by Siriwardane et al. [47] indicated that natural zeolite with highest sodium content and highest surface area showed the highest CO_2 adsorption capacity during volumetric gas adsorption studies and highest rates of adsorption during TGA studies. Hernández-Huesca et al. [48] studied adsorption equlibria and kinetics of CO_2 adsorption in natural zeolites, namely erionite (ZAPS), mordenite (ZNT) and clinoptilolite (ZN-19). Erionite (ZAPS) was found to have highest CO_2 adsorption capacities over the entire equilibrium pressure range. For example, CO_2 adsorption capacity of ZAPS was about 2.8 mmol.g^{-1} at 290 K and atmospheric pressure. An extensive screening study of about 13 synthetic zeolites, including 5A, 13X, NaY, ZSM-5, HiSiV-3000 (based on ZSM-5 structure with silica to alumina ratio, Si/Al>1000) was conducted Harlick and Tezel [86] for CO_2 removal from flue gas. From pure component isotherm data, it was observed that adsorption capacities of the adsorbents increased in the following order (in the pressure range of about 0-2 atm): 13X (Si/Al=2.2) > NaY(Si/Al=5.1)> H-ZSM-5-30(Si/Al=30)> HiSiv3000> H-Y-5 Si/Al=5.1) (***Figure 5***). This might be due to low silica to alumina ratio with cations (sodium) in the structure that show strong interactions with CO_2. Five commercial zeolites, namely 13X, 4A, 5A, WE-G 592(UOP) and WE-G(UOP) were tested by Siriwardane et al. [90]. They reported that CO_2 adsorption capacity was significantly lower at 120°C than at ambient temperature. Zeolites 13X and WE-G 592 showed the highest adsorption capacity. These two zeolites have the largest pore diameters and sodium to silica ratio. Zukal et al [98] performed

Table 3 CO_2 Adsorption Capacity of Zeolites

Sorbent	T (K)	p_{CO2} (atm)	Adsorption Capacity (mmol.g^{-1})	Experimental Procedure	Ref.
Zeolite 13X	293	0.15	2.63		75
Zeolite 13X	295	1	4.61		86
Zeolite 13X	298	1	4.66		87
NaX	305	1	5.71	Gravimetric analysis	78
NaY	305	1	5.5	Gravimetric analysis	79
NaY	295	1	4.06		86
NaM	298	1	2.95	Gravimetric analysis	78
Silicalite	303	0.15	0.48	Calorimeter-Volumetric Apparatus	100
Na-ZSM-5	303	1	0.75	GC	82
Molecular sieve 13X	298	1	2.8-3.6^{a}	PSA	32
Molecular sieve 4A	298	1	2.3-3.1^{a}	PSA	32
Molecular sieve 13X	293	0.15	2.18		101
Molecular sieve 4A	293	0.15	1.65		101
Molecular sieve 13X	-	0.1	2.33	Fluidized Bed	97
Molecular sieve 5A	-	0.1	2.35	Fluidized Bed	97
Erionite (ZAPS)	290	1	2.8		48
Mordenite (ZNT)	290	1	1.8		48
Clinoptilolite(ZN-19)	290	1	1.7		48
ZSM-5^{b}	313	0.1	0.32^{c}	GC	85
HZSM-5-30	295	1	1.9		86
HiSiv 3000	295	1	1.44		86
HY-5	295	1	1.13		86

a. Cyclic tests
b. SiO_2/Al_2O_3 ratio = 280
c. Experimental data

investigation on CO_2 adsorption on six high silica zeolites (SiO_2/Al_2O_3>60), TNU-9, IM-5, SSZ-74, ferrierite, ZSM-5, ZSM-11. The highest CO_2 adsorption capacity was found with TNU-9 and IM-5 attaining 2.61 and 2.42 $mmol.g^{-1}$ at the pressure of 100kPa, respectively.

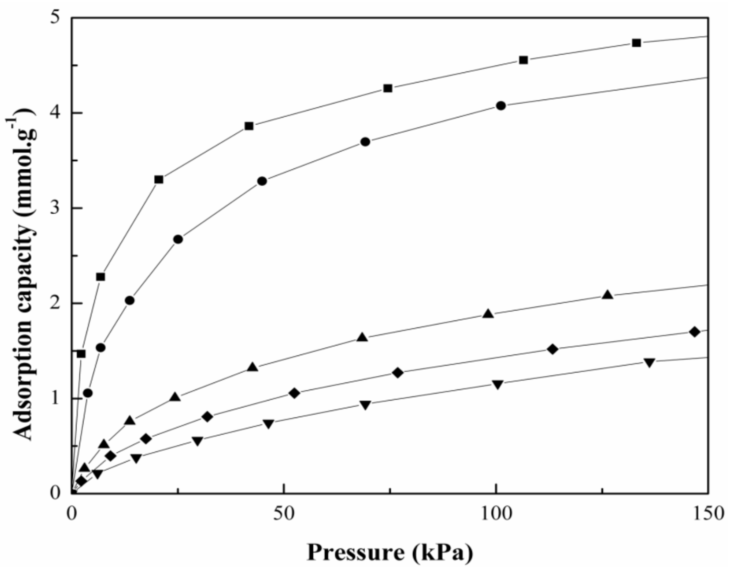


Figure 5 Comparison of CO_2 Adsorption Isotherms for Fresh Zeolites at 295 K (Reproduce from Harlick and Tezel [86]. —■— 13X; —●— NaY; —▲— HZSM-5-30; —◆—HiSiv 3000; —▼—HY-5

Recent studies also focused on modification of zeolites by the introduction of large and electropositive, polyvalent cations to enhance the adsorption of CO_2. Khelifa et al. [89] demonstrated that NaX(Si/Al=1.21) zeolite exchanged with Ni^{+2} and Cr^{+3} had shown a decrease in CO_2 adsorption capacity as compared to that of parent NaX zeolite due to a weak CO_2-sorbent interaction. NaX and NaY and those resulting of ion exchanged with Cs, since it is the most electropositive metal of the periodic table, were tested in the adsorption of CO_2 by Diaz et al. [42,43] Cs treated zeolites performed better were very active for adsorption at higher temperatures (100^{o}C). Zhang et al. [94] prepared chabazite (CHA) zeolites (Si/Al<2.5) and exchanged them with alkali cations (e.g., Li, Na and K) and alkaline earth cations (e.g., Mg, Ca, Ba) to assess their potential for CO_2 capture from flue gas by VSA for temperatures below 120^{o}C. From adsorption isotherm it was found that NaCHA and CaCHA hold comparative advantages for high temperature (>100°C) CO_2 separation whilst NaX zeolite shows superior performance at relatively low temperatures. According to Katoh [82] the selectivity of ion-exchanged ZSM-5 zeolites, M-ZSM-5(M=Li, Na, K, Rb, and Cs) might be due to the fact that almost all CO_2 molecules strongly adsorbed on the cation sites, while N_2 interacted with the wall of the H-ZMS-5.

Adsorption kinetics is an important parameter to value the adsorption performance of an adsorbent. Kinetic studies of CO_2 adsorption on zeolite are rarely reported. According to the results shown by Hernández-Huesca et al. [48], adsorption of CO_2 on erionite (ZAPS) occurred fast and about 70% of total capacity achieved at both 273K and 293K. Zhang et al. [39] investigated the adsorption kinetics of CO_2 adsorption on zeolite 13X and adsorption activation energy for CO_2 on 13X decreased with the increase of pressure. The adsorption kinetics were described by the linear driving force (LDF) model.

Most of the research in adsorption using zeolitic adsorbents have focused on PSA/VSA adsorption for separating CO_2 from flue gas in power stations that use coal as fuel [17,41,47,83,88,95]. TSA process has also been suggested by various research groups for the separation of CO_2 from flue gas using zeolites [93,96]. Using TSA process Merel et al. [93] obtained best performance with zeolite 5A in terms of CO_2 capture rate (18%) and volumetric productivity (+23%) when simulated 10%CO_2/90%N_2 gas was used. Konduru et al. [96] employed TSA process to capture CO_2 from a 1.5%CO_2/98.5%N_2 using zeolite 13X. Based on average CO_2 recovery of 84% after five consecutive cycles, they concluded that zeolite 13X showed promise as an adsorbent with substantial CO_2 uptake capacity. Lee et al. [97] pointed out one potential difficulty with the zeolite sorbents when used in fluidized beds. They observed significant sorbent carried over due to attrition. Zeolites 5A and zeolites 13X presented 2.1- 4.0 fold higher attrition than AC and activated alumina. This would possibly cause high maintenance cost for dry sorbent and problems in the operation of fluidized bed process.

In summary, zeolites have been studied extensively to determine the effect of type of ions incorporated into the structure on the adsorption equilibrium and energetics. In general, adsorption kinetics of CO_2 on zeolites is comparatively fast and achieved equilibrium capacity within a few minutes. However, CO_2 adsorption on zeolites is strongly influenced by the temperature and pressure. Adsorption of CO_2 decreases with increase in temperature and increases with rise in gas phase partial pressure of CO_2. Presence of water vapor may limit the application of zeolite sorbents by decreasing its capacity. It is therefore obvious that by carefully considering and optimizing different important factors, such as basicity and pore size of zeolites, electric field strength caused by the presence of exchangeable cations in their cavities may significantly influence the CO_2 adsorption capacities of zeolites [99].

2.5 Metal organic frameworks (MOFs)

Metal-Organic Frameworks are relatively new class of solid sorbent materials with a great potential for CO_2 capture. These are crystalline compounds consisting of metal ions or clusters coordinated to form rigid organic molecules to one-, two-, or three-dimensional structures that can be porous. In some cases, the pores are stable to elimination of the guest molecules (often solvents) and can be used as a sorbent for CO_2.

Professor George Shimizu, Department of Chemistry, University of Calgary, is one of the leading experts in MOF materials. "Gap Analysis of Metal Organic Frameworks (MOFs) for Solid Sorbents for Postcombustion CO_2 Capture" by Prof. Shimizu is included in Appendix I.

In summary, MOFs may be promising materials for CO_2 removal provided that more favorable CO_2 adsorption isotherms are obtained. Their selectivity and capacity at low partial pressure of CO_2 in gas mixtures are low gas. They may not always be sufficiently stable for the conditions under which they would need to be applied in flue gas treatment. Additionally, the stability over multiple adsorption and desorption cycles under practical adsorption conditions needs to be examined in more detail. However, MOFs likely will also play an increased role in future methodologies for postcombustion CO_2 capture.

3. Chemisorbents

Most of the conventional physisorbents, such as zeolites, ACs, CMS and CNTs described above suffer from low CO_2 adsorption capacities at relatively low CO_2 partial pressure and lower selectivity towards CO_2. Recently, modifications in the surface chemistry of the porous materials by incorporating basic sites capable of interacting strongly with acidic CO_2 in order to increase CO_2 adsorption capacity and to keep high selectivity for CO_2 are considered very promising. The common modifying functional groups include alkaline carbonates and various amine groups.

3.1 Regenerable Alkali Metal Carbonates Based Sorbent

Chemical adsorption of CO_2 with a regenerable alkali metal carbonate (M_2CO_3; M: Li, Na, K) solid sorbent (dry scrubbing) can be considered as a potential technique for CO_2 capture from flue gas. Alkali metal carbonates have been studied as sorbents for a post combustion CO_2 capture since its operating temperature <200°C and its moisture tolerance, in fact moisture is needed for adsorption reaction. These classes of sorbents were investigated for their commercial feasibility by Hoffman et al [102] in 2001. The carbonation and decarbonation reactions for Na2CO_3 system are:

Carbonation: $M_2CO_3 + H_2O + CO_2 = 2MHCO_3$ (1)

$$\Delta H = -135 \text{ kJ.mol}^{-1} \text{ when M = Na}$$

$$= -141 \text{ kJ.mol}^{-1} \text{ when M = K}$$

Decarbonation: $2MHCO_3 = M_2CO_3 + H_2O + CO_2$ (2)

In the adsorption process (carbonation), CO_2 and moisture react with the carbonate sorbent at 60-110°C and formed alkali metal bicarbonate. Heat treatment of bicarbonate at 100-200°C regenerates (decarbonation) the alkali metal carbonate releasing the CO_2 and water vapour. Cooling the offgas condenses the steam producing nearly pure CO_2. 1g of Na_2CO_3 potentially can capture 415 mg or 9.43 mmol of CO_2. In USA RTI International is the leading developer of sodium carbonate based process and in Asia, Korea Energy Research Institute (KERI) and Korea Electric Power Research Institute (KEPRI) have a joint effort to develop potassium carbonate based technologies for retrofitting existing power plants.

Japanese researchers Hayashi et al [103] in 1998 had noted the poor performance of CO_2 capture by zeolite and carbon molecular sieve in the presence of moisture in pressure swing adsorption (PSA) method. They developed temperature swing adsorption (TSA) and regeneration cyclic process for CO_2 capture using potassium carbonate supported on activated carbon. For regeneration, pure steam was utilized for bench-scale unit. *It is important to note recently several group proposed and applying steam stripping in case of amine impregnated solid.* K_2CO_3 performs the best out of three carbonates as it is shown ***Figure 6***; it has a wide carbonation temperature range where sorbent efficiency is 100%. They had shown that there was an optimum loading of K_2CO_3 on AC support and suggested that above the optimum loading, excess K_2CO_3 blocks micropores of AC, restricting CO_2 supply at the active reaction sites, resulting in reduction of adsorption kinetics and working CO_2 capture capacity.

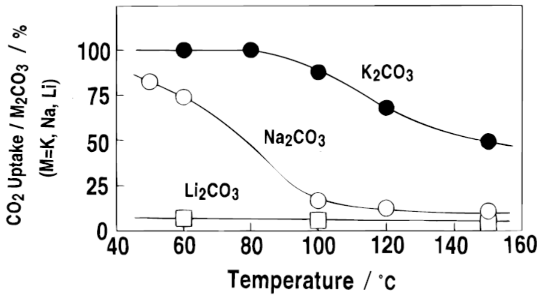


Figure 6 Effect of temperature on the efficiency of CO_2 capture by alkali metal carbonates. Feed gas composition: 13.8% CO_2, 10% H_2O and balance He [103].

3.1.1 Regenerable Sodium Carbonate Sorbent Systems

Harrison et al from Louisiana State University (LSU) and Gupta et al RTI International's collaborative research work on Na_2CO_3 sorbent in 2004 [104] had utilized TGA and lab fixed-bed reactor. Authors concluded that multicyclability/durability and the energy requirement for sorbent regeneration are the two key factors to the economic viability of the process. To satisfy the durability and needs of high kinetics, they suggest that the active sodium compound must be dispersed on a ceramic support such as Al_2O_3. RTI International has over the last several years through their publications and presentations [104-110] reported the status of its dry carbonate process. RTI's process development group identified [110] that fixed-bed and dense-phase fluidized-bed systems were not optimal reactor schemes for the Dry Carbonate Process due to its exothermic nature of chemical reaction. The schematic of RTI's Dry Carbonate process for CO_2 capture from flue gas is shown ***Figure 7*** [110]. It is intended that this technology can be retrofitted to existing power plants and it is ideally suited for coal-fired power plant. Economic analyses indicated that this technology has potential to achieve lower cost requirements and a lower energy penalty compared to conventional MEA technology. RTI's sorbent R&D has progressively narrowed the scope of the potential sorbent and process designs that can be combined to create a commercially-feasible CO_2 capture process. In field testing of RTI's prototype co-current down flow gas-solid contactor system was operated for a total of 235 hours using fossil fuel-derived flue gas. The system has been demonstrated to run continuously for extended periods of time and has achieved greater than 90% capture of CO_2 under various process conditions.

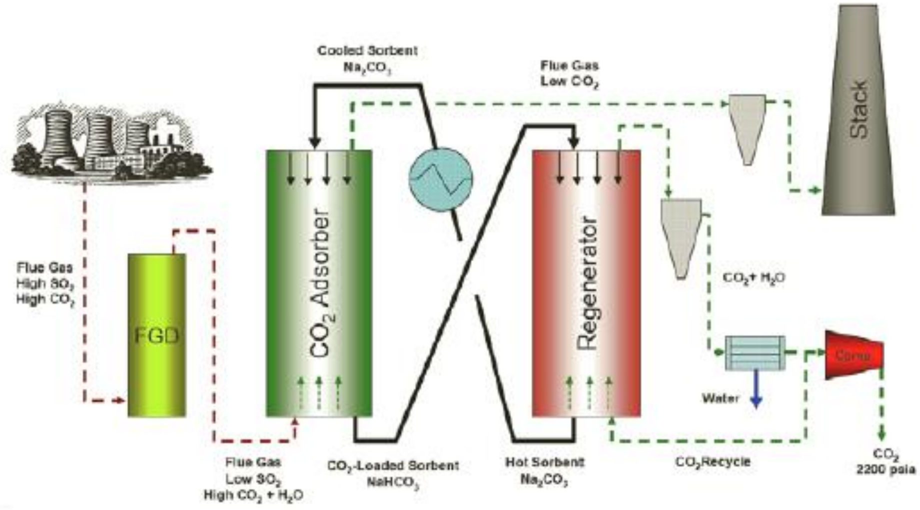


Figure 7 **Schematic of the RTI's Dry Carbonate CO2 Capture Process [110].**

Korean scientists from research institutes and university studied [111] the effect of water vapour pretreatment on Na_2CO_3-based sorbent-system in a bubbling fluidized-bed reactor. The spray-dried sorbent was pretreated with water vapour before carbonation to increase reactivity and CO_2 removal rate in the initial stage. It was established that greater than 90% regeneration capacity in the temperature range between 135° and 300°C. Korean researchers had published [112] a comprehensive article on supported Na_2CO_3-based sorbent systems prepared by spray dry technique. Of six types of spray dried sorbent-systems, three samples had better CO_2 sorption capacity than MEA (33.3 wt% MEA solution was used as the reference and its CO_2 absorption capacity is 6 wt %).

3.1.2 Regenerable Potassium Carbonate Sorbent Systems

Russian scientists Okunev at al [113-115] had studied the influence of porous support matrix on CO_2 sorption of K_2CO_3. For support, both hydrophilic (silica gel, alumina, vermiculite) and hydrophobic (activated carbons) materials were used. This study found that initially porous alumina/K_2CO_3 sorbent-system possesses the highest dynamic capacity but drops immediately after the first cycle. A completely reversible regeneration was observed in case of activated carbons impregnated sorbent-system. The sorbent-systems dynamic capacity decreases in the sequence alumina > activated carbon > vermiculite > silica gel.

To identify the best sorbent-support system Korean researchers [116,117] had prepared several K_2CO_3-based sorbents by impregnating supports such as activated carbon (AC), TiO_2, Al_2O_3, MgO, SiO_2 and various zeolites. It was found that the CO2 capture capacity of K_2CO_3/AC, K_2CO_3/TiO2, K_2CO_3/MgO, and K_2CO_3/Al_2O_3 sorbent-systems was 86, 83, 119, and 85 mg CO_2/g sorbent-system (active phase loading ~30 wt%), respectively. They noticed that spent sorbents such as K_2CO_3/AC, K_2CO_3/TiO2, K_2CO_3/Al_2O_3, and K_2CO_3/MgO could be completely regenerated at 150°, 150°, 350° and 400°C respectively. The CO_2 capture capacities of K_2CO_3/Al_2O_3 and K_2CO_3/MgO, after regeneration at ≤200°C, decreased due to the formation of $KAl(CO_3)_2(OH)_2$, $K_2Mg(CO_3)_2$, and $K_2Mg(CO_3)_2.4(H_2O)$ phases during carbonation, which were not completely converted to the original K_2CO_3 phase. But regeneration was not a problem in 130°–150°C in the case of K_2CO_3/AC and K_2CO_3/TiO_2 sorbent-systems, due to the formation of a $KHCO_3$ during CO_2 absorption. In 2009 [118] a new dry sorbent-system, called 'KZrI30' (30 wt.% K_2CO_3/ZrO_2 sorbent-system) was developed. This sorbent has CO_2 capture capacity ~96% of the theoretical value, in the presence of 1vol.% CO_2 and 9 vol.% H_2O at 50°C and able to maintain the capacity in multicycle operation.

It is reported [119] that the enhanced CO_2 capture capacity can be obtained by converting the entire $K_2CO_3 \cdot 1.5H_2O$ phase to the $KHCO_3$ phase if the sorbents are fully activated with excess water. KIER & KEPRI 2007 [120] summarizes the results of performance of the two fluidized-bed reactors (fast fluidized bed for carbonation & bubbling fluidized bed for regeneration) in the continuous solid circulation mode. KEPRI prepared spray-dried sorbent 'Sorb KX35' (35% K_2CO_3; support material was not disclosed) had an attrition index (AI) of 0.1%. This sorbent-system had a CO_2 removal capacity of 50–73% at steady state and regenerable. Yi et al [121, 122] 2009 had reported that in a continuous solid circulating mode, potassium carbonate CO_2 capture system evaluation in coal-fired flue gas slip-stream and average CO_2 removal was >70% during 2 hrs of operation. Average CO2 removal was >85% in a simulated flue gas stream during 50 hr continuous operation.

Chinese researchers Zhao et al [123, 124] found that K_2CO_3 with hexagonal crystal has superior carbonation kinetics over monoclinic K_2CO_3 due to crystal structure similarities between K_2CO_3 hexagonal and $KHCO_3$. After identifying the crystal structure and carbonation kinetics relationship have moved to study K_2CO_3-impregnated composite sorbent-systems (support materials: coconut activated charcoal (AC1), coal active carbon (AC2), silica gel (SG), activated alumina (Al_2O_3)) and dolomite [125, 126]. In 2010 Zhao et al [127] had focused their attention on the effect of carbonation temperature, CO_2 concentration, and H_2O concentration and operation pressure on carbonation conversion rate and reaction rate of K_2CO_3 calcined from $KHCO_3$. These basic operational parameters were collected by the group for designing and operating a large scale CO_2 capture process.

Recently Korean researchers from National University in Daegu, Pohang University of Science & Technology and KEPRI reported [127] a new regenerable modified K_2CO_3/Al_2O_3 sorbent was developed for CO_2 capture at ≤200°C. But earlier works [113] had reported though initial CO_2 capture capacity of K_2CO_3/Al_2O_3 is good but capture capacity of the sorbent drops during multiple tests at temperatures below 200°C. To overcome this problem, a new alumina-modified support containing the $KAl(CO_3)(OH)_2$ phase was used for preparation of the new K_2CO_3/Al_2O_3 sorbent system. The regenerable modified K_2CO_3/Al_2O_3 sorbent system maintained it's CO_2 capture capacity during multiple tests even at a regeneration temperature of 130°C. This excellent regeneration property was due to the characteristics of the modified K_2CO_3/Al_2O_3 sorbent producing only a $KHCO_3$ phase during CO_2 carbonation step. ***Figure 8*** shows that the CO_2 capture capacity of this new sorbent increased with the amount of K_2CO_3 loading. In particular, the CO_2 capture capacity of the 48 wt.% loaded sorbent was about 128 mg CO_2/g sorbent (2.9 mmol/g of sorbent). In addition, it was confirmed that the CO_2 capture capacities the new sorbents did not drop in 5 cycles. Also, around 80-90 percent of active phase was taken part in the carbonation step (theoretical values of CO_2 sorption is 318.3 mg CO_2/g K_2CO_3).

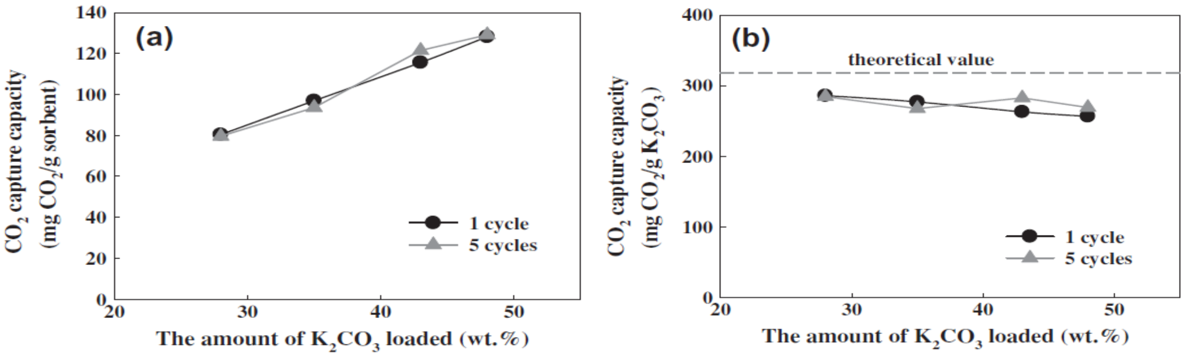


Figure 8 The CO_2 capture capacities of sorbent system (a) and the amount of CO_2 sorption per gm of K_2CO_3 (b) of the modified K_2CO_3/Al_2O_3 sorbent system as a function of the amount of K_2CO_3 loading in 1 vol.% CO_2 and 9 vol.% H_2O at 60°C [128].

Table 4 sumarizes the literature data of the dry carbonate process and ***Table 5*** lists the major developers around the world.

Table 4 Alkali Carbonate Sorbents for CO_2 Capture

Active phase	Support	Temperature of operation (°C)	Wt% active phase	Gas composition	Capacity (mmol.g^{-1})	Method of testing	Ref
K_2CO_3	AC, Activated Coke & Silica	**Ads.**:100° **Reg.**:150°	~35 in AC	Simulated flue gas & actual flue gas in slip stream	~2.1 (Ads. efficiency ~80%)	Fix-bed lab scale and Bench scale	103
Na_2CO_3	Ceramic Supported sorbents	**Ads.**:60-70° **Reg.**:120-140°	10-40	Simulated flue gas & actual flue gas	~0.5-3.2	TGA, Fixed-Bed, Entrained-bed Reactor, Field testing by co-current moving bed, Limited no. of cycles	104-110
Na_2CO_3	Ceramic Supported sorbents	**Ads.**:50-70° **Reg.**:>135° (in N_2)	35 wt%	10% CO_2, 12.2% H_2O & 77.8% N_2	~2.6 (~80% sorbent efficiency with a 35% active phase)	Bubbling bed	112
Na_2CO_3	Ceramic Supported sorbents	**Ads.**:50-70° **Reg.**:120° (in N_2)	20-50	Simulated flue gas: 14.4% CO_2, 5.4% O_2, 10% H_2O & 70.2% N_2	~2.3 (>80% sorbent efficiency with a 30% active phase)	TGA	113
K_2CO_3	AC, TiO_2, Al_2O_3, MgO, ZrO_2, CaO, SiO_2 and zeolites	**Ads.**:60-100° **Reg.**:130-400° (moisture up to 9% & balance N_2)	30	1% CO_2, 0-11% H_2O & N_2 balance	~1.1-2.7	Fixed-bed, Multiple cycle	116-119
K_2CO_3	'Sorb KX35' (proprietary recipe)	**Ads.**:60-100° **Reg.**:120-220° (in N_2)	35	Simulated Flue Gas: Dry basis-12% CO_2 and 88% N_2; 7-30% moisture	~2.1(~96% sorbent efficiency)	Coupled fluidized bed reactor: Adsorber- fast fluidized bed and Regenerator- bubbling fluidized bed, multiple cycle	120
K_2CO_3	'Sorb A' (proprietary recipe)	**Ads.**:70-90° **Reg.**:≥150° (in N_2)	35	Slip stream- coal-fired flue gas: 7-9% CO_2 (dry basis), 10-19% H_2O	CO2 >85% (capacity not available)	Coupled fluidized bed reactor: Adsorber- fast fluidized bed and Regenerator- bubbling fluidized bed, multiple cycle	121
K_2CO_3	AC, Silica Gel, Activated Al_2O_3	**Ads.**:60° **Reg.**:200° (in N_2)	~25	15% CO_2, 15% H_2O & N_2 balance	~0.34-1.7	TGA & Bubbling Fluidized Bed	124
K_2CO_3	Modified Al_2O_3 support- $KAl(CO_3)(OH)_2$	**Ads.**:70-90° **Reg.**:130 ° (in N_2)	~28-48	1% CO_2, 9% H_2O & N_2 balance	~2.9(~48 wt% K_2CO_3 loading)	TGA & Fixed-bed, multiple cycle	127

Table 5 Research Group working for development of Alkali Carbonates Based solid sorbents for post combustion CO_2 Capture

Sorbent Systems	Name of the Research Group & Lead Researches	Comments	Reference
K_2CO_3-based system	H. Hayashi, S. Hirano et al: *Department of Chemical Science and Technology, University of Tokushima, Japan*	Last activity reported 1998	[103]
Na_2CO_3-based system	P. Harrison: *Department of Chemical Engineering, Louisiana State University,USA*	No recent activities	[104]
Na_2CO_3-based system	T.O. Nelson, R.P. Gupta et al: RTI International, North Carolina, USA	Leading Developer in USA; last two years very little activities/information	[104-110]
K_2CO_3-based system	S.C. Lee et al: Department of Chemical Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea	Collaborating with other Korean groups	[116,119]
K_2CO_3-based system	T.J. Lee: Department of Chemical Engineering, Yeungnam University, Republic of Korea	Collaborating with other Korean groups	[19], [21]
K_2CO_3-based system	Y.S. Ahn et al: Korea Institute of Energy Research (KIER), Republic of Korea	Leading developer in the world; collaborating with other Korean groups	[116,119]
K_2CO_3-based system	C.K. Ryu et al:Korea Electric Power Research Institute (KEPRI), Republic of Korea	Leading developer in the world; focussed on sorbent development & scale up	[116,118-120,122,128]
K_2CO_3-based system	*C. Zhao et al: School of Energy and Environment, Southeast University, China*	Started with studying the mechanism of carbonation moving towards bench scale CO2 capture	[123-127]

In summary, due to high CO_2 capture capacity of Na_2CO_3 (9.43 mmol.g^{-1}) and K_2CO_3 (7.23 mmol.g^{-1}) and carbonation/regeneration temperature between 60°-200°C alkali metal sorbents have good potential for post combustion CO_2 capture. These sorbents in pure form lack mechanical strength, loss of kinetics and adsorption efficiency in cyclic uses. To overcome these issues composite/supported sorbents are made. Dry regenerable alkali-metal based sorbents have the added advantage of being relatively inexpensive. However, to be commercially viable, the long-term stability and long-life performance of these sorbents under real flue gas conditions of postcombustion applications remains to be established.

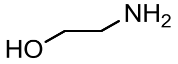
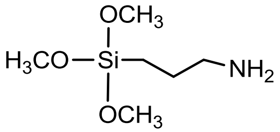
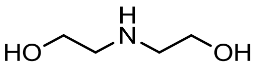
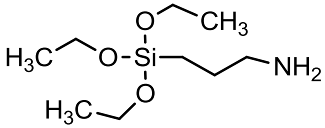
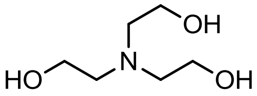
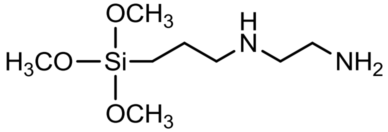
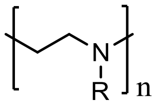
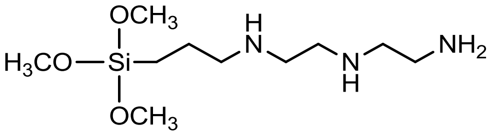
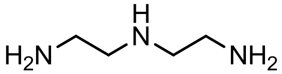
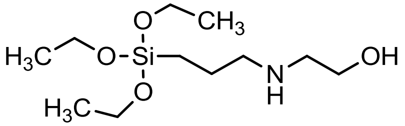
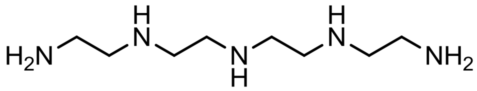
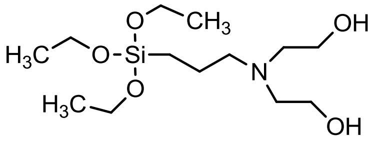
3.2 Amine Functionalized Solid Sorbents

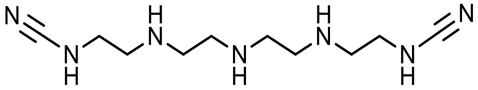
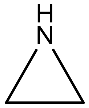
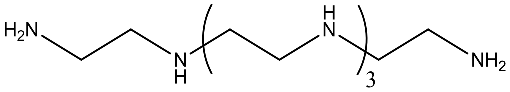
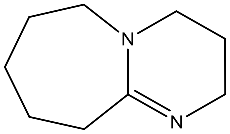
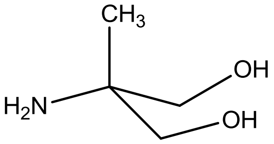
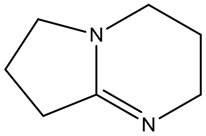
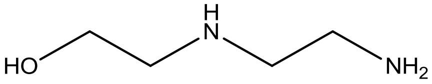
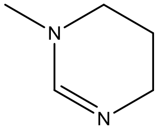
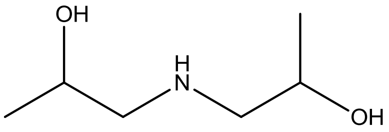
A variety of micromeso-porous materials loaded with basic nitrogen functionality, more specifically, organic amine functionality has been synthesized and characterized to chemisorb CO_2 from flue gas streams. Supported amine sorbents have been classified into three classes [130,131].

- **Class 1:** This class of supported sorbents is prepared by physically loading monomeric or polymeric amine species into or onto the porous support, typically porous silica by impregnation technique.
- **Class 2:** This class of supported adsorbents is that in which the amine, mainly amine-containing silane is covalently tethered to a solid support, such as porous silica. This is accomplished by binding amines to oxides via the use of silane chemistry or via preparation of polymeric supports with amine-containing side chains. This provides covalently tethered amine sorbents the potential to be completely regenerable through multi-cycle adsorption/desorption uses.
- **Class 3:** These supported adsorbents are based on porous supports upon which amino-polymers are polymerized in situ. This category of supported sorbents can be considered a hybrid of the other two classes [130].

The structure of widely used amines for sorbent functionalization is given in ***Table 6***.

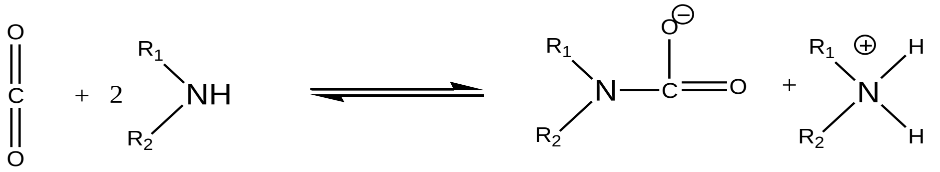
Table 6 Structure of Widely Used Amines for Sorbents Functionalization

Name	Structure	Name	Structure
Amines		Silanes	
Monoethanolamine (MEA)		3-aminopropyltrimethoxysilane (APTS)	
Diethanolamine (DEA)		3-aminopropyltriethoxysilane (APTES)	
Triethanolamine (TEA)		N-[3-(trimethoxysilyl)propyl]-ethylenediamine (AEAPTS)	
Polyethyleneimine (PEI)	 (R=H for linear, R=H or CHx for branched)	N-[3-(trimethoxysilyl)propyl]-diethylenetriamine (DAEAPTS)	
Diethylenetriamine (DETA)		Ethylhydroxyl-aminopropyl-trimethoxyslane (EHAPTS)	
Tetraethylenepentamine (TEPA)		Diethylhydroxyl-aminopropyl-trimethoxyslane (DEHAPTS)	

Tetraethylenepentamine-acrylonitrile (TEPAN)		Cyclic Aziridine	
Pentaethylenehexamine (PEHA)		1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	
2-Amino-2-methyl-1,3-propanediol (AMPD)		1,5-diazobicyclo [4.3.0]non-5-ene (DBN)	
2-(2-Aminoethylamino)ethanol (AEAE)		N-methyltetrahydropyrimidine (MTHP)	
Diisopropanolamine	DIPA		

3.2.1 Reaction Scheme of CO_2 with Amines

Adsorption of CO_2 using amine functionalized sorbents involves chemical reaction and it is therefore necessary to know how the nature of amine influences the rate of adsorption and kinetics in terms of amine efficiency, defined as the number of CO_2 molecules adsorbed for each nitrogen atom in the amine functional group present. The zwitterion mechanism originally proposed by Caplow [132] and reintroduced by Danckwerts [133], is generally accepted mechanism for the reaction of primary and secondary amines CO_2. The mechanism involves two steps: formation of zwitterion (not shown by reaction here), followed by base catalyzed deprotonation of zwitterion. However, overall reaction can be written as

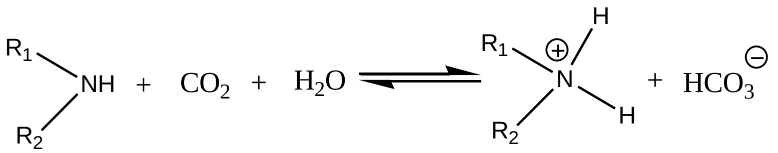


(3)

[R_2 = H for primary amine]

If we consider only the amine as a base, the equilibrium CO_2 loading capacities of primary and secondary amines are limited by the overall stoichiometry of the reaction (3) to 0.5 mol.(mol. of amine)$^{-1}$.

The only reaction of importance between CO_2 and the sterically hindered primary or secondary amine [134] would be the formation of bicarbonate (reaction (4), as in the case of tertiary amines, the stoichiometry of which allows loading of CO_2 up to 1 mol.(mol. of amine)$^{-1}$ for hindered primary or secondary amine.



(4)

The reaction of CO_2 with moderately hindered amines includes the formation of a carbamate as in the case of non-hindered amines. The stoichiometry of which allows loading of CO_2 up to 0.5 mol. (mol. of amine)$^{-1}$. Tertiary amines do not react directly with CO_2 as the primary and secondary amines do. They lack the free proton needed in the deprotonation step. Instead, the reaction produces protonated amine and bicarbonate ion in presence moisture, resulting in a higher capacity for CO_2. The mechanism of this reaction is suggested to be base catalyzed hydration of CO_2 as reaction (4) above [135]. In general, the formation of bicarbonate allows a high equilibrium capacity. But, the kinetics is relatively slow.

3.2.2 Amine functionalized activated carbonaceous materials

Amine impregnation on different carbon based supports shows promise to improve CO_2 adsorption and selectivity. It has been shown that by incorporating certain functional groups into its porous structure, thus enhancing the CO_2-adsorbent interactions, the adsorption capacity of carbonaceous materials could be significantly improved.

3.2.2.1 Amine functionalized activated carbon sorbents

Przepiórski et al. [136] found that commercial AC treated with ammonia at high temperatures (200 to 1000°C) indicated significant enhancement in adsorption of CO_2. The sample treated with ammonia at 400°C showed the best adsorption capacity of 1.73 mmol g^{-1}. This was attributed to the presence of N-containing groups introduced to carbon structure. However, samples treated at temperature above 400°Cindicated a decreasing trend to adsorb CO_2. Pevida and his group [137,138] also functionalized a series of carbonaceous materials, obtained from a commercial AC to introduce nitrogen into carbon structure by heat treatment with gaseous ammonia. They observed that nitrogen-functionalities vary depending on the temperature of the ammonia treatment. They finally concluded that CO_2 capture capacity is not directly related to the total nitrogen content of sorbents but to specific nitrogen functionalities that are responsible for increasing the CO_2-adsorbent affinity. Particularly, for one of the ACs, CO_2 capture capacities rose from 1.6 to1.9 mmol.g^{-1} after treatment at 800°C. Plaza et al. [139] reported that aminated sorbents prepared from biomass residue and almond shell first activated with CO_2 and then heat treatment with ammonia gas exhibited significant differences in texture and surface chemistry and therefore, shown significantly higher capacities than starting char.

Several amine impregnated solid sorbents were developed by chemical treatment of carbon-enriched fly ash concentrates with various amine groups by Gray et al., [139,141] Maroto-Valer and others, [35, 142] and Arenillas et al [142]. In 2004, Gray et al. [141] treated fly ash with 3-chloropropylamine-hydrochloride (CPAHCL) solution. The best sample had the CO_2 capture capacity of 0.18 mmol.g^{-1}. However, one-step activation by steam before impregnation can successfully increase the surface area and pore volume of carbon-enriched fly ash and thereby, CO_2 capture capacity [35,142]. Activated fly ash derived sorbents were also examined after impregnated with polyethyleneimine (PEI) [35,143]. Maroto-Valer et al. [35] showed that the impregnation of PEI could significantly improve the adsorption capacity as much as 2.13 mmol.g^{-1} at 75°C, much more than that of counterpart without impregnation (0.22 mmol.g^{-1} at 75°C). However, in 2005, Arenillas and others [143] showed that its highest CO_2 adsorption capacity was 1.02 mmol.g^{-1} at 75°C. Besides, they also impregnated AC derived from fly ash with PEI and its blend with polyethylene glycol (PEG). They confirmed that addition of PEG into the PEI-loaded sorbents improves the CO_2 adsorption capacity and kinetics. This might be due to the bicarbonate formation reaction in presence of PEG that attracts more water. Further studies conducted by Maroto-Valer and his group [142] showed the change in surface areas of the activated fly ash (372-1075 $m^2.g^{-1}$) and its pore volume (02.34-0.774 $m^3.g^{-1}$) due to changes in chemical and physical properties of the raw fly ash. A typical comparison of CO_2 adsorption capacities of activated fly ash carbon and its alkanolamine modified counterparts at various temperatures is shown in ***Figure 9*** based on the maximum possible adsorption capacity data reported by Maroto-Valer and others [142].

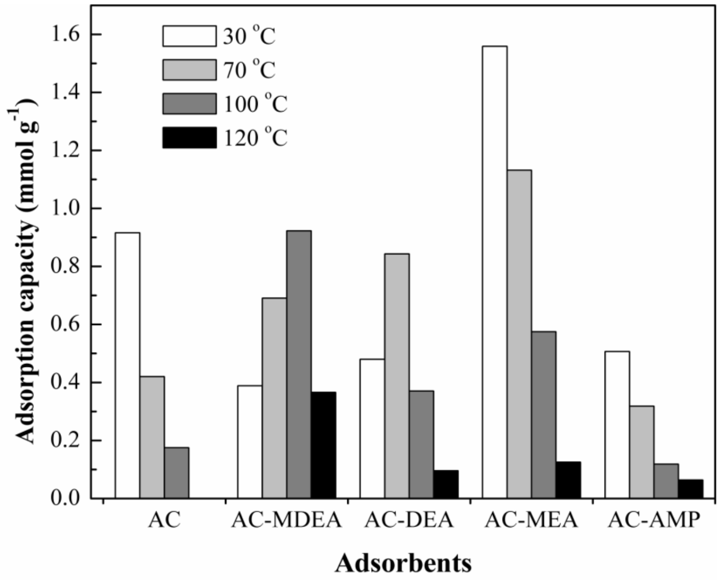


Figure 9 CO_2 Adsorption Capacity of Activated Fly Ash Carbon and Impregnated Fly ash at Different Temperatures Based on the Data Reported by Maroto-Valer et al [142].

Two surface treatment methods, including ammonia heat treatment and PEI impregnation were used to modify and evaluate the feasibility of high surface area sorbent from low-cost anthracites by Maroto-Valer and his group [36,37]. At higher activation temperature, both treatments increased the CO_2 capture capacity of activated anthracites because of the introduction of basic nitrogen groups onto the surface. PEI impregnated deashed anthracite sorbent could adsorb as much as 2.13 mmol.g^{-1} at 75°C [36]. In 2007, Plaza et al. [143] impregnated commercial AC (Norit CGP super) with different alkylamines, such as diethylentriamine (DETA), polyethylenimine (PEHA) and PEI. The adsorption capacity of AC significantly reduced with increasing temperature. Other research group [37] also reported similar negative effects on capture capacities of activated anthracites impregnated with PEI.

More recently, Alesi et al. [144] studied CO_2 capture and regeneration conditions of tertiary amidine N-methyltetrahydropyrimidine (MTHP) derivatives supported on AC in the temperatures ranging from 29-50^{o}C**.** Capture capacities were measured for 1,5-diazo-bicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazobicyclo[5.4.0]-undec-7-ene (DBU) supported on AC at a amine loading of approximately 2.7 (mmol.amidine).g^{-1}. It was found that CO_2 capture on the amidines only occurred in moisture. However, adsorption of moisture on the hydrophilic AC support put limit on the CO_2 capture capacities. DBN was shown to have a higher capture capacity of 0.8 mmol.g^{-1} with an amine efficiency of 0.30 (mol CO_2).(mol of amidine)$^{-1}$ at an adsorption temperature of 29°C compared to DBU.

3.2.2.2 Amine functionalized carbon nanotubes sorbents

The potential application of CNT as support for amine impregnated sorbents has been studied by Fifield and others [58]. Pyrene methyl picolinimide (PMP) was introduced as anchors to increase the affinity of carbon structure and amine groups. In 2008, Lu and others [31] reported a comparative study of CO_2 capture by CNT, granulated AC (GAC) and zeolite modified by 3-aminopropyltriethoxysilane (APTES). After surface functionalization CNT showed the significant enhancement in CO_2 adsorption capacity followed by the zeolite. ***Figure 10*** shows the CO_2 adsorption capacities of raw and modified adsorbents.

Dillon et al. [65] synthesized and characterized PEI-functionalized SWNT. The maximum absorption of 2.1 mmol.g^{-1} was reported for PEI (25000)-SWNT at 27°C. Desorption of CO_2 was done by heating under argon at 75°C. CNT modified by APTS solution were also tested for its CO_2 adsorption potential at multiple temperatures (20–100°C) by Su et al [40]. The adsorption capacities of CO_2 via CNT and CNT (APTS) decreased with temperature indicating the exothermic nature of adsorption process and increased with water content in air at 0–7%. They observed that CO_2 adsorption capacity of CNT (APTS) was about 2.59 mmol.g^{-1} at 20°C and suggested that the CNT(APTS) could be a promising low-temperature adsorbents for CO_2 capture from flue gas. Recently, Hsu et al. [63] studied regeneration behavior of CO_2 adsorption on CNT (APTS) sorbent. A combination of thermal and vacuum desorption at 120^{o}C was suggested to shorten the regeneration time. The adsorption capacities and other physicochemical properties were preserved after 20 cycles of adsorption/regeneration.

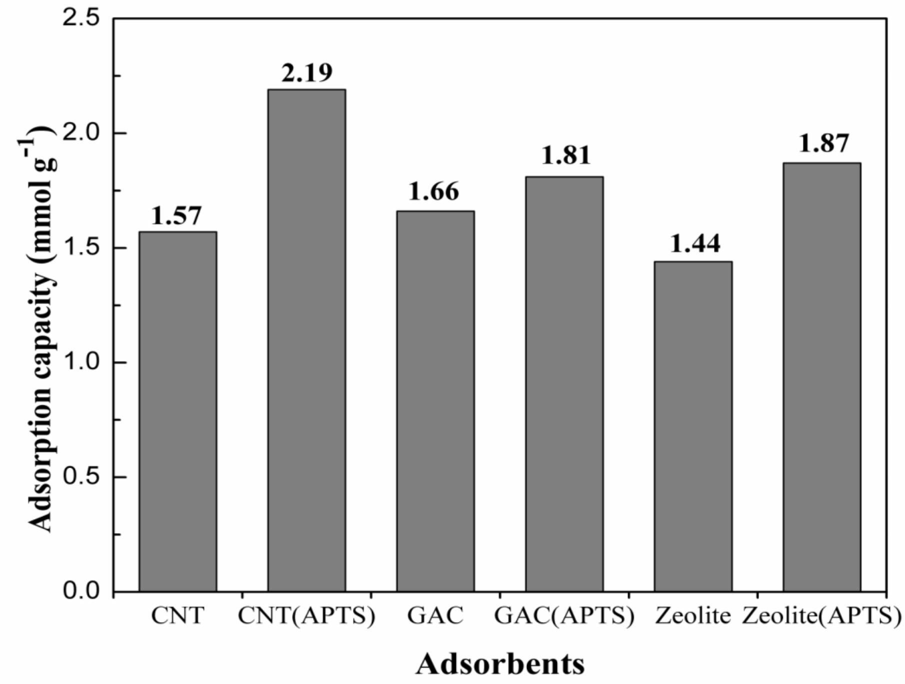


Figure 10 CO_2 Adsorption Capacities of Raw and Modified Adsorbents at 25^{o}C with a [$CO_{2,in}$] = 50% [31].

3.2.2.3 Amine functionalized solid resin sorbents

Amine functionalized solid resins are also being studied to use them as sorbents for CO_2 capture. Drage et al. [146] synthesized high nitrogen content carbon adsorbents prepared from the activation of urea–formaldehyde (UF) and melamine–formaldehyde (MF) resin, using K_2CO_3 as activating agent. By varying the temperature of activation, a range of adsorbents were prepared and characterized for CO_2 adsorption. CO_2 adsorption capacity was determined to be dependent upon both nitrogen functionality and textural properties of resins. Best performing adsorbent was capable of capturing about 1.86 mmol. g^{-1} at 25°C under pure CO_2 produced from the chemical activation of UF resin at 500^{o}C. Besides, both categories sorbents showed rapid adsorption half times. However, there was substantial decrease in capacities (~56%) of both the resins with increasing adsorption temperature from 25^{o}C to 75^{o}C.

In summary, the nitrogen enrichment of carbonaceous materials is found to be effective in enhancing the specific CO_2-adsorbate interactions. However, impregnation of amines resulted in a significant decrease of the surface areas, as well as meso- or micropore volume [142,144]. It is probably due to the pore filling or blockage because of the amine incorporation assumed to be affected by the molecular size and shape of alkanolamines used, although the mechanism of pore filling is still not well understood [142].

3.2.3 Functionalized zeolite based sorbents

Zeolites with significant surface area and pore volume present a potential option for CO_2 capture. However, we have seen that CO_2 adsorption on zeolite sorbents decreases significantly with increasing temperature and it also shows very low capacity in presence of moisture in flue gas. Therefore, there have been a few investigations (***Table 7***) to synthesize aminated zeolites as an alternative sorbents.

Zeolite 13X was modified with MEA by impregnation method by Jadhav et al. [161] MEA loadings were in the range of 0.5 - 25 wt%. The aminated zeolites showed improvement in CO_2 adsorption capacity over unmodified zeolite by a factor of ca. 1.6 at 30°C. The experimental results showed that the highest CO_2 adsorption capacity at the room temperature was not observed at the MEA loading of either 0.5 wt% or 25 wt%. This was attributed to reduced surface area and pore volume and restricted access to adsorption sites for CO_2 at higher loadings. However, a higher capacity at the temperature of 120°C was obtained with higher MEA loading of 50 wt% compared with unmodified zeolite and modified zeolite with low amine loading level. Unlike at the room temperature, where physisorption is dominant, the chemical interaction between CO_2 and amine may be playing a significant role in sorption of CO_2 at 120 C despite reduced pore volume and lower surface area. The same conclusion was also reached by Su et al [162]. They dispersed TEPA into commercial available Y-type zeolite (Si/Al = 60) and analyzed separately the equilibrium capacities of CO_2 resulting from physisorption and chemisorption. For their proprietary adsorbent, as the adsorption temperature increases, the contribution of physisorption to the overall sorption capacity decreases significantly, contrary to the general trend of that of chemisorption. The highest adsorption capacity reported was 4.27 $mmol.g^{-1}$ at 60 ^oC in presence of 15% CO_2 and 7% water vapor in gas stream. In addition, CO_2 adsorption and other physicochemical properties of the sorbent were preserved after 20 cycles of adsorption and regeneration.

Fisher et al. [163] employed β-zeolite as a solid support for TEPA impregnation and compared it with TEPA impregnated silica and alumina. The TEPA modified β-zeolite exhibited the highest CO_2 adsorption capacity up to 2.08 mmol g^{-1} at 30°C under the 10% CO_2/90% Ar flow, outperforming TEPA/SiO_2 and TEPA/Al_2O_3 sorbents. It was suggested that the higher capacity of TEPA/β-zeolite could be related to zeolite's high surface area. TEPA/β-zeolite maintained its CO_2 capture capacity for more than 10 adsorption/ regeneration cycles.

Table 7 CO_2 Adsorption Capacity of Amine Impregnated Solid Sorbents

Support	Amine	Amine loading (wt%)	Adsorption Capacity[a] (Humid) (mmol. g^{-1})	Experimental Conditions		No. of Cycles	Ref.
				P_{CO_2} (atm)	T (°C)		
MCM-41	PEI	75	3.02	1	75		146
MCM-41	PEI	50	2.05	0.1	75		146
PE-MCM-41	DEA	77	2.93	0.05	25		45
PE-MCM-41	DEA	73	2.81 (2.89)	0.05	25		45
MCM-41	PEI	50	(3.08)	0.13	75	10	147
MCM-41	TEPA	50	4.54	0.05	75	6	148
SBA-15	TEPA	50	3.23	0.05	75	6	156
SBA-15	DEA+TEPA	50 (30% TEPA, 20% DEA)	3.61	0.05	75	6	157
SBA-15	PEI	50	3.18	0.15	75		158
SBA-15	PEI	50	1.36	0.12	75		159
SBA-15	APTS		(2.01)	0.10	25		49
KIT-6	PEI	50	1.95	0.05	75		149
Monolith	PEI	65	3.75	0.05	75	5	150
Mesoporous Silica	PEI	40	2.4	1	75		151
MC400/10	TEPA	83	5.57 (7.93)	0.1	75	50	152
Precipitated silica	PEI[b]	67	4.55	1	100		153
R-IAS[c]	E-100[d]		(4.19)	0.10	25		49
PMMA	TEPA	41	(14.03)	0.15	70		154
PMMA	DBU	29	(3.0)	0.10	25	1	13
PMMA	DBU	29	(2.34)	0.10	65	6	13
PMMA (Diaion)	PEI	40	2.40(3.53)	0.10	45		155
SiO_2 (CARiACT)	PEI	40	2.55(3.65)	0.10	45		155
Zeolite 13X	MEA	10	1.0	0.15	30		160
Zeolite Y60	TEPA	50	(4.27)	0.15	60	20	161
β-zeolite	TEPA	38	2.08	0.10	30		162

a. CO_2 adsorption capacity in mmol.g^{-1} sorbent, within parenthesis indicates humid condition result
b. Low molecular weight PEI (MW ~ca. 800)
c. Reformulated immobilized amine sorbent[16]
d. E-100: ethyleneamine

3.2.4 Functionalized polymer based sorbents

Polymeric amine sorbents have been used for years in closed environment, such as aircraft, submarine, and space shuttles to capture CO_2 for CO_2 concentration less than 1% [164,165]. However, the cost of these sorbents is too high for large-scale applications in the industry, such as CO_2 capture from flue gas. There are two ways to make polymeric amine sorbents – (i) impregnation method or covalent functionalization by chemical reaction of polymers/oligomers with high amine content into polymer support, and (ii) synthesis of copolymers with amine containing monomers or monomers that can be subsequently aminated easily through reaction of functional groups like chloride etc [129].

Satyapal et al. [165] reported proprietary adsorbent, HSC^+ consisting of PEI bonded to a high surface area, solid polymethyl methacrylate (PMMA) polymeric support. In addition, the polyethylene glycol, PEG was also coated on the HSC^+ support to improve the cyclic capacity of the sorbent material. The heat of adsorption of the HSC^+ sorbent was estimated to be -94 ± 8 kJ.(mol $CO_2)^{-1}$ and its CO_2 adsorption capacity was about 0.91 mmol.g^{-1} at ambient pressure and 40^oC. A range of primary, secondary and tertiary ethanolamines and their mixtures were impregnated within the pores of PMMA beads with high surface areas by Filburn et al [50]. The results demonstrated the advantage of secondary amines over other amine types in removing low levels of CO_2 using a pressure swing adsorption process [50]. In further studies, they investigated a screening test of PMMA supported various amine sorbents for CO_2 capture [155]. The amines used were MEA, modified TEPA (referred to as TEPAN), mixture of ethyleneimine (E-100), reaction-modified ethyleneimine with acrylonitrile (E-100AN) etc. TEPAN and E-100AN demonstrated remarkably higher cyclic CO_2 capacities and reproducibility. For example, PMMA supported TEPAN exhibited as high as a cyclic capacity of 10.21 mmol.g^{-1} at 40^oC.

In 2005, Gray et al. [166] immobilized Michael addition reaction products of ethylenediamine and TEPA with acrylonitrile within the pores of PMMA solid beads. They evaluated the performance of the sorbents in a temperature swing system using (10 % CO_2 + 2 % H_2O) in helium gas over the temperature range of 20-65°C. The average CO_2 capture capacities for the sorbent over 4 adsorption/desorption cycles was in range of 3.4 -6.6 mmol.g^{-1}. The thermal stability of the sorbent was also investigated over a ten cycle study and suggested that these sorbents could be one of the potential sorbents for the capture of CO_2 from flue gas streams. Furthermore, in an effort to achieve the higher CO_2 capture capacity, Gray et al. [13] immobilized a two-ring tertiary amine, DBU in PMMA beads. With the DBU loading of ca. 29 wt%, the modified sorbent showed an adsorption capacity of 3.43 mmol.g^{-1} at the room temperature under the simulated flue gas containing 10% CO_2 and 2% H_2O. However, the CO_2 capacity decreased considerably to 2.34 mmol.g^{-1} as the temperature increased to 65^oC, which is contrary to amine impregnated mesoporous inorganic sorbents.

Besides PMMA (diaion), other supports such silicon dioxide (CARiACT) and polystyrene (Macronet) were also compared [156]. The heat of reaction (ΔH_r) was also determined as key criteria for sorbent screening. It was found that both CARiACT and PMMA supported PEI sorbents with ΔH_r values of 26.7 and 24.6 kJ. (mol.$CO_2)^{-1}$, respectively were within the acceptable value of about 30.66 kJ. (mol$CO_2)^{-1}$. Moreover, the sorbents exhibited acceptable CO_2 capture loading capacities of 2.5-3.5 mmol.g^{-1} under humid condition and stable over the temperature range of $25\text{-}105^oC$ for 10 cycles.

Li et al. [167,168] reported development of fibrous sorbents for CO_2 capture by coating PEI onto commercial glass fiber matrix with high surface areas using and epoxy resin (EP) [167] and epichlorohydrin (ECH) [168] as cross-linked agent. CO_2 adsorption capacities obtained were 6.30 $mmol.g^{-1}$ for PEI cross-linked with EP coated fiber and 4.12 $mmol.g^{-1}$ for PEI cross-linked with ECH coated fiber at 30°C at 1 atm and under humid condition. Both modified fibrous adsorbents could be completely regenerated at 120°C. However, these modified glass fibrous adsorbents were most efficient at room temperature. At a higher temperature of 50°C, the adsorption capacity drops drastically.

Recently, Yang et al. [168] synthesized and characterized amine-containing fibrous adsorbent (PAN-AF) by grafting copolymerization of allylamine onto polyacrylonitrile (PAN) fiber. They reported a CO_2 adsorption capacity of 6.22 mmol $CO_2.g^{-1}$ with 60.0 wt % grafting degree. However, regeneration of PAN-AF is proposed to be done by heating PAN-AF in boiled water. ***Table 7*** shows CO_2 adsorption capacity of few impregnated polymer based solid sorbents.

3.2.5 Functionalized silica supported sorbents

3.2.5.1 Impregnated silica supported sorbents

The first amine-impregnated silica used to capture CO_2 was reported by Song and others in 2002 [147]. They used wet impregnation of hydrothermally synthesized MCM-41, a high-surface-area mesoporous silica with cylindrical pores of relatively small diameter (2.8 nm), with PEI to create an adsorbent, termed as "molecular basket" [147,148,170-172]. In 2003, Xu et al. [170] reported the highest CO_2 adsorption capacity of 3.02 $mmol.g^{-1}$ at PEI loading of 75 wt% in MCM-41-PEI under pure CO_2 atmosphere at 75^{o}C. The adsorbent prepared by a one-step wet impregnation method showed a higher CO_2 adsorption capacity than that of prepared by a two-step impregnation method and mechanical mixing method. It was found that the adsorption and desorption performance of MCM-41-PEI strongly influence by the concentration of CO_2.

When PEI loading was higher than 30 wt%, MCM-41 showed synergetic adsorption gain. It was hypothesized that there was a synergetic effect of MCM-41on the PEI for the adsorption of CO_2 [170]. When the PEI loading was low, the pore size of the adsorbent slightly decreased and the PEI was mostly adsorbed on the inner pore wall of the silica support. Both physical adsorption and chemical adsorption by reaction with PEI contribute to CO_2 adsorption capacity in this case. The adsorption capacity was even smaller than that of the linear adsorption capacity. With increasing PEI loadings, the pore size further decreased. At the same time, because more PEI was loaded into the channels, the chemical adsorption of CO_2 became much more dominant than that of with low PEI loadings. The physical adsorption on the unmodified pore wall of MCM-41 (and the capillary condensation in the mesopore) became negligible in comparison with the chemical adsorption. Moreover, MCM-41 had a synergetic effect on the adsorption of CO_2 by PEI in the confined mesoporous pores. Therefore, the CO_2 adsorption capacity increased. The highest synergetic adsorption gain was obtained when the mesoporous pores were fully loaded with PEI at about 50 wt% of PEI loading. When the PEI loading further increased to 75 wt%, the synergetic adsorption gain was smaller than that with PEI loading of 50 wt%. The largest amount of PEI that can be theoretically loaded into MCM-41 is 50 wt%. For the adsorbent with PEI loading of 75 wt%, theoretically, only 50wt% of the PEI could be loaded into the MCM-41 pores and other 25 wt% of the PEI would be coated on the external surface of the molecular sieve crystals.

Compared with conventional adsorbents, PEI-impregnated MCM-41 showed an increase in adsorption capacity with increase of temperature, though the adsorption capacity was expected to decrease with the increase of temperature as CO_2 adsorption into MCM-41 or PEI is an exothermic process. Xu et al [170] hypothesized that the low adsorption capacity at low temperature could be a result of low adsorption rate caused by kinetic limitation and overall process is kinetically (diffusion) controlled. It has been verified by the authors that the adsorption capacity at low temperature will be even larger than that high temperature if the adsorption time is sufficiently long to allow CO_2 to reach more affinity sites overcoming the diffusion limitation.

A series of performance and stability studies using MCM-41-PEI sorbent was also carried out by Song and his groups [148,171,172] to separate CO_2 from simulated flue gas, flue gas of natural gas fired boiler, and simulated humid flue using packed bed adsorption column. The adsorbent was tested with simulated flue gas (CO_2: 14.9%, O_2:4.25% and N_2: 80.85% by volume) at temperature range of 25-100^oC and feed gas flow rate range 10-30ml.min^{-1} by Xu et al. [171]. The adsorbent showed separation selectivity >1000 for CO_2/N_2 and about 180 for CO_2/O_2. The cyclic adsorption/desorption operation indicated that the adsorbent was stable at 75^oC after 10 cycles of operation. However, it was not stable when operation temperature was higher than 100^oC. MCM-41-PEI adsorbed very little N_2, O_2 and CO in the flue gas (CO_2: 7.4-7.7%, H_2O: ~14.6%, O_2: 4.45%, CO: 200-300 ppm, NO_x: 60-70 ppm, and N_2: 73-74%) from natural gas-fired boiler [172]. However, it adsorbed simultaneously CO_2 and NO_x indicating the need for pre-removal of NO_x before subsequent capture of CO_2 [148,172]. In addition, the presence of moisture in the simulated flue gas and flue gas from natural gas-fired boiler was shown to enhance the adsorption capacity when moisture concentration in feed is lower than that of the CO_2. The possible reasons could be the formation of bicarbonate ion (eq. (4)) during the chemical interaction between PEI and CO_2 in presence of moisture. No further increase in CO_2 adsorption capacity was observed when feed concentration of moisture was higher than that of CO_2.

More recently, nanoporous SBA-15 supported sorbent (SBA-15-PEI) was developed by Ma et al. [159] loading 50 wt% PEI. This sorbent showed a sorption capacity of 3.18 mmol.g^{-1} at 75^oC under a CO_2 partial pressure of 15 kPa. The reported CO_2 adsorption capacity is about 50% higher than that of their previously developed MCM-41-PEI sorbent. This may be ascribed to the higher pore diameter and pore volume of SBA-15 compared to those of MCM-41. This allows PEI modified sample prepared from SBA-15 to have a higher surface area after the same PEI loading (50%). A two-stage sorption approach was also proposed in this study by Ma et al. [159] to remove CO_2 and H_2S respectively from gas streams using this sorbent. The sorbent and process have shown high sorption capacity and selectivity for CO_2 and H_2S and capable of removing H_2S to less than 60ppbv.

Franchi et al. [43] impregnated DEA, a secondary alkanolamine on different support, such as MCM-41(d_p = 3.6) pore-expanded MCM-41(PE-MCM-41, dp = 9.7), silica gel. PE-MCM-41 with high pore diameter and volume allowed for a higher loading level of amine agents and exhibited better CO_2 adsorption performance, which shows a good agreement with observations of Ahn's group [150,151]. The most promising adsorbent had a maximum CO_2 capacity of 2.93 mmol.g^{-1} with 77% DEA loading at 25^oC in the presence of 5% CO_2 in N_2. In addition, the effect of moisture on the uptake capacity of DEA loaded PE-MCM-41 appeared to be insignificant. Moreover, DEA impregnated PE-MCM-41showed good cyclic stability in comparison to other impregnated sorbents, such as DEA impregnated zeolites 13X (***Figure 11***) [43]. The authors also reported an improved performance of sorbent obtained by using ethanol during impregnation stage. A similar observation was also reported by Xu et al. [147] for impregnation of MCM-41 using methanol as solvent.

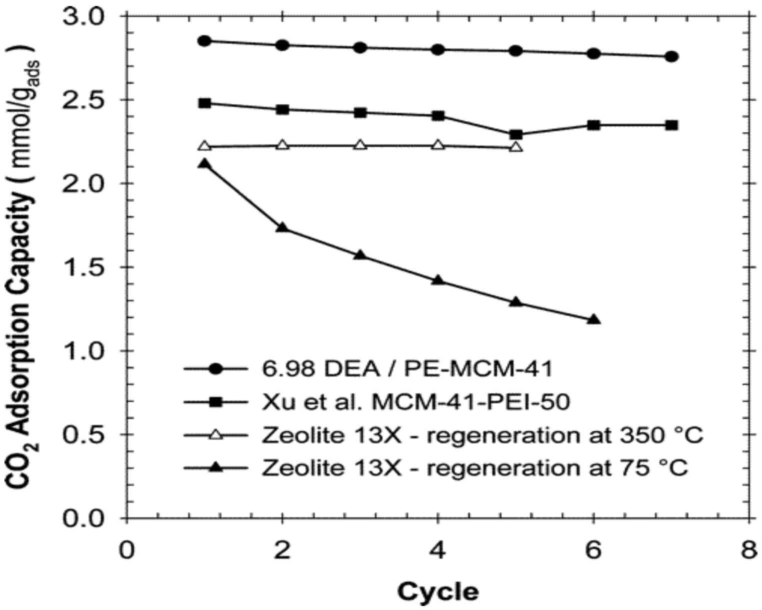


Figure 11 CO_2 adsorption capacity as a function of adsorption cycle for 6.98 DEA/PE-MCM-41 and other CO_2 adsorbents [43]. Amine content of 6.98 DEA/PE-MCM-41= 6.98 mmol DEA.g^{-1} [147].

Gargiulo et al. [173] synthesized, characterized and compared PEI functionalized mesoporous MCM- 48 and SBA-15. Functionalized sorbents showed CO_2 adsorption capacities at 75°C (up to 1.36 mmol.g^{-1}). It was evident from pore size distribution of the non-functionalized and PEI-loaded MCM-48 and SBA-15 silicas that pore filling reduces gradually the actual pore size. PEI loaded SBI-15 showed constantly a little higher CO_2 adsorption capacity than that of PEI loaded MCM-48.

The significant role of the distribution of the amine groups impregnated in the porous materials has been demonstrated by Zhu and his group [157]. They utilized as-prepared mesoporous SBA-15 occluded with organic template (Pluronic P123), to load the TEPA through impregnation. The reported CO_2 adsorption capacity of the modified SBA-15 with the TEPA loading of 50 wt% reached 3.27 mmol.g^{-1} at 75°C with 5% CO_2 in N_2, outperforming those supported by calcined SBA-15. However, TEPA itself exhibits a smaller CO_2 adsorption capacity due to its high viscosity and tendency to aggregate. This performance is attributed to the synergistic effect on adsorption capacities for TEPA and as-prepared SBA-15 support. The presence of P123 template optimized the accessibility of TEPA to CO_2, by better dispersion and distribution of amine agents inside the as-synthesized support. Further, Yue et al. [156] also fabricated as-synthesized SBA-15 supported sorbents through dispersing amine blends of TEPA and DEA. The existence of hydroxyl group in DEA was found to significantly promote the adsorption of CO_2 in the amine containing SBA-15. Hydroxyl group facilitate the formation of carbamate zwitterion and therefore, equilibrium CO_2 loadings of amine can reach 2 mol CO_2. (mo1 amine)$^{-1}$. The synthesized sorbents with 30 wt% TEPA and 20% DEA exhibited adsorption capacity of ca. 3.61 mmol.g^{-1} in the sixth adsorption cycle at 5% CO_2 concentration at 75°C.

As a new strategy to further improve efficiency for CO_2 capture, Yue et al. [149] impregnated TEPA into as-prepared MCM-41 prepared with ionic surfactant cetyltrimethylammonium bromide (CTAB). The optimal loading of 50% TEPA, as synthesized MCM-41 exhibited CO_2 adsorption capacity of 4.16 $mmol.g^{-1}$ in 5% CO_2. The highest equilibrium capacity reported up to 5.39 $mmol.g^{-1}$with 60% loaded TEPA. The higher CO_2 adsorption capacity of MCM-41 supported sorbent than previously mentioned SBA-15 supported adsorbent is probably due to the effect of ionic surfactant templates used in case of former support, which resulted in stronger interaction between silica wall and templates and better amine distribution [149]. They concluded that the amount, type, and the distribution of the surfactant occluded in the pores of the silica support have significant influences on the CO_2 adsorption capacities of the hybrid sorbents. However, their studies showed that TEPA impregnated as synthesized MCM-41 took only 1.5 min to reach adsorption halftime but 140 min to reach nearer to adsorption capacities. This might be due to the fact that adsorption of CO_2 in this type of sorbent is a kinetically (diffusion) controlled process [149]. Therefore, Choi et al. [129] suggested that adsorption halftime or working capacities defined for short adsorption time should be used instead of equilibrium capacities in real application cases.

In 2008, Ahn and coworkers [150] synthesized and studied a series of PEI loaded (50 wt%) ordered mesoporous silica supports, namely MCM-41, MCM-48, SBA-15, SBA-16 and KIT-6 to assess their CO_2 adsorption performance. All impregnated sorbents showed faster adsorption kinetics and substantially higher CO_2 sorption capacities than that of pure PEI. The CO_2 adsorption capacities were found to be varied in the order:

KIT-6 (d_p: 6.5 nm)> SBA-15(d_p: 5.5) ≈ SBA-16(d_p: 4.1) > MCM-48(d_p: 3.1) > MCM-41(d_p: 2.1)

where, d_p is the average pore diameter in nm. The performance was proposed to be influenced by the pore diameter and pore arrangement of mesoporous silica materials. Bulky PEI is assumed to be introduced to the pore easily as pore size of support increases. The best sample, KIT-6-PEI-50 exhibited the highest CO_2 adsorption capacity of 3.07 $mmol.g^{-1}$ at 75°C under pure CO_2. In addition, the stability and reproducibility of KIT-6-PEI-50 were confirmed after three consecutive adsorption/desorption cycles without any deterioration (up to 15 hours) at 75°C. On the basis of these results, the same group [151] developed PEI impregnated silica monolith showing hierarchical pore structure as support. For 5% diluted CO_2 sorption tests, the amine-impregnated monolith with 65% PEI loading exhibited the maximum adsorption capacity of 3.75 $mmol.g^{-1}$ at 75°C, outperforming the previous sorbent (KIT-6-PEI-50) reported with adsorption capacity of 1.95 $mmol.g^{-1}$ under the same conditions [150] 176.

Recently, Goeppert et al. [154] impregnated nanostructured fumed silica using various organoamines, namely PEI, MEA, DEA, TEPA, and PEHA, 2-amino-2-methyl-1-3-propanediol(AMPD), 2-(2-amino-ethylamino)ethanol (AEAE), etc. Precipitated and fumed silica with various surface areas showed essentially similar in adsorption characteristics. Precipitated silica/PEI containing 67wt% PEI adsorbed up to 4.55 $mmol.g^{-1}$, whereas silica supported AEAE containing 67 wt% AEAE showed highest adsorption capacity of 5.23 $mmol.g^{-1}$ at 70°C. However, silica supported AEAE suffered from leaching problems like other shorter chain oligomers of ethyleneimine, TEPA, PEHA. Moreover, those oligomers showed lower desorption efficiency, though they had higher adsorption capacity for CO_2. They observed that simple amines like MEA, DEA etc. were not suitable because of amine leaching problem at higher temperature.

More recently, Qi et al. [153] proposed a novel high efficiency CO_2 capture platform obtained by using PEI, TEPA supported on specially design mesoporous capsules. The novel composite sorbent showed excellent CO_2 capture capacity of 6.6 mmol.g^{-1} under 1 atm moisture-free CO_2 at 75^oC and exceptional CO_2 capture capacity of 7.9 mmol.g^{-1} under simulated humid flue gas with 10% CO_2 at 75^oC. The CO_2 capture kinetics was found to be relatively fast and attained 90% of the total capacity within the first few minutes (***Figure 12***). Besides, sorbents could be regenerated below 100^oC and exhibited good cyclic stability over repetitive adsorption/regeneration cycle (~50 cycles).

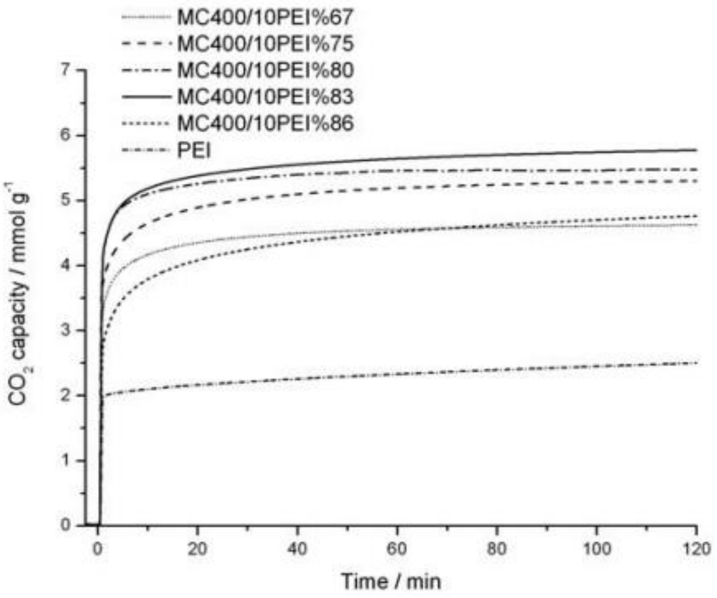


Figure 12 CO_2 Capture Kinetics of Mesoporous Silica Sorbents with Different Amine Loadings [153].

Further studies took into consideration the mode of regeneration and the lifetime of adsorbents during the evaluations of amine impregnated adsorbents. Drage et al. [152] demonstrated thermal swing desorption for PEI functionalized proprietary mesoporous silica using pure CO_2. Thermal swing regeneration was shown to give good cyclic regeneration capacities (2 mmol. g^{-1}). However, successive loss of cyclic adsorption capacity of the sorbent and therefore lifetime of sorbents was observed over numerous regeneration cycles. It was probably due to the secondary reaction between CO_2 and PEI above 135^oC to form a stable product e.g. urea, which leads to the irreversible degradation of the adsorbents. The use of nitrogen as stripping gas instead of CO_2 was also suggested in overcoming the problems identified for the thermal regeneration of the adsorbents. In addition to TSA process, Dasgupta et al. [160] investigated a single column five-step PSA option using PEI impregnated SBA-15 as adsorbent. A strong adsorptive rinse cycle was suggested for CO_2 recovery during PSA process. Pirngruber et al. [174] conducted a preliminary analysis of the performances in a VSA or TSA process for varieties amine immobilized solid support for postcombustion CO_2 capture and concluded that neither conventional TSA or VSA mode seem to be viable option for these sorbents.

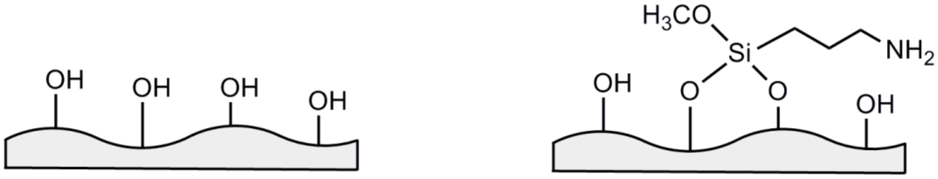
In summary, novel amine impregnated silica supports as shown in ***Table 8*** are promising and can effectively adsorb CO_2 with relatively higher working capacity, even some cases greater than the 4 mmol.g^{-1} stipulated industrial requirements for solid sorbents. Moreover, their adsorption capacities are not impaired by the presence of moisture (in many cases moisture helps for higher capacity). However, durability and regeneration kinetics of the amine impregnated solid sorbents have not been tested adequately under real flue gas conditions. Their desorption kinetics are still slower. Considerable leaching of amines may also put a major drawback for the use of impregnated amine functionalized sorbents for CO_2.

3.2.5.2 Grafted silica supported sorbents

A number of groups have reported synthesis and characterization of amine-grafted ordered mesoporous silica sorbents (Class 2 Category) for CO_2 capture. Here amine, mainly amino-silane, is covalently tethered to the silica support [130]. Three methods can be used for the grafting of amine on silica support: postsynthesis grafting, direct synthesis by co-condensation, and anionic template synthesis with help of the interaction between the cation head in aminosilane and anionic surfactants [175]. Various kinds of silica, such as silica gel, MCM and SBA type silica were used as the support. The mesoporous nature of the support permits good diffusivity of organic amine into the pore space and, following functionalization, good mass diffusion of CO_2 gas molecules into and out of the structure (except when the pores are blocked). In addition, a wide variety of aminosilanes (***Table 8***) were grafted onto the surface of porous silica to investigate the impact of amine type and amine loadings on the CO_2 adsorption capacity of resulting sorbent composites.

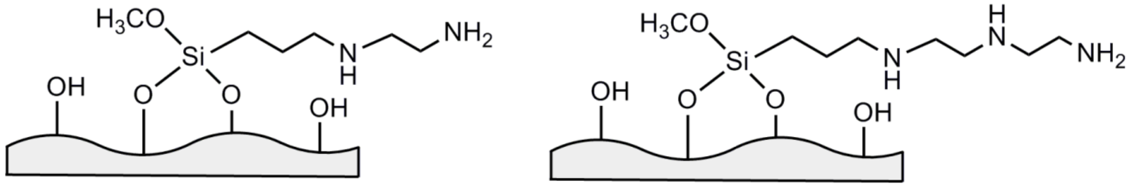
Leal et al. [176] first described the chemisorption of CO_2 on an APTES modified surface of silica gel. They confirmed that each molecule of CO_2 uses two surface amino groups to form an ammonium carbamate species in absence of H_2O and ammonium bicarbonate surface species in presence of H_2O. The sorbent was capable of adsorbing about 0.44 mmol.g^{-1} of dry CO_2. It was far below the requirement for industrial application of the sorbents.

A series of aminopropyl- functionalized hexagonal mesoporous silica (HMS) were prepared and characterized by Chaffee's group [177-181] to enhance CO_2 adsorption due to their high porosity to facilitate rapid gas diffusion to and from their surface. The modified HMS materials as shown in ***Figure 13*** were developed by Delaney et al. [177] using 3-aminopropyltrimethoxysilane (APTS), aminoethyl-aminopropyl-trimethoxysilane (AEAPTS) and *N*-[3-(trimethoxysilyl)propyl) diethylenetriamine (DAEAPTS), ethylhydroxyl-aminopropyl-trimethoxysilane (EHAPTS) and diethylhydroxyl-aminopropyl-trimethoxysilane (DEHAPTS). The modified silica produced very high surface area material with varied concentrations of surface bound amine and hydroxyl functional groups. These sorbents were found to have substantial reversible CO_2 adsorption capacities under dry conditions at 20°C. The modified HMS sorbents have also been shown to reversibly adsorb substantially more than modified silica gel reported by Leal et al. [176]. Another observation that for HMS-APTS, HMS-AEAPTS and HMS-DEAPTS the ratio of CO_2 molecules adsorbed per available N atom was approximately 0.5. This is consistent with the carbamate formation mechanism as presented by eq (3). With HMS-DEHAPTS the ratio was approximately 1. As tertiary amines cannot form stable carbamates (section 3.2.1) so it is proposed that the hydroxyl groups may serve to stabilize carbamate type zwitterions.



Raw silica

APTS grafted silica



AEAPTS grafted silica

DAEPTS grafted silica

Figure 13 Modified HMS Materials

Based on a systematic investigation of CO_2 adsorption on different mesoporous silica substrates and their amine functionalized hybrid product, Knowles et al. [178,179,181] also pointed out that the extent of surface functionalization was found to depend on substrate morphology (e.g. available surface area, pore geometry and pore volume), diffusion of reagents to the surface, as well as the silanol concentration on the substrate surface. Their results showed that the higher N content of the tether leads to a higher CO_2 capacity on the adsorbent surface. The CO_2 adsorption performance of hybrid materials exhibited good adsorption kinetics, reaching saturated within 4 minutes for each sample, and highest CO_2 capacity of about 1.66 $mmol.g^{-1}$ at 20^oC in dry 90% CO_2/10% Ar mixture [178]. Moreover, when the grafted sorbents are exposed to humid stream of CO_2, the adsorption capacity slightly reduced.

As an extension of their previous work on APTS and AEAPTS–functionalized HMS, to explore the potential of the longer side chain and greater number of N atoms/tether to achieve still higher CO_2 capacities, Knowles et al. [181] assessed *N*-[3-(trimethoxysilyl)propyl]- diethylenetriamine (DAEAPTS) functionalized HMS. The sample with best CO_2 adsorption performance was found to have CO_2 adsorption capacity of 1.2 $mmol.g^{-1}$ at 20^oC which was less than previously observed for the analogous APTS and AEAPTS-functionalized silicas (1.66 $mmol.g^{-1}$) [180]. In comparison with APTS and AEPTS-functionalized silica sorbents, the DAEAPTS- functionalized sorbents had a greater CO_2 adsorption capacity for a given surface tether loading (tethers per substrate surface area) under anhydrous conditions at 20^oC. However, the amine efficiencies of DAEAPTS -functionalized sorbents were less than those reported for analogous APTS and AEPTS- functionalized materials. It was thought to be due to reduced accessibility of CO_2 to the surface-bound amine groups brought about by entanglement (reduced mobility) of the longer hydrocarbon chains within the mesoporous domain and the relative proximity of amine pairs. All functionalized HMS sorbents were found to be thermally stable up to 170^oC in both pure

N_2 and mildly oxygenated (2%) N_2 atmosphere and showed no affinity for N_2 and O_2. However, DAEAPTS-functionalized sorbents were found to degrade in highly oxygenated atmosphere.

Recently, Liang et al. [182] synthesized a series of functionalized SBA-15 with melamine based dendrimers up to the fourth generation to study their CO_2 adsorption properties. They prepared using the similar stepwise polymerization reaction scheme proposed by Acosta et al. [183]. It was found that CO_2 adsorption capacities of the dendrimer functionalized SBA-15 did not show substantial improvement over that of the aminopropyl modified SBA-15. The CO_2 adsorption capacities of these adsorbents were improved relative to the non-functionalized SBA-15 except for the fourth generation dendrimer functionalized SBA-15. The exception was thought to be associated with the completely filled pores of the sorbent which blocked CO_2 to access the amino groups. The highest adsorption capacity was shown by the third generation dendrimer functionalized SBA-15 and it was about 0.98 mmol/g at 20^oC in 90% CO_2/10% Ar.

Hiyoshi et al. [184,185] demonstrated the potential application of aminosilane-modified mesoporous silica in separation of CO_2 from gas streams containing moisture. A series of aminosilane-modified mesoprous silica materials were prepared by grafting various aminosilanes (mono-, di- and tri-) onto the walls of SBA-15. The characterization of these prepared adsorbents showed the significant decrease of surface area or pore volume after grafting, which was close to the predicted values for each adsorbent. Among those aminosilane grafted SBA-15, DAEAPTS modified material (DAEAPTS-SBA-15) exhibited the best CO_2 adsorption capacity of 1.10 $mmol.g^{-1}$ in a gas flow containing 15% CO_2 at 60 ^oC and 1.21 $mmol.g^{-1}$ in the gas mixture of 15% CO_2, 12% H_2O with N_2 balance, respectively [184]. In their subsequent researches [185], they found that the DAEAPTS -SBA-15 showed improved CO_2 adsorption capacity after SBA-15 was boiled in water for 2h followed by grafting of aminosilanes. The amount of CO_2 adsorbed reached 1.58 $mmol.g^{-1}$and 1.80 $mmol.g^{-1}$ corresponding to absence as well as presence of water vapor under the same experimental conditions. The efficiencies of the aminosilanes at identical surface density of amine were found to be in the order APTES>AEAPTS> DAEAPTS.

In an effort to develop selective sorbents for CO_2 and H_2S removal from natural gas mixtures 3-aminopropyl-functionalized silica xerogel and MCM-48 silica sorbents were also synthesised and studied by Huang et al. [186]. The CO_2 uptake capacity of amine grafted MCM-48 sorbent was always higher than that of amine grafted xerogel. With the respect to pure CO_2, the amount of CO_2 adsorbed reached to 2.05 $mmol.g^{-1}$ at 25^oC. In the presence of water, the CO_2 adsorption capacity doubled as the adsorption mechanism changed from carbamate formation to bicarbonate formation.

Mesoporous SBA-15 silica possesses high surface area for grafting and large uniform pore size to facilitate CO_2 diffusion inside the pore. Gray and coworkers [48,185-188] prepared a series of amine grafted SBA-15 sorbents suitable for CO_2 adsorption. They grafted SBA-15 with γ-(aminopropyl) triethoxysilane (APTES), a primary amine to study the CO_2 adsorption/desorption relying on a high temperature/pressure diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectrometry (MS) technique. They reported APTS grafted SBA-15 could adsorb up to 0.4 $mmol.g^{-1}$ at 25°C. Whereas, SBA-15 grafted with [*N*-(2-aminoethyl)-3-aminopropyl] trimethoxysilane (AEAPTS) [189], a diamine adsorbed 0.79 $mmol.g^{-1}$ at $25^{\circ}C$ which is about twice the amount of monoamine-treated SBA-15 [187]. CO_2 was found to adsorb on the amine sites in the form of bicarbonate and carbonates which desorb as CO_2 by temperature-programmed desorption (TPD) in He/H_2O flow in temperature range of 80-120^{o}C. The enhanced CO_2 adsorption capacity was obtained in the presence of H_2O in gas flow compared to that in the absence of H_2O. H_2O is needed to react with CO_2 to produce carbonate and bicarbonate [187], which was confirmed later on by Khatri et al. [190] on the basis of the isotopic shift results from H_2O and corresponding isotopic D_2O.

APTS enriched SBA-15 with surface area 227 $m^2.g^{-1}$ and surface nitrogen loading of about 7.1% was also compared with commercially available immobilized amine sorbent (IAS) with surface area 219 $m^2.g^{-1}$ and surface nitrogen value of loading 17.7% in a humid 10% CO_2/90%He stream over the temperature range of 25-60^{o}C by this research group [188]. The average CO_2 capture capacity values over three cycles were 1.89 mmol/g-adsorbent for SBA-15 and 1.82 mmol.g^{-1} for IAS at 25^{o}C. Though both sorbents had similar basicities and surface areas, the key factors for performance improvement of SBA-15 sorbent was ascribed to more accessibility and distribution of amine sites in case of SBA-15. In another work, this group compared APTS grafted SBA-15 with reformulated immobilized amine sorbent (R-IAS) impregnated with a secondary amine prepared by reacting ethyleneamine with acrylonitrile [50]. The reported average capacity of the R-IAS which has surface nitrogen loading of about 21.9% was 3.02 mmol. g^{-1} under at 25^{o}C. The higher CO_2 capcaity of R-IAS was attributed to the increase loading of secondary ethyleneamine. However, all three sorbents showed poor stability after two consecutive adsorption and regeneration cycles. This might be due to instability in the amines used in those sorbents.

In an attempt to investigate the thermal stability of APTS-SBA-15 sorbent, Khatri et al. [190] conducted the temperature-programmed degradation study of fresh APTS-SBA-15 in the presence of air with the air to He ratio of 1:2 and flow rate of 30 mL/min. The results showed that the APTS-SBA-15 sorbent was stable up to 250^{o}C. A long-term adsorption/desorption test, however, is still required to learn further about the stability of sorbent. Additionally, the SO_2 adsorption on APTS-SBA-15 resulted in a negligible CO_2 adsorption capacity, indicating the necessity of SO_2 removal before amine-based CO_2 adsorption.

Zheng et al. [191,192] synthesised SBA-15 mesoporous silica material grafted with AEAPTS and characterized its CO_2 adsorption properties. They reported CO_2 adsorption capacity of 1.95 mmol.g^{-1} in pure CO_2 at 22°C. However, this value decreased to around 0.45 mmol.g^{-1} when the AEAPTS -SBA-15 was tested at 25°C with 15% CO_2 in the N_2 flow system. Moreover, the AEAPTS -SBA-15 showed a reduced thermal stability (around 200°C) in air due to the occurrence of oxidation. However, the current CO_2 adsorption capacity of AEAPTS -SBA-15 was not adequate for large scale CO_2 separation and the further improvement regarding to adsorption capacity was still one of the concerns.

As a continuous effort to develop high-capacity, water-tolerant amine grafted silica based sorbent with large amine loadings as well as with large pore volume and pore size, Sayari and coworkers [193-202] developed pore-expanded MCM-41 mesoporous silica (PE-MCM-41) grafted with amine and conducted a series of experiments on those sorbents under both dry and humid conditions and compared with other available physisorbents and chemisorbents available in the literature. The amines used for grafting were 3-[2-(2-aminoethylamino) ethylamino] propyltrimethoxysilane (DAEAPTS) and APTS. The sorbent silica was prepared through postsynthesis hydrothermal treatment of the as-synthesized MCM-41 [195]. DAEAPTS grafted PE-MCM-41support showed an adsorption capacity of 2.05 mmol.g^{-1} at 25°C and 1.0 atm for a dry 5% CO_2 in N_2 feed mixture with amino-silane loading of 5.98 mmol (N).g^{-1} [193]. They showed that the effect of amine surface density of the sorbent has a strong impact on the adsorption efficiency. However, presence of moisture did not enhance significantly the performance of the amine-impregnated PE-MCM-41 sorbents as expected toward bicarbonate formation pathway. Subsequently, Harlick and Sayari [194] also focused on optimizing the grafting conditions and concluded that in comparison to the dry grafting procedure, wet grafting by co-addition of water at 85°C showed a 33% increase in total amine content and a 43% increase in CO_2/N ratio, resulting in a 90% overall improvement.

To evaluate the cyclic stability and working adsorption capacity of amine grafted PE-MCM-41, TSA, temperature-vacuum swing adsorption (TVSA), as well as PSA regeneration modes were performed by this research group for DAEAPTS -PE-MCM-41 [197-201]. It was found that regeneration under vacuum at 70°C, the sorbent showed a good stability over 100 adsorption-desorption cycles with average working adsorption capacity of 2.28 mmol.g^{-1} for pure CO_2 [197], while temperature swing regeneration process was suitable desorption above 120°C [198]. In addition to thermal stability, it also showed infinitely high selectivity for CO_2 over N_2 and O_2 [198-201]. It was also confirmed by Belmabkhout and Sayari [201] that SO_2 has an adverse effect on CO_2 removal and its removal is required prior to CO_2 adsorption.

Recently, Belmabkhout and Sayari [202] noted that under dry conditions the deactivation of the amine grafted MCM-41 silica sorbents took place through the urea formation reaction (***Figure 14***) even at mild conditions of 20°C and deactivation was dependent on the adsorption-desorption conditions and nature of adsorbent. TRI-PE-MCM-41 sorbent underwent over 700 cycles without any loss of sorption capacity when adsorption and regeneration was carried out using humid gas containing about 7.5% relative humidity at 70°C. Therefore, they suggested that the stability of sorbent could be enhanced significantly by inhibiting the formation of urea using moisture containing gases.

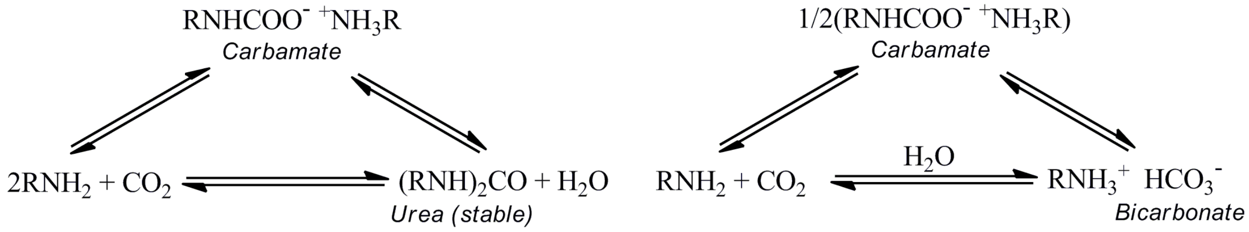


Figure 14 Relationship between amine, CO_2, carbamate, and urea species during CO_2 adsorption-desorption under dry and humid conditions [202].

A novel covalently tethered hyperbranched aminosilica (HAS) sorbent (***Figure 15***) with high amine content capable of capturing CO_2 rervesibly from flue gas was developed and compared with other covalently supported solid sorbents by Jones and his research group [203,204]. HAS was synthesized via one-step surface polymerization reaction inside SBA-15 pores where aziridine monomer (also known as ethylene imine) undergoes a ring opening polymerization in presense of catalytic amounts of acetic acid to form hyperbranched aminoplolymers that were covalently bound to SBA-15 support [204]. The HAS sorbent had an amine loading of 7.0 mmol N.g^{-1} and CO_2 adsorption capacity of 3.08 mmol g^{-1} under a flow of 10% CO_2/90% Ar saturated with water at 25°C tested in a packed bed reactor. It was stable over 12 cycles with regeneration at 130°C.

Following their early research work, Drese et al. [204] proposed modification of the HAS synthesis conditions, such as aziridine-to-silica ration and solvent to further tune the sorbent's composition, adsobent capacity and kintetics. They found that higher amine loadings and therefore, higher potential active adsorption sites contributed to a better adsorption capacity. The reported amine loadings for modified HAS ranged from 2.27 to 9.78 mmol N g^{-1} adsorbent and resulted adsorption capacities in the range of 2.0-5.55 mmol.g^{-1} from a simulated flue gas consisting of humidified 10% CO_2/90% Ar test gas measured at 25°C, although a sufficiently long adsorption time was chosen (200 min) rendering kinetic effects less important.

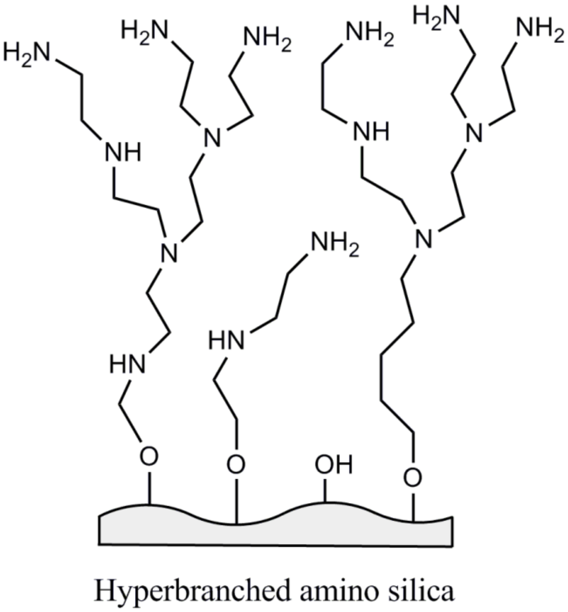


Figure 15 Hyperbranched Amino Silica

Knofel et al. [205], functionalized SBA-16 silica was with AEAPTS, a diamine. The functionalization of SBA-16, which has a 3D cubic pore matrix with interconnected pores, allows good accessibility for the grafting species as well as the gas molecules during adsorption. The most promising sorbents adsorbed about 1.4 mmol.g^{-1} at 27°C under atmospheric pressure and in pure CO_2. The grafted silica sorbent showed high enthalpies for adsorption for CO_2 (-100 kJ/mol), indicating the high energy requirement for sorbent regeneration in cyclic adsorption/desorption.

The comparison of three amine functionalized mesoporous silica materials with different pore sizes was made by Zelenak et al. [206] MCM-41 (d_p = 3.3), SBA-12 (d_p = 3.8) and SBA-15 (d_p = 7.1) were modified by APTES. The authors suggested that the key parameter influencing the CO_2 adsorption by amine modified materials was not surface area but the pore size and density of $–NH_2$ active sites on the surface of the support. The total amount of CO_2 adsorbed was 0.57 mmol.g^{-1} for APTES -MCM-41, 1.04 mmol.g^{-1} for APTES -SBA-12 and 1.53 mmol.g^{-1} for APTES -SBA-15 sorbent, which was in accordance with the order of pore size as well as amine surface density. Kim et al. [207] developed and tested series of amine functionalized mesoporous silica sorbents via anionic surfactant-mediated synthesis method for CO_2 adsorption at room temperature. Higher amine loading on mesoporous structure was found to be governing factor to achieve high CO_2 adsorption.

Table 8 CO_2 Adsorption Capacity of Amine Grafted Solid Sorbents

Support	Amine	Amine loading (mmol. g^{-1} sorbent)	Adsorption Capacity[a] (Humid) (mmol. g^{-1})	Experimental Conditions		Ref.
				P_{CO_2} (atm)	T (^oC)	
SBA-15	APS	2.7	0.52 (0.5)	0.15	60	184
SBA-15	AEAPS	4.2	0.87 (0.9)	0.15	60	184
SBA-15	TA	5.1	1.1 (1.21)	0.15	60	184
SBA-15[b]	APS	2.61	0.66 (0.65)	0.15	60	185
SBA-15[b]	AEAPS	4.61	1.36 (1.51)	0.15	60	185
SBA-15[b]	TA	5.8	1.58 (1.80)	0.15	60	185
SBA-15	MAPS	1.88	0.25 (0.25)	0.15	60	185
SBA-15	AEAPMS	3.52	0.91 (0.93)	0.15	60	185
SBA-15	EDA		0.45	0.15	25	192
SBA-15	EDA		1.95	1	22	192
SBA-15[c]	EDA		0.91	0.15	25	191
SBA-15	APTS		0.4	0.04	25	187
SBA-15	AP	2.72	1.53	0.1	25	206
SBA-15	Aziridine polymer	9.78	(5.55)	0.1	25	204
SBA-15	Aziridine polymer	9.78	(4)	0.1	75	204
SBA-15	Aziridine polymer	7	(1.98)	0.1	75	203
SBA-15	Aziridine polymer	7	(3.11)	0.1	25	203
SBA-16	TEDA (AEAPTS)	0.76	1.4	1	27	205
SBA-12	AP	2.76	1.04	0.1	25	206
MCM-41	AP	3	0.57	0.1	25	206
PE-MCM-41	TRI	7.95	2.65	0.05	25	194
PE-MCM-41	TRI	7.8	2.28	0.05	70	197
MCM-48	APTES	2.3	2.05	1	25	186
MCM-48	APTES	2.3	1.14	0.05	25	186
HMS[d]	APTS	2.29	1.59	0.9	20	179
HMS[d]	DT	4.57	1.34	0.9	20	181
MSP[e]	EDA		0.73	0.1	60	208
Silica gel	AP	1.26	0.89	1	50	176
CNTs	APTS		1.32	0.15	20	63
CNTs	APTS		2.59	0.5	20	40

a. CO_2 adsorption capacity in mmol.g^{-1} sorbent, within parenthesis indicates humid condition result
b. SBA-15 support is boiled in water for 2h followed by grafting of aminosilanes
c. EDA-SBA-15 enhanced by backfilling with propylsilane (C3) in supercritical fluid propane
d. Hexagonal mesoporous silica
e. Mesoporous spherical-silica particles

Table 8 summarized the CO_2 adsorption capacity of amine functionalized adsorbents. Though functionalization of mesoporous silicas with amine functional groups significantly improves the CO_2 adsorption capacity of silica substrate, the reported equilibrium CO_2 adsorption capacities are not as high as those reported with amine impregnated mesoporous silicas. Moreover, the low hydrothermal stability of mesoporous silicas in presence of water vapor at elevated temperature is still one of the major concerns.

3.2.6 Impregnated alumina supported sorbents

Due to its high resistance to steam and good mechanical and thermal stability properties, porous alumina was also considered for impregnation [209]. Plaza et al. [210] synthesized and tested a series of solid sorbents by immobilizing six different liquid amines, such as DETA, DIPA, TEA, AMPD, PEHA and PEI on the surface of a mesoporous alumina through wet impregnation. Alumina sorbent impregnated with 40 wt% DETA (A-DETA) presented the highest CO_2 adsorption capacities throughout the temperature range of 298–373 K (ca. 1.82 $mmol.g^{-1}$ at 373 K). A-DETA doubled the CO_2 capture capacity of the raw alumina at 298 K (i.e. 1.36 vs.0.68 $mmol.g^{-1}$). It is also worth noting that alkanolamine-impregnated samples (A-TEA, A-AMPD and A-DIPA) showed a gradual decrease in CO_2 adsorption with increasing temperature, whereas the alkylamine-impregnated samples (A-DETA, A-PEHA and A-PEI) presented a gradual increase in CO_2 capture capacity. The probable reason for this could be an improvement of CO_2 mass diffusivity through the amine film with temperature, as this would allow more amine groups to react [147].

List of the research organizations working in development of amine functionalized solid sorbent are given in ***Table 9***. During the testing of these sorbents, the adsorption/desorption conditions are often highly varied, leading to difficulty in comparing their performance systematically. Most R&D evaluations are currently being conducted on lab-scale using compressed CO_2 gas in a thermogravimetric apparatus (TGA) and most commonly at temperature below 75°C. During the testing of these materials, the adsorption and desorption conditions are often very different leading to difficulty in comparing material performance. Limited literatures are available on testing sorbents under actual flue gas conditions. Therefore, to advance the development to the next level, it is essential to test sorbents on actual flue gas conditions. Development of adsorbent with high selectivity and high CO_2 capacity, which can be operated at elevated temperature (~60-120°C) is desired for more efficient and cost-effective CO_2 capture by adsorption method.

Table 9 Research Group working for development of solid sorbents for postcombustion CO_2 capture

Support	Amine	Name of the Research Group	Ref
MCM-41, AC, Silica gel	Triamine silane, DEA	Sayari, A. Department of Chemistry and Department of Chemical Engineering, **University of Ottawa**, Ottawa, Ontario, K1N 6N5, Canada	[193-202]
Zeolite 13X	MEA	S. S. Rayalu, **National Environmental Engineering Research Institute**, Nehru Marg, Nagpur 440 020, India	[161]
MCM-41	PEI	Song, C., Clean Fuels and Catalysis Program, The Energy Institute, and Department of Energy & Geo-Environmental Engineering, **The Pennsylvania State University**,USA	[10,171,148,147]
SBA-15	γ-(aminopropyl)-triethoxysilane	Rajesh A. Khatri, Chemical Engineering Department, The University of Akron, Akron, Ohio 44325-3906, and National, Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, Pennsylvania	[9, 189,190]
SBA-15	alkyl amines, adenine , imidazole and guanine	S. P. Ratnasamy, National Chemical Laboratory, Homi Bhabha Road, Pune 411 008, India	[5]
Mesoporous silica	N-[3-(trimethoxysilyl)propyl]diethylenetriamine	Alan L. Chaffee and his group, CRC for Greenhouse Gas Technologies School of Chemistry, **Monash University**, Victoria 3800, Australia	[177-182]
Fly-ash, **SBA-15** **R-IAS** **IAS**	CPAH APTS Ethyleneamine, E-100 Proprietary	M.L. Gray,T, Y. Soong, K.J. Champagne, H. Pennline, J.P. Baltrus, US Department of Energy, **National Energy Technology Laboratory**, P.O. Box 10940, Pittsburgh, PA 15236, United States	[49,140,141,166,188,203,204]
Fly-ash, AC	MEA, DEA, MDEA	M. Mercedes Maroto-Valer, School of Chemical and Environmental Engineering, **University of Nottingham**, University Park, Nottingham, UK	[34-37,142]
		Ranjani V. Siriwardane, U.S. Department of Energy, National Energy Technology Lab, 3610 Collins Ferry Road, P.O. Box 880, Morgantown, West Virginia 26507-0880	[32,47,88]
		Sjostrom, **ADA Environmental Solutions**, 8100 Southpark Way, Unit B, Littleton, USA	[212]
Silica, resin	PEI	C.E. Snape, Nottingham Fuel and Energy Centre, School of Chemical, Environmental and Mining Engineering, **University of Nottingham**, UK	[143,146]
SBA-15	EDA	F. Zheng and his group, **Pacific Northwest National Laboratory** P.O. Box 999, MSIN: K6-28 Richland, WA 99352	[11,191,192]
PMMA	ED, TEPA	T. Filburn College of Engineering, **University of Hartford**, Hartford, CT 06117, United States	[49,50,155,165]

Support	Amine	Name of the Research Group	Ref
SBA-15	Aziridine	Christopher W. Jones, School of Chemical & Biomolecular Engineering, **Georgia Institute of Technology**, Atlanta, Georgia 30332	[129-131,153, 203, 204]
SBA-16	TEDA	C. Knofel, Laboratoire Chimie Provence, **Universités d'Aix-Marseille** I,II et III – CNRS, UMR 6264, Centre de Saint Jérôme, 13397 Marseille, France	205]
β-zeolite, SiO_2, and Al_2O_3	TEPA	Steven S.C. Chuang, Department of Chemical and Biomolecular Engineering, **The University of Akron, Akron**, OH 44325-3906	[163,187,189]
Biomass residue, Alumina	Ammonia DETA, DIPA, TEA, AMPD, PEHA, PEI	M.G. Plaza, C. Pevida, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis, **Instituto Nacional del Carbón**, CSIC. Apartado 73. 33080 Oviedo, Spain	[137-139,144]
Glass fiber	PEI	Shuixia Chen and his group (Peiyuan Li, Bingqing Ge, Sujuan Zhang, Qikun Zhang, and Yongning Zhao), PCFM Lab, OFCM Institute, School of Chemistry and Chemical Engineering, and Materials Science, Institute, **Sun Yat-Sen UniVersity**, Guangzhou 510275, PR China,	[167-169]
Y-Zeolite	TEPA	Chungsying Lu and his group (Fengsheng Su, Shih-Chun Kuo, and Wanting Zeng), Department of Environmental Engineering, **National Chung Hsing University** 250 Kuo Kuang Road, Taichung 402, Taiwan	[162,208]
SBA-15	PEI	R. Sanz , G. Calleja, A. Arencibia, E.S. Sanz-Pe´ rez, Department of Chemical and Environmental Technology, **ESCET Universidad Rey Juan Carlos**, Madrid, Spain	[20]
MCM-48, SBA-15	PEI	N. Gargiulo, D. Caputo and C. Colella Dipartimento di Ingegneria dei Materiali e della Produzione, Università Federico II, Napoli, Italy	[173]
MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6	PEI	Wha-Seung Ahn and his group (Won-Jin Son, Jung-Sik Choi), Department of Chemical Engineering, **Inha University**, Incheon 402-751, Republic of Korea	[116,119,150,151]
SBA-15	TEPA	Zhu, J. H. and cowokers, Key Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering **Nanjing University**, Nanjing 210093 (P.R. China)	[149,157]
Silica	PEI	C. E. Snape and co workers Nottingham Fuel and Energy Centre, School of Chemical, Environmental and Mining Engineering, **University of Nottingham**, Nottingham NG7 2RD, UK	[143,146]
Anthracite	Ammonia, PEI	M. Mercedes Maroto-Valer, The Energy Institute and Department of Energy and Geo-Environmental Engineering, **Pennsylvania State University**, 405 Academic Activities Building, University Park, PA 16802, USA	[35-37,142]

Support	Amine	Name of the Research Group	Ref
AC, Carbon black	Calcium acetate solution	Kun-Hong Lee, Department of Chemical Engineering, **Pohang University Of Science and Technology**, San 31. Hyoja-Dong, Nam-Ku, Pohang. Kyungbuk, 790-784, South Korea	[26]
Biomass	Ammonia	C. Pevida, **Instituto Nacional del Carbón**, CSIC. Apartado 73. 33080 Oviedo, Spain	[137-139,144, 146]
AC	Ammonia	Przepiorski, J., Institute of Chemical and Environment Engineering, **Technical University of Szczecin**, ul. Pulaskiego 10, 70-322 Szczecin, Poland	[136]
AC, CNT, Zeolite	APTS	Chungsying Lu, Department of EnVironmental Engineering, **National Chung Hsing UniVersity**, Taichung 402, Taiwan	[208]
SWNT	PEI	Eoghan P. Dillon, Christopher A. Crouse, and Andrew R. Barron, Richard E. Smalley Institute for Nanoscale Science and Technology, Center for Biological and Environmental Nanotechnology, Carbon Nanotube Laboratory, and Department of Chemistry, **Rice University**, Houston, Texas 77005	[65]

CPAH: 3-chloropropylamine-hydrochloride, PMMA: poly (methyl methylacrylate), ED: ethylenediamine, TEPA: tetraethylenepentamine, TEDA: N$^{/}$-[3-(trimethoxysilyl)propyl]-ethylenediamine, DETA: diethylenetriamine, DIPA: diisopropanolamine, TEA: triethanolamine, AMPD: 2-amino-2-methyl-1,3-propanediol, PEHA: pentaethylenehexamine, PEI: polyethyleneimine

4. Performance of solid sorbent

Adsorption is considered to be one of the more promising technologies for CO_2 capture from power plant flue gases. The success of this approach is dependent on the development of a sorbent material that has a high adsorption capacity, high CO_2 selectivity and long term durability. Selection of the suitable solid sorbent material is an important step in the existing and upcoming thermal power plant with CO_2 capture processes. However, it is not straightforward to select the most promising sorbent material from the existing sorbent inventory because several parameters affect the overall CO_2 capture process, performance and economics. Truly, there is and will be no single, ideal solid sorbent. Instead, sorbents need to be compared in light of the specific process they will be adapted to, ranking the importance of adsorbent parameters as they apply to the specific constraints of the system. However, some generalizations can be drawn from the reviewed literature. This section compares the potential advantages of solid sorbent system over MEA process and identifies potential solid sorbent.

4.1 Comparison of ideal solid sorbent with MEA process

In this section an attempt is made to do some preliminary comparison (first order approximation only, as the solid sorbent technology is still at an early stage of development) between an ideal solid sorbent and a bench mark MEA process.

Basis of Calculation: The scope of the present report does not allow comprehensive analysis/cost calculation of the two processes. However, a simplified cost calculation (first order approximation) for basic comparison is given below in ***Table 10*** for a 1000t/d CO_2 capture from coal-fired power plant flue gas. For simplicity, the impurities in the flue gas were not considered.

Table 10 Flue gas parameters for CO_2 capture

Flue Gas		
Volumetric rate	2800	m^3/min
CO_2 concentration in flue gas	14	%
Pressure	1.22	Bar
Temperature	423	K
CO_2 Capture		
CO_2 removal	90	%
Amount of CO_2 captured	1000	t/d
CO_2 volumetric rate	400	m^3/min

4.1.1 Cost Calculation for Ideal Solid Sorbent

We would like to define a hypothetical ideal sorbent with all the desired properties such as high adsorption capacity (>10 $mmol.g^{-1}$), low regeneration energy (<1000 $kJ/(kgCO_2)^{-1}$), infinite selectivity and multi-cycle durability and very low overall cycle time (<10 mins) to reduce the energy penalty to ¼ of the benchmark 30% MEA wet scrubbing system (provide the MEA regeneration energy). This area is in early stage of development and most of the studies are in lab scale. Due to this key parameters are not available in open literature. Therefore, in this first order simplified calculations we used solid sorbent parameters as given in ***Table 11*** from the available literature which is close to the defined hypothetical ideal sorbent.

Basis: The adsorption–desorption process can work on the principle of temperature swing adsorption (TSA) or pressure swing adsorption (PSA). However, in this report the preliminary cost calculations are based on a1000 tCO_2/day capture plant using TSA, as shown in ***Figure 16***. The capture plant is comprised of a number of parallel trains. Each train will have a number of units. The unit consists of one column in adsorption mode and other is in regeneration mode so that the plant will produce a continuous output of CO_2. The flue gas is first fed to the adsorber unit through a blower after cooling it to the adsorption temperature (about 60°C, for this case) using a heat exchanger. In practice, a direct contact cooler is used to remove some of the impurities in the flue gas, in addition to cooling. The regeneration of the CO_2 is conducted using a blower and low pressure steam. It is heated to the desorption temperature (about 105°C, for this calculation). When the bed reaches the desorption temperature, CO_2 is released. The regenerator is cooled again to the adsorption temperature by blowing fresh air through it. It should be noted that this flow-sheet is conceptual and will require significant further development as there is no data on the time for the sorbent to cool from the regeneration temperature back to the adsorption temperature.

Data-sheet based on the simplified calculations (first order approximation) is given in ***Table 11***. This table consists of input-output parameters for bed sizing, pressure drop calculation, and preliminary cost estimation for CO_2 capture using impregnated sorbent.

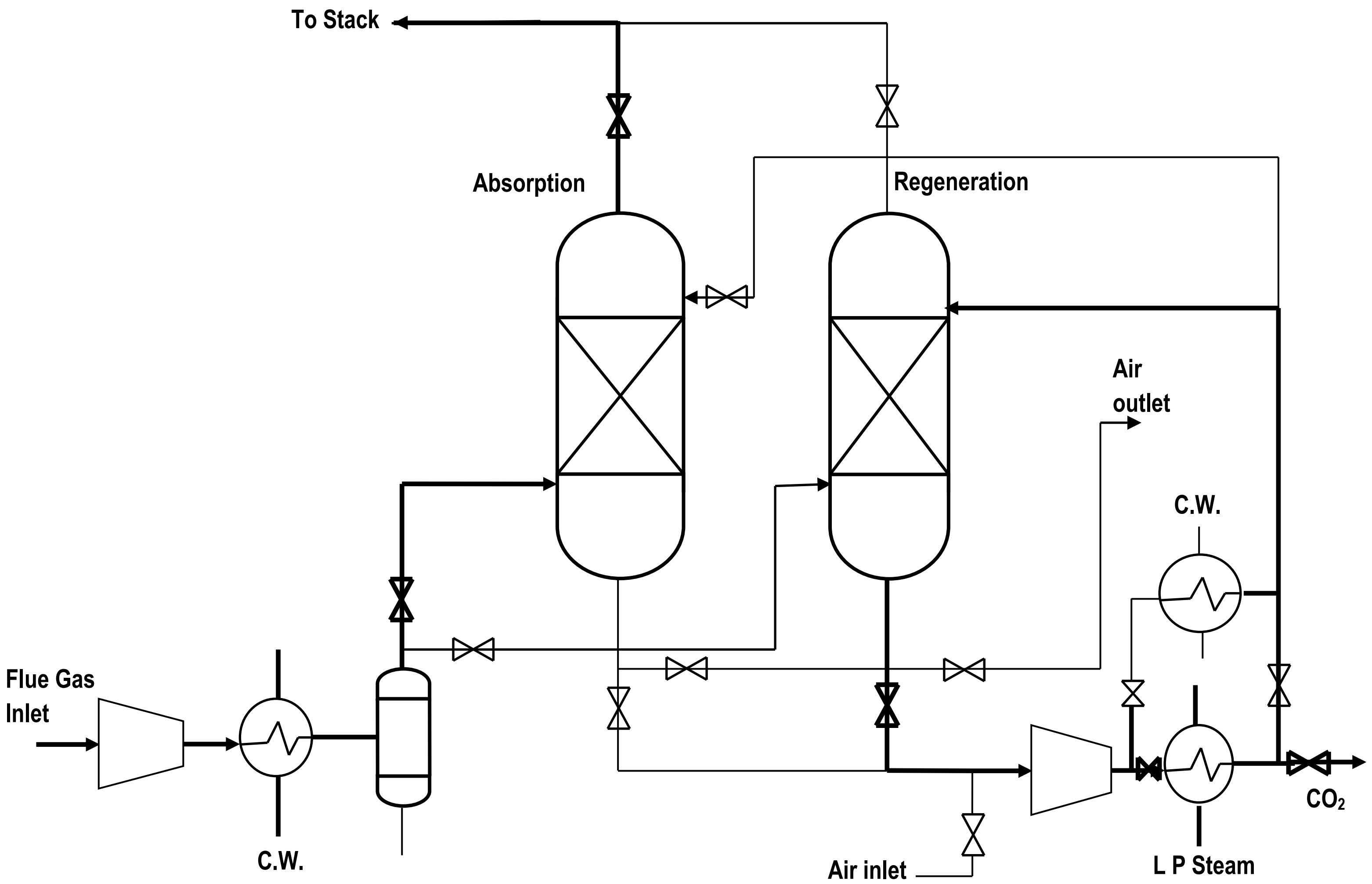


Figure 16 Schematic of TSA sorbent system for CO_2 capture.

Table 11 Data Sheet Summary for Fixed Bed Adsorber/Regenerator Module

Solid Sorbent Properties		
	Ideal case	
Particle density	2600	kg/m^3
Particle size	75	µm
Adsorption capacity	0.187	$KgCO_2/kg$ sorbent
Energy for regeneration	1644.7	$kJ/kg\ CO_2$

Parameters		
Adsorption temperature	333	K
Adsorption time	7	Min
Regeneration temperature	378	K
Regeneration time	30	Min
CO_2 captured	41.67	t/hr
Bed voidage	0.7	
Adsorber Design		
Numbers of fixed beds per train	5	
Numbers of paralleled trains	5	
Sorbent needed per bed	6.24	Ton
Superficial velocity	0.5	m/s
Bed diameter	4.9	M
Bed height	0.43	M
Pressure drop across bed	32.5	kPa

Utilities	Solid Sorbent-Ideal Case	
	Consumption	Annual Cost
Cold Water[t/hr]	133	$605,450
L. P. Steam [t/hr]	29.98	$6,068,000
Electric Energy [Mwh]	0.5	$357,878
Equipment	**Numbers**	**Capital Cost**
Columns	25	$2,000,000
Condenser	5	$1,800,000
Heat Exchanger	1	$180,000
Blower	1	$1,000,000
Material	Consumption	Cost
Solid Sorbent [tons]	156	$1,560,000

The capital costs are based on purchased equipment costs, taken from charts given in Chemical Engineering Process Design and Economics – A Practical Guide (2^{nd} Ed.) by G.D. Ulirch and P.T. Vasudevan: Process Publishing, Durham, New Hampshire, 2004. Equipment purchase costs are then updated to 2010 basis, using the CE Plant Cost Index.

For operating costs, a natural gas price of $6/MCF and an electricity price of $80/MWh are assumed. The sorbent is priced at $10/kg.

Please note that the capital costs in ***Table 11*** are “bare module” costs using the methodology described in Ulirch’s book. Therefore, it is difficult to compare these costs to the costs of other solvent processes in the literature. However, the effect of the two cases on the capital and operating costs can still be studied.

4.1.2 Comparison to the Base Case MEA

A review of the current status of the amine based capture processes for post combustion CO_2 capture is included in the Appendix II. Without going through detailed economics, a comparison between the key process parameters of the solid sorbent and MEA processes can be revealed.

The base MEA process is based on a 30 wt% MEA with inhibitor. MEA has the highest theoretical absorption capacity for CO_2. This theoretical upper absorption capacity of MEA, however, is not realized in practice due to corrosion problems. This 30 wt% MEA seems to be the upper limit at one time, but it was reported that Flour Daniel has pushed it to close to > 35 wt% for its Econamine FG PLUS^{SM} process.

In terms of absorption and desorption temperatures, it was 50°C and 120°C respectively for MEA and 60°C and 105°C for the ideal solid sorbent case. The heat for regeneration is 4503 kJ/kg CO_2 for MEA and 1644.7 kJ/kg CO_2 for the ideal sorbent. A good industry number for the steam consumption for the amine based process is 1.18 tonne steam per tonne of CO_2 (or 2.4 GJ/t). For the ideal sorbent it is 0.72 t/t CO_2. So, a better energy performance compared to the base MEA is expected from the solid sorbent. However, this has to be demonstrated in larger scale test. A lower electrical load is also expected for solid sorbent because of the elimination of the solvent pump. However, this must be weighed against the additional power required for the air blower to cool the sorbent from the regeneration temperature back to the adsorption temperature.

A more rigorous cost analysis based on 400 MW_{net} supercritical power plant data (Table 12) has been carried out for solid sorbent using fixed bed and fluidized bed configuration [211]. The key parameters for conventional MEA system, parallel flow fixed-bed and fluidized-bed contactors for solid sorbent CO_2 capture system are compared in ***Table 13***. It can be seen from the ***Table 13*** that % cost of electricity (COE) increase is 14% less in case of solid sorbent fluidized-bed system in comparison to the MEA system. Moreover, it is shown that for their novel fixed bed configuration, % COE increase is 25% less in comparison to the MEA system.

Table 12 Potential advantages of solid sorbent system over MEA process

Design Conditions

Based on: 400 MW$_{net}$ Supercritical PC Plant
Flue gas flow rate: 1,200,000 acfm
CO_2 Concentration:14 vol%
Flue Gas temperature = ~55°C
Total Pressure: 0.95-1.16 bar
CO_2 Removal: 9,000 tons of CO_2/day (90% CO_2 removal efficiency)
Pressure drop: < 6 psi

Amine Functionalized SBA-15 Silica Based Sorbent

Particle Size: 50-100 µm
Density: 2.6 g/cm^3
Capacity: 6 mmol.g^{-1}
Cost of Sorbent (Estimate): $10/kg
Regeneration Time: 30-60mins.

Operating Conditions

Adsorption: ~50-70° C
Regeneration: ~110-120° C

Table 13 Comparison of Key Parameters for Solid Sorbent with MEA System[211]

	Conventional MEA	Amine Impregnated SBA-15 Sorbent	
		Fixed Bed	Fluidized Bed
Flow rate per unit, m^3.s^{-1}	118	36	71
No. of Absorber Units	8-10	63	8
Total Sorbent Required, tons	N/A	1600	1100
Pressure Drop, Pa	7-41	41	2
Total Foot Print, m^2	460-840	5295	650
ID Fan Load, MW	22.4	15.9[+]	6.5
Solvent Pump Load, MW	3	N/A	N/A
Gross Plant Size, MW	491	474[+]	465
Cost of Electricity(COE), ¢/kWh	7.56	6.93[+]	6.88
Cost of Electricity(COE) increase, %	55	42	41
Initial Sorbent Cost, M$	94[*]	15	11
Annual Sorbent Replacement Cost, M$/y	8.1[*,#]	7.5[¶]	22[¶]

[+] Based on Parallel Flow Fixed bed; [*] MEA Cost listed is total system cost;
[#] For MEA Plant, Solvent make-up rate: ~995 kg/hr;
[¶] Sorbent Replacement: Every 6 months (For fluidized bed) and every 2yrs (For fixed bed)

On the basis of the above energy and cost analysis, it is evident that solid sorbents have a potential to be an acceptable alternative to the benchmark MEA process for post combustion CO_2 capture.

4.2 Desired potential solid sorbent

There are several types of solid sorbent materials which can capture CO_2 below 200°C, as discussed in Section 2 & 3. ***Figure 17*** is a solid sorbents mapping where CO_2 capture capacity of sorbents plotted as a function of adsorption temperature. At this point, it can be considered that any sorbent with a working capacity ≥2.0 and multi-cycle stability for extended time period is a potential sorbent. Using this information and the MEA theoretical regeneration energy from Appendix II as a benchmark, a more generalized table is developed, ***Table 14***. In this table activated carbon and zeolite are not included since their capacities are not acceptable for flue gas condition. This table shows that broadly three types of sorbents have potential to provide performance which will exceed benchmark MEA system. Dry carbonate process regeneration energy is higher than functionalized amine system. Grafted amine has a better thermal stability than impregnated amine since it is chemically bonded with the substrate. According to this metrics table functionalized amines (grafted & impregnated) are the most promising candidates for post combustion CO_2 capture.

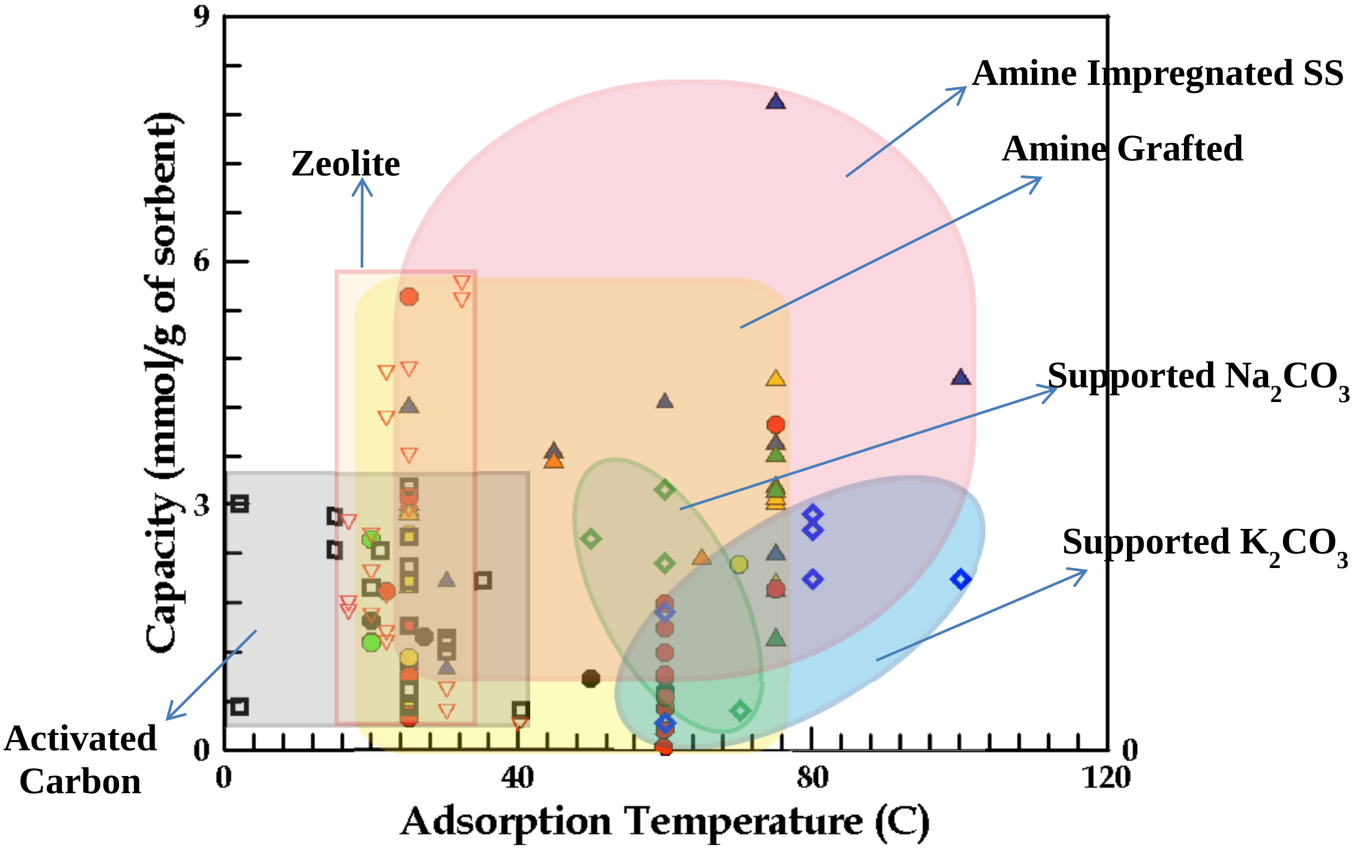


Figure 17 Solid sorbens CO_2 capture capacity as a function of adsorption temperature.

Table 14 Relative comparison of three classes of solid sorbent group.

Parametrs	Grafted Amine	Impregnated Amine	Supported Carbonates
Working Capacity	High	High	medium
Regeneration Energy	lower	lower	Similar
Thermal Stability	Carbonates > Grafted Amine > Impregnated Amine		
Issues	SO_2	SO_2	High heat of Reaction with SO_2

A typical comparison of functionalized solid sorbents with ideal sorbent is shown in ***Table 15***. Based on the present literature review and analysis, most potential solid sorbents for CO_2 capture are compared with the ideal sorbent. Listed amine systems have accepted regeneration energy, capture capacity, adsorption/regeneration temperature range. In the adsorption-desorption cycles row, the number represents the maximum number of cycles tested in the literatures.

Table 15 Comparison of Functionalized Solid Sorbent with Ideal Solid Sorbent in Terms of Key Performance Requirement[*]

	Ideal Sorbent[+]	PEI Impregnated MCM-41[171-172]	TRI-Grafted PE-MCM-41[193-197]	TEPA Impregnated MCM[153]	TEPA Impregnated Zeolite Y[162]	TEPA Impregnated PMMA[155]
Working Capacity($mmol.g^{-1}$)	10	3.02	2.65	7.93	4.27[162]	14.03
Regeneration Energy (kJ. $(kgCO_2)^{-1}$)	1000	na	2045	na	835	na
Total cycle time (min)	<10	50	100	na	120	30
Selectivity	∞	>1000	∞	na	na	na
Ads/Reg Temp/(ΔT) [°C]	60/90/Δ=30	75/125	25-50/70-150	75/<100	30-60/75	40/75
Adsorption-Desorption Cycles	∞	20	750	50	20	3
Cost ($\$.kg^{-1}$)	<5	na	Na	na	na	na

[*] Most of the studies conducted in Lab scale and sufficient data is not available for comparison of the performance in terms of key performance requirement (na: data not available);

[+] Define Ideal Solid sorbent with respect to 1/4th of energy requirement of 30wt% MEA base case.

During this study we have contacted several major solid-sorbent-for-post-combustion developers and ***Table 16*** listed them. At present, ADA Environmental Solution (ADA-ES) is using regeneration energy as one of the main criteria for selecting the solid sorbent technology. ADA-ES had done high level design and captical cost estimation by an engineering consultant company and found it is comparable with MEA process. Their main justification for them selecting & developing solid sorbent technology is its potential of considerable amount of reduction of energy penalty, high sorbent capacity and long term durability which will reduce the materials replacement cost. Sjostrom and Krutka [212] compared about 24 different sorbent materials in a cyclic temperature swing adsorption (TSA)/regeneration CO_2 capture process using simulated coal combustion flue gas. The comparison showed that supported amines exhibited the highest working CO_2 capacities and several of the sorbents tested have theoretical regeneration energies significantly lower than that of the industry benchmark. Ten of these sorbents were supported amine based.

Table 16 List of North American developers contacted for this project.

Organization	Contact Name	Email/Phone#	Comments
ADA Environmental Solution (ADA-ES)	**Dr. Holly Krutka**, Research Scientist	<hollyk@adaes.com>/(303) 962-1949	Talk with Holly Krutka in several times regarding solid sorbents for CO_2 capture. They have done high level design and capital cost estimation through an engineering company. It is comparable to MEA process. According to her major *saving is the energy*. Working capacity lower than 3mmol is ok as long as the kinetics is good. Their kinetic study mostly qualitative. Plan is to scale up from 1kW to 1MW in 2013. For this scale up NETL & other will be doing modelling and simulation.
National Energy & Technology Laboratory (NETL)	**Dr. McMahan L. Gray**, Physical Scientist	<mcmahan.gray@netl.doe.gov>/(412) 386-4826	NETL is a leading developer of CO_2 capture technologies. Recently has done licensing agreement with ADA-ES for two of its patented solid sorbents. Tried to contact Dr. Gray but got no feedback.
RTI	**Dr. Thomas O. Nelson**	tnelson@rti.org	Working on dry carbonate process for CO_2 capture. Tried to contact but got a feedback.
TDA Research Inc.	**Dr. Jeannine Elliott**, Principal Eng.,	jelliott@tda.com/(303) 261-1142	Received DoE funding to develop low cost carbon based sorbents system. Tried to contact but got no feedback.
SRI International	**Dr. Gopola Krishnan,** Principal Scientist	gopala.krishnan@sri.com/(613) 562-5800, x6480	Had a teleconference with Dr. Krishnan. Developing functionalized carbon based (proprietary) low cost sorbent for post combustion CO2 capture. Regeneration energy is around 1/3 of MEA because functionalized carbon sorbent work as a physisorbent. Unique reactor design, single column host adsorption & regeneration. Run results >50H is very good. Building 24" diameter and 60ft talk reactor for 0.25-0.5 MW system. Partnering with NETL, ATM Inc.
University of Ottawa	**Dr. Abdel Sayari,** Professor	abdel.sayari@science.uOttawa.ca/(613) 562-5800, x6480	I had a couple of teleconference with Prof. Sayari. He is a leading developer of amine grafted solid sorbents. According Holly Krutka of ADA, Prof. Sayari's sorbents is one of the best. ADA contracted a chemical synthesis company to synthesize few hundred pounds of the sorbents for pilot scale testing. Dr. Sayari believes capacity & kinetics both are important. Looks like some of his IP right are given to 'Carbon Capture Technology', small US company.

5. Gap Analysis

In order for carbon capture and storage schemes to be economically viable, development of highly efficient and economic CO_2 capture process of capturing CO_2 from fossil fuel based power plant flue gas streams is important today. As a result, there is an increasing interest in using less energy intensive processes, such as adsorption technique. From the foregoing discussions, it is obvious that solid sorbent based CO_2 adsorption is relatively new technology but post combustion CO_2 capture using solid sorbents holds great potential to overcome the huge energy penalties and capital cost associated with amine (e.g. MEA process) based regenerative absorption process for post combustion CO_2 capture. Amine functionalized solid sorbent has the most potential. It is also evident from the above discussion that all the identified sorbents are in early development stages, there are several parameters undetermined and not much work has been done so far to evaluate the sorbents to the small pilot plant scale. These parameters need to be determined for further evaluation of the potentials of these sorbents. In view of this, this section identifies the potential technology gaps; predominantly R&D gaps for impregnated amine sorbents for postcombustion CO_2 capture and recommends steps needed to close those gaps.

5.1 Gap Analysis for Potential Solid Sorbents

Table 14 assists to select the class of solid sorbent that has the most potential. ***Table 15*** listed some of the most promising amine functionalized solid sorbents. It can be seen from the ***Table 15***, most of the key parameters are available for TRI-Grafted PE-MCM-41. Its working capture capacity is considerably lower than ideal sorbent but it is demonstrated that it has a very good multi-cycle capability. In this case, one needs to study its synthesis process, its scalability and reproducibility in large scale with low cost. Followed by first order of manufacturing cost estimation, identify the process steps which can be improved or simplified. PEI Impregnated MCM-41 again has a considerably lower capture capacity, its regeneration energy is not known and it is only evaluated for 20 cycles. Since it is an impregnated amine, therefore, its synthesis is less complicated but we need to estimate the manufacturing cost. TEPA impregnated zeolite Y has a capture capacity above 4 and only been studied 20 cycles but its regeneration energy is shown to be 16.5% lower than that of ideal sorbent. TEPA Impregnated MCM-41 has capture capacity which is close to 80% of the ideal sorbent and TEPA impregnated PMMA capture capacity is 40% above the ideal sorbent. However, most of the other parameters are not available for these sorbents. Cycle time is another key parameter in determining the amount of sorbent needed for the capture and the foot print of the adsorption system. Diffusion distance and mass transfer rates play an important role. Therefore, cycle time can be improved by proper microstructure designing (nanoscale microstructural manipulation) of the sorbent. All sorbents list in ***Table 15*** have considerably high cycle time. This table clearly shows several parameters are not available which need to be determined and all of them synthesis procedure needs to be examined carefully to estimate a 1st order approximation of their cost.

Contactor/bed configuration is another very important area for the overall success of the solid sorbent system. To meet low pressure drop criteria, to reduce cycle time and footprint, and to maintain uniform bed temperature, efficient bed configuration is essential. The conventional configurations for contacting CO_2-laden flue gas streams with solid sorbents are fixed-bed, fluidized bed and moving bed. Fixed-bed contactor could not meet the constraints, required very large footprint. Due to some inherent advantages of the fluidized bed contactors, such as (i) excellent gas-solid contact due to vigorous agitation of sorbent particles, (ii) minimum diffusional resistance, (iii) uniformity of temperature, and (iv) faster overall kinetics, etc. over fixed bed contactors, fluidized bed contactors is likely to be superior to the fixed bed adsorber and requires relatively small footprint. However, fluidized bed requires robust mechanical properties due to high rate of sorbent attrition. Recently, new innovative bed configurations have been suggested by Inventys [216] (honeycomb bed where honeycomb itself is made of activated carbon sorbent), PNNL (porous metal based structured bed where porous metal separating gas flow channel from the solid sorbent) and University of Arkon (metal monolithic made of FeCr alloy and surface coated with solid sorbent) to overcome some of the problems associated with fluidized bed. These structure beds also have certain drawbacks. Manufacturing of honeycomb structure may not be possible using certain types of sorbents or replacement of sorbents with new generation sorbents may also face manufacturing challenges. However, these bed configurations are still in developing stage and need to be demonstrated its long term durability under actual flue gas conditions (e.g., high volumetric flow rate and cyclic thermal shock).

5.2 Major Gaps

Based on the above discussion, following key gaps are identified for solid sorbents based post combustion CO_2 capture process:

- Technology still at development stage
  - most of the data available in open literature are based on thermogravimetric analysis and small laboratory scale fixed bed reactor
  - regeneration time for most of the impregnated solid sorbents is still higher than 30 minutes
  - heat of regeneration data is not available
  - information like mass transfer and diffusional effects and particle-bed characteristics of solid sorbents are scarce
  - sorbent tolerance tests under reactive flue gas contaminants such as moisture and SO_x, NO_x are not demonstrated
  - sorbent stability and multi-cycle performance tests under various bed configurations are not reported
  - synthesis of impregnated/grafted solid sorbents is not still established for large scale application
- Techno-economic analysis for impregnated solid sorbents is not available
- Critical mass of technical personnel to support solid sorbent development activities is limited in Alberta
- Industry involvement to support technology developers for scale-up technologies to the pilot scale demonstration and ultimately full-scale commercial sizes using solid sorbent is still lacking.

5.3 Recommendation

Section 4.1 has shown that solid sorbents has potential to keep the cost of electricity increase within 30%. Therefore, adsorption process using solid sorbents is an important technology area for carbon capture and it is worthwhile to invest in this technology area.

From the above gap analysis, we suggest TRI-grafted PE-MCM-41, TEPA impregnated MCM-41 and zeolite Y are the potential solid sorbents which fulfills some of the key performance requirements of ideal solid sorbents.

TRI-grafted PE-MCM-41: This is one the most advanced and tested sorbent developed by Prof. Sayari's group, University of Ottawa. This has an acceptable working capacity together with good cyclic ability. However, bench scale study using this solid sorbent should be performed in actual flue gas condition. Special attention is also needed to improve the kinetics and cycle time by further modifying particulate morphology and using structure bed configuration. Appropriate design of structure bed may allow use of finer sorbent particle which in turns improve the adsorption/desorption kinetics of the sorbents. Here recommendation would be working in collaboration with Prof. Sayari to address the cost effective large scale synthesis of the sorbent, kinetics issues, further rigorous testing in actual flue gas condition and finally techno-economic analysis of the process using various bed configuration.

TEPA Impregnated MCM-41/Zeolite Y: These sorbents have high capacity. Impregnated Zeolite –Y sorbent has comparatively low heat of regeneration. Moreover, Zeolite-Y could be inexpensive substrate for impregnation. Here recommendation would be to take a systematic approach to initially synthesize this sorbent in lab scale and evaluate important characteristics of these sorbent. Once these characteristics are confirmed, more rigorous testing in bench scale should be performed using simulated/actual flue gas condition for long term stability and selectivity. In next step, address the sorbent manufacturing scalability issues and techno-economic feasibility of post combustion CO_2 capture process.

Once we complete above development to close the gap, sorbent will be ready for further evaluation in pilot scale.

The amount of support materials in a solid sorbent system varies from 40-70%, therefore, it is important to stress that inexpensive natural or easy manufacturable sorbent support will play a vital role in the economic viability of the solid sorbent system.

Other than the above recommendations, we also suggest systematic studies/development of various bed configurations to close the gap. Suitable bed configuration may provide more flexibility in the sorbent robustness requirement, finer sorbent particle or coating of sorbent and consequently provides opportunity to enhance the kinetics, reducing the footprint and sorbent requirement.

As discussed in ***Section 5.1***, honeycomb structure has the potential to overcome drawbacks of fluidized and packed bed. However, honeycomb structure may not be possible using certain types of sorbents or replacement of sorbents with new generation sorbents may also face manufacturing challenges. Therefore, honeycomb made of support material coated with solid sorbent may provide flexibility in the design and future technology upgrading. It is worth to mention that AITF from 2010 considering honeycomb type of structure (made of high thermal conductivity materials, e.g., Al, Mg, Fe or their alloys, AlN etc. and low thermal mass, since this combination will have good heat transfer and thermal cyclic ability) bed with a porous wall where alternate channel filled with solid sorbent. AITF's proposed configuration is similar to PNNL design. Presently AITF and University of Alberta are jointly considering monolithic honeycomb structure with unique feature for application in post combustion CO_2 capture application. This design concept may have a potential for protectable IP. Detail experimental and modelling work is also recommended for quick development of potential bed configuration. It is also recommended to collaborate with structure bed user like Inventys and developer like PNNL.

In summary followings are the key suggestions for closing the gap:

- Synthesis and micro-structural modification of the potential sorbents to reduce overall cycle time, improve working capacity, selectivity and multicycle durability under actual flue gas conditions
- Performance study of the potential sorbents in actual flue gas conditions using various bed configurations such as structured bed
- Detailed techno-economic analysis for different reactor configuration
- Active participation of Industries and leading developers

6. Conclusion

Improved cost effective processes for post combustion CO_2 capture from flue gas streams of fossil fuel based power plants are essential today in order to mitigate the global warming problem. Among several different process technologies, solid sorbents for CO_2 capture from flue gas is one of the promising options today. This study has identified several potential sorbents, technology gaps and technical approach to bridge the gaps to facilitate further development.

Activated carbon and zeolite based sorbents are low cost with fast adsorption kinetics and require low regeneration energy. However, their CO_2 capture capacity and selectivity is not in an acceptable range for post combustion CO_2 capture condition. On the other hand, MOFs as sorbents for post combustion CO_2 capture need more systematic research attention. The performance of this type of sorbent still remains to be established under actual flue gas conditions. It has been recognized that these materials also suffer in CO_2 uptake in the presence of moisture. Alkali carbonates such as sodium and potassium carbonates have reached pilot scale trials. But still these sorbent based systems have challenges such as high heat of reaction, slow kinetics and working capacity. Further development will be seriously impacted unless appropriate technological solutions are found to mitigate these issues.

The available literature data and information analysis indicate that a number of amine functionalized sorbents have shown promise to meet the desired working capture capacity target in simulated flue gas conditions. Analysis showed that the sorbents have theoretical regeneration energies significantly lower than that of the industry benchmark 30% MEA process. However, the long-term stability and consistent performance of these sorbents under flue gas conditions remains to be established through bench scale and pilot-scale studies before commercialization. Moreover, at this stage, from a design point of view, several important key characteristics, such as kinetic data for adsorption and desorption, mass transfer and diffusional effects, effects of flue gas contaminant, particle characteristics and other physicochemical properties of candidate sorbents are not available. Because of the lack of adequate data on solid sorbent performance in various contactor configurations, limited process design and economics analysis exists.

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Appendix I: Gap Analysis of Metal Organic Frameworks (MOFs) as Solid Sorbents for Post Combustion CO_2 Capture.

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Preamble: Metal organic frameworks are a relatively new class of porous solids that have received considerable attention as prospective gas storage and separation materials. This confidential report will provide an overview of the state of development of this broad class of materials regarding their potential for CO2 capture from flue gas streams. Rather than providing a broad summary of all existing work (accounts such as these are already in existence in the available literature), this report has been prepared as a more critical assessment of the technology. While there is abundant opportunity, it is also readily apparent that it is only very recently that the researchers in this field have begun to address the most crucial questions for real-world capture. That said, progress in this field has been rapid (it essentially began as an active field of study in the late 1990s). Much greater insight into the appropriate materials exists now, versus even three years ago, and options exist for making materials that could not be made by any other competing approach.

1. What MOFs are being developed around the world and by whom? What development stages and scale of testing are these solid sorbents at?

To begin, MOFs are crystalline networks of metal ions or metal ions clusters linked by organic molecules to form either neutral or charged frameworks that contain pores typically in the range from 0.05- 0.3 nm (Figure 1). They are also reported in the literature as porous coordination polymers (PCPs).

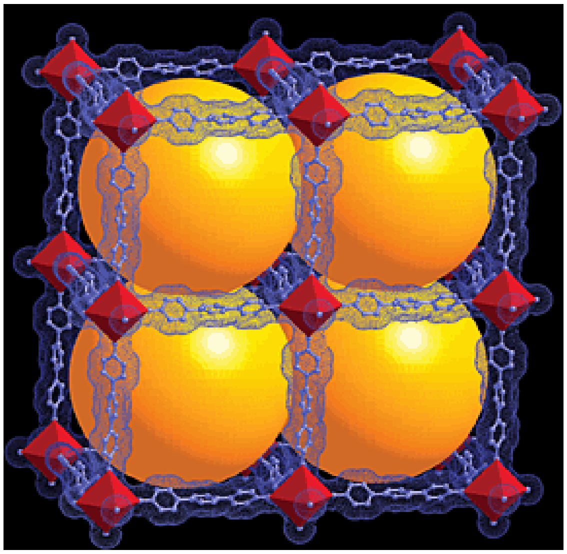

Figure 1. Representation of a porous MOF derived from single crystal X-ray diffraction data.

This shows a cubic structure where octahedral corners are formed Zn4O carboylate clusters and the spacers are triphenyl linkers. The yellow sphere represents the pore. From http://yaghi.chem.ucla.edu/gallery/

MOF chemistry has several appealing features for materials science with the hallmark features being:

i) Crystallinity. This equates to order and the ability to perform X-ray diffraction experiments to assess structure at a molecular level.

ii) Ease and modularity of synthesis. MOFs can be prepared often by simple precipitation reactions under the right conditions (solvents, temperature, and stoichiometries). The modularity of MOFs refers to the fact that often entire components can be exchanged in a systematic manner allowing for preparation of sequential members of a family.

iii) Porosity. This is the most notable feature of MOFs as they can have enormous internal surface areas.

iv) Design. The crystallinity and the modularity of MOFs converge to offer a sense of rational design of these materials versus “shake and bake” or “heat and beat” methods often employed for solid state science.

What MOFs are being developed?

The answer to this question is quite vast as the type of organic linker that can be incorporated in a MOF is literally limitless. Even restricting a researcher to commercially available linkers, with the range of metal ions, synthetic conditions, and combinations of linkers possible, the number of potential new MOFs is vast and ongoing research reflects that there is quite a bit of “low fruit.” That said, there are many publications where researchers have grown crystals of a “new MOF” with solvated pores and characterized the material exclusively by X-ray crystallography. It is quite possible that the pores in such a material would collapse upon removal of the included solvents rendering the material, for all intents and purposes, non-porous. Such manuscripts appear in very low calibre publications and report only the preparation and structural determination of the framework. In an attempt to provide a meaningful response to the above query, the materials considered for discussion will be restricted only to those that have demonstrated a CO2 sorption isotherm and true porosity.

Even with the above caveat, the ongoing research in CO2 capture in MOFs is expansive. Two recent review articles have provided comprehensive surveys of the literature on CO2 capture in MOFs.[1,2] A modified table of ambient pressure CO2 sorption in MOFs has been adapted from the more recent work (Table 1).[3-119] The type of components in MOFs have the following general similar characteristics: the organic linkers are able to bridge multiple metal centers and they typically have a rigid molecular structure (i.e. aryl groups versus alkyl groups); the linkers are often anionic as this both augments the strength of the interaction with the metal ions and also removes counter ions from any pores augmenting the porosity; they are readily accessible either commercially or by facile and high yielding synthetic procedures. By far, the most widely studied linkers are polycarboxylates as they address all the above criteria. Carboxylate linkers were employed in MOF-210, a MOF that presently has the highest surface area for any reported MOF at 6210 m^2/gm.[108] The next most widely employed would be anionic N-heterocycles such as imidazolates, triazolates. Neutral aromatic amine donors, such as polypyridines, are also widely used, often in conjunction with anionic linkers to maintain pores free of counter anions. The imidazolate MOFs, so-called zeolitic imidazolate frameworks (ZIFs), [120] have however been tested to be very stable. This class of MOFs is based on the fact that the N-donor atoms in the anionic imidazolate unit are situated at ~145°, a value comparable to the Si-O-Si angle in zeolites. Thus, it can be expected (and this has been largely verified, that MOF analogues of zeolites and indeed even more structures, could

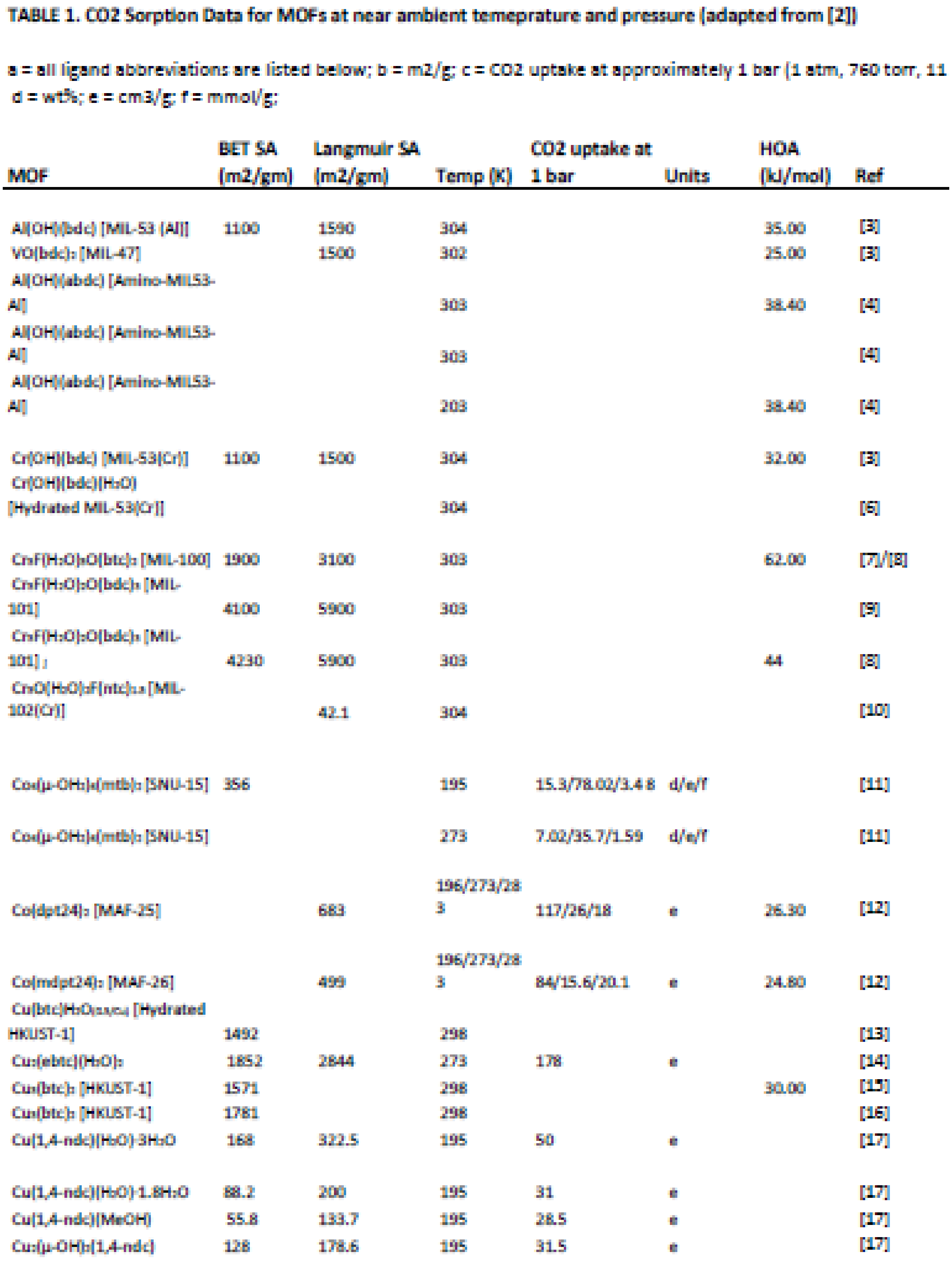

TABLE 1. CO2 Sorption Data for MOFs at near ambient temeprature and pressure (adapted from [2])

a = all ligand abbreviations are listed below; b = m2/g; c = CO2 uptake at approximately 1 bar (1 atm, 760 torr, 11
d = wt%; e = cm3/g; f = mmol/g;

MOF	BET SA (m2/gm)	Langmuir SA (m2/gm)	Temp (K)	CO2 uptake at 1 bar	Units	HOA (kJ/mol)	Ref
Al(OH)(bdc) [MIL-53 (Al)]	1100	1590	304			35.00	[3]
VO(bdc)$_2$ [MIL-47]		1500	302			25.00	[3]
Al(OH)(abdc) [Amino-MIL53-Al]			303			38.40	[4]
Al(OH)(abdc) [Amino-MIL53-Al]			303				[4]
Al(OH)(abdc) [Amino-MIL53-Al]			203			38.40	[4]
Cr(OH)(bdc) [MIL-53(Cr)]	1100	1500	304			32.00	[3]
Cr(OH)(bdc)(H_2O) [Hydrated MIL-53(Cr)]			304				[6]
$Cr_3F(H_2O)_2O(btc)_2$ [MIL-100]	1900	3100	303			62.00	[7]/[8]
$Cr_3F(H_2O)_2O(bdc)_3$ [MIL-101]	4100	5900	303				[9]
$Cr_3F(H_2O)_2O(bdc)_3$ [MIL-101]	4230	5900	303			44	[8]
$Cr_3O(H_2O)_2F(ntc)_{1.5}$ [MIL-102(Cr)]		42.1	304				[10]
$Co_4(\mu\text{-}OH_2)_4(mtb)_2$ [SNU-15]	356		195	15.3/78.02/3.4 8	d/e/f		[11]
$Co_4(\mu\text{-}OH_2)_4(mtb)_2$ [SNU-15]			273	7.02/35.7/1.59	d/e/f		[11]
Co(dpt24)$_2$ [MAF-25]		683	196/273/283	117/26/18	e	26.30	[12]
Co(mdpt24)$_2$ [MAF-26]		499	196/273/283	84/15.6/20.1	e	24.80	[12]
Cu(btc)H_2O[illegible] [Hydrated HKUST-1]	1492		298				[13]
$Cu_2(ebtc)(H_2O)_2$	1852	2844	273	178	e		[14]
$Cu_3(btc)_2$ [HKUST-1]	1571		298			30.00	[15]
$Cu_3(btc)_2$ [HKUST-1]	1781		298				[16]
Cu(1,4-ndc)(H_2O)·3H_2O	168	322.5	195	50	e		[17]
Cu(1,4-ndc)(H_2O)·1.8H_2O	88.2	200	195	31	e		[17]
Cu(1,4-ndc)(MeOH)	55.8	133.7	195	28.5	e		[17]
$Cu_2(\mu\text{-}OH)_2(1,4\text{-}ndc)$	128	178.6	195	31.5	e		[17]

$Cd_3(Tz)_6$	310	338					[18]
$Cu_3(Tz)_6$	232	282	195	49.7	e		[19]
$Cu(tpim)_{1.5}(OH)_{0.5}$	258	286	298	25.2	e		[20]
$Co_3(tmitb)_2$			295				[21]
$Co(dhtp)(H_2O)_2$ [MOF-74, CPO-27-Co]							[22]
Co/DOBDC	1080		296	11.7/30.6	d	37.00	[22]
$Mg(dhtp)(H_2O)_2$ [MOF-74Mg, CPO-27-Mg]	1542		278				[24]
Mg/DOBDC	1495	1905	296	23.6/35.2/63	d	47.00	[22]
$Mg_2(DOT)$ [Mg-MOF-74]				89	h	39.00	[23]
$Ni(dhtp)(H_2O)_2$ [MOF-74-Ni, CPO-27-Ni]	1218		278				[24]
Ni/DOBDC	1070		296	11.6/25.6	d	41.00	[22]
$Ni_2(dhtp)$	1083	1312	303[313/353]	11/22.5	d	40.00	[25]
Zn/DOBDC	816		296	5.8/24.4	d		[22]
MOF-74	816		298				[16]
$Cu_2(Hbtb)_2(H_2O)EtOH$	600		298				[26]
Cu(pydc)(bpp)	600.26		195	103	e	32.47	[27]
$Ni_2(dpze)(bptc)$		505	195	24.3/123.5/5.5	d/e/f		[28]
$Ni_2(dpze)(bptc)$			195	24.4/124.0/5.5 4	d/e/f		[28]
$Ni(cyclam)_2(mtb)$	141.2	154.2	195	11.2/2.53	d/f		[29]
$Zn_2(abtc)(DMF)_2$ [SNU-4]		1460	195	55.1	d		[30]
$Cu_2(abtc)(DMF)_2$ [SNU-5']		1260	195	53.8	d		[30]
$Cu_2(abtc)$ [SNU-5]		2850	195	112.3	d		[30]
$Cu_2(bpndc)_2(4,4'\text{-bipy})$ [SNU-6]	2590	2910	195	113.8/25.8	d/f		[31]
$Pd(H\text{-pymo})_2$	600		273	69	e	44	[32]
$Pd(F\text{-pymo})_2$	600		273	84	e	48.00	[32]
$Cu(F\text{-pymo})_2$			273	7.6	d	55.00	[33]
$Co(F\text{-pymo})_2$	300		273				[34]
$Zn(F\text{-pymo})_2$			273				[34]
$Cu_{24}(bxyb)_{12}(dmf)_6(H_2O)_{18}$	1840	2020	195	725	g/L		[35]
$Be_4O(bdc)_3$ [MOF-5-Be]	3500	4100	195	1600	h		[36]
Zn(pydc)(dma)			195	142	e		[37]
Zn(pydc)(dma)			273	37	e		[37]
$Cu(4,4'\text{-bipy})_2(BF_4)_2$			248/258/273	180/170/153	h		[38]
$Co_3(OH)_2(p\text{-cdc})_2DMF_2$	1080		273	100	e		[39]

Co(p-cdc)(py)$_2$(H$_2$O)	351		273	33	e		[39]
Zn$_3$(ntb)$_2$ [SNU-3]		419	195	6.75/159	f/g		[40]
Zn$_3$(ntb)$_2$ [SNU-3]			273	1.57/37	f/g		
PdNPs@[SNU-3]		242	195	151	e		[41]
Cu$_2$(cis -chdc)$_2$(bpee)		168	195	32.4	e		[42]
Cu$_2$(4,4'-bipy)$_{1.5}$(2,6-ndc)$_2$		113	195	11	d		[43]
Cu(bpe)$_{0.5}$(2,6-ndc)		337	195	13.2	d		[43]
Al(OH)(1,4-ndc)		546	195	138	e		[44]
Al(OH)(2,6-ndc)	1308	1996	303				[45]
Al(OH)(bpdc)	1613	2334					[45]
Zn$_2$(bdc)$_2$(dabco) [DMOF-1]	1450		195	409	e		[46]
Zn$_2$(abdc)$_2$(dabco) [DMOF-1-NH2]			195	338	e		[46]
Zn$_2$(am1)$_2$(dabco) [DMOF-1-AM1]			195	123	e		[46]
Zn$_2$(am2)$_2$(dabco) [DMOF-1-AM2]			195	233	e		[46]
Zn$_2$(am3)$_2$(dabco) [DMOF-1-AM3]			195	206	e		[46]
Zn$_2$(am4)$_2$(dabco) [DMOF-1-AM4]			195	187	e		[46]
Cu(4,4'-bipy)$_2$(OTf)$_2$	390		195	365	h		[47]
Co(4,4'-bipy)$_2$(OTf)$_2$	400		195	235	h		[47]
Ni$_2$:Ni$_3$(μ$_3$-OH)(pba)$_3$(ndc)$_{1.5}$ [MCF-19]	2667	2316	195	510	e		[48]
Zn$_2$(OH)(azpy)(bdc)$_{1.5}$	32		273	1.04			[49]
Zn$_4$O(fma)$_3$	1120	1618	300			16.10	[50]
Ni$_8$(5-bbdc)$_6$(μ$_3$-OH)$_4$ [MAMS-1]			195	91.175	e		[51]
Zn$_2$(H$_2$O)$_2$(bbpdc)$_2$ [MAMS-2]			195	83.974	e		[52]
Cu(etz)			195/273/298	126/49/19	e	26.60	[53]
Al$_4$(OH)$_8$(btec) [MIL-120]	308	432	303	3.15	f	37.50	[54]
[H$_3$O][Zn$_7$(μ$_3$ -OH)$_3$(bas)$_6$]		649	273	2	f		[55]
Cu$_2$(hbptb)(H$_2$O)$_2$		1217/*604 4		12.63	d		[56]
Cu$_3$(egbb)(H$_2$O)$_3$		*4186		6.36	d		[56]
Zn$_4$(μ$_4$-O)(hbptb)$_2$(hbptb-H$_2$)		*5712		6.08	d		[56]
Zn$_5$Na$_2$(egbb)$_2$(dmf)$_2$		*1307					[56]
[Cu(4,4'-bipy)(H$_2$O)$_2$(BF$_4$)$_2$](4,4'-bipy)			273	161	h		[57]

Ag$_2$(bpz)	240	280	195	79	e		[78]
CdNa(2-stp)(dabco)$_{0.5}$			195	92.6	e		[79]
H$_2$[Ni$_3$O(H$_2$O)$_3$(tatb)$_2$ [PCN-5]		225	195	4.8	f		[80]
Co$_3$(2,4-pdc)$_2$(μ$_3$-OH)$_2$	630		195	156	e		[81]
Zn$_4$O(adc)$_3$ [PCN-13]	150						[82]
Zn$_2$(ip)$_2$(4,4'-bipy)$_2$	300		195	58	e		[83]
Cd$_3$(OH)$_2$(apta)$_4$	210		195	67	e		[84]
Zn(pur)$_2$		800		7.4	h		[85]
Ni$_3$(OH)$_2$(1,4-cdc)$_2$		146	195	45	e		[86]
Mn(2,6-ndc)		191	195	13/71	f/g		[87]
Dy(btc)	655		273	189	e		[88]
[Cd(bbib)$_3$](ClO$_4$)$_2$	148	174	195	40	e		[89]
Co$_2$(ad)$_2$(CO$_2$CH$_3$)$_2$	1040		273/298	6.0/4.1	f	45.00	[90]
Cu$_2$(pzdc)$_2$dap			195	98	e		[91]
Cu$_2$(pzdc)$_2$azp			195	148	e		[91]
Mn(tcnq)$_2$(4,4'-bipy)			195	48	e		[92]
Zn(tcnq)$_2$(4,4'-bipy)			195	200	e		[92]
Cu(hbdc)	397	584	296	52	e	26.20	[93]
Cu(Hoxonic)(4,4'-bipy)$_{0.5}$			273				[94]
Cu$_2$(pzdc)$_2$(4,4'-bipy) [CPL-2]	633		298	6.5/1.6	d/f	18.6-21.5	[95]
Ca[Co(en)(ox)$_2$]$_2$			298	14	d		[96]
Cu-bdc		241	u	17.5	e		[97]
Cr-bdc		404	u	48.5	e		[97]
Fe(Tp)(CN)$_3$]$_2$[Co]	154		298	15.9	e	12.50	[98]
LiZn(btc)	725	962	195	174	e		[99]
Sm(ntb)Cl$_3$-mon			298	13.6	e		[100]
Sm(ntb)Cl$_3$-hex			298	45.1	e		[100]
Zn(mial)$_2$	802		253/298/343	109/48/21	e		[101]
Zn$_2$(btdc)$_2$(4,4'-bipy) (3-int)			195	55	e		[102]
Zn$_2$(btdc)$_2$(4,4'-bipy) (2-int)			195	201	e		[102]
Zn(dabco)$_{0.5}$(dctp)			195	69.6/3.10	e/f	76.80	[103]
Zn$_4$(bhfp)$_{10}$	378		298	4.5	d		[104]
Zn$_2$(BPnDC)$_2$(4,4'-bipy) [SNU-9]	824	1034	195	43.0/219	d/e		[105]
Zn$_2$(bdc)$_2$ [MOF-2]	345		298				[16]
Cu$_2$(bptc)$_3$ [MOF-505]	1547		298				[16]
Zn(bdc)(4,4'-bipy)$_{0.5}$ [MOF-508b]			303				[106]
Zn$_4$O(abdc)$_3$ [IRMOF-11]	2096		298				[16]
Zn$_4$O(abdc)$_3$ [IRMOF-3]	2160		298				[16]

$Zn_4O(C_2H_4\text{-}bdc)_3$ [IRMOF-6]	2516		298				[16]
$Zn_4O(btb)_2$ [MOF-177]	4508		298				[16]
$Zn_4O(bdc)_3$ [MOF-5, IRMOF-1]	3800	4400	298				[16]
MOF5-EHI			298	37	g		[107]
MOF5-EI			298	23	g		[107]
$Zn_4O(bte)_2$ [MOF-180]			298				[108]
$Zn_4O(bbc)_2$ [MOF-200]	4530	10400	298				[108]
$Zn_4O(btb)_{4/3}(ndc)$ [MOF-205]	4460	6170	298				[108]
$Zn_4O(bte)_{4/3}(bpdc)$ [MOF-210]	6240	10400	298				[108]
$Zn_4O(bdc)(btb)_{4/3}$ [UMCM-1]	4160	4730/6500					[109]
$Zn_4O(bdc)(btb)_{4/3}$ [UMCM-1]	4100		298/313/338			14.9	[110]
$Zn(mim)_2$ nano-ZIF-8	1264	0.51		7.9	f		[111]
Zn(bim)(nim) [ZIF-68]	1090		298	39.9/37.6	g/e		[112]
Zn(cbim)(nim) [ZIF-69]	950		298	49.2/40.6	g/e		[112]
$Zn(im)_{1.13}(nim)_{0.87}$ [ZIF-70]	1730		298	45.4/55.0	g/e		[112]
Zn(nbim)(nim) [ZIF-78]	620		298	60.2/51.5	g/e		[112]
Zn(cbim)(nim) [ZIF-69]	810		298	36.1/33.5	g/e		[112]
Zn(bbim)(nim) [ZIF-81]	760		298	49.3/38.2	g/e		[112]
Zn(cnim)(nim) [ZIF-82]	1300		298	49.3/52.7	g/e		[112]
ZIF-95	1050		298	19.2/19.7	g/e		[113]
ZIF-100	595		273	28.2/32.6	g/e		[113]
$Zn_2(tcpb)(dpg)$	740		273	64	e		[114]
$Zn_{3.68}Co_{0.32}O(bdc)_3$		2900	273				[115]
$Zn_{3.16}Co_{0.84}O(bdc)_3$		2900	273				[115]
$Zn_2(bttb)(dpni)$			273	86	e		[116]
$Zn_2(bttb)(dpni)$			298	26.5	e		[116]
$Zn_2(bttb)$	1370		273	129	e		[117]
$Zn_2(bttb)(py\text{-}CF3)_2$	390		273	36	e		[117]
$[Zn_8(ad)_4(bpdc)_6O](dma)$	1680		273/313	3.41/1.25	f		[118]
$[Zn_8(ad)_4(bpdc)_6O](tma)$	1460		273/313	4.46/1.63	f		[118]
$[Zn_8(ad)_4(bpdc)_6O](tea)$	1220		273/313	4.16/1.66	f		[118]
$[Zn_8(ad)_4(bpdc)_6O](tba)$	830		273/313	3.44/1.36	f		[118]
$Zn_4(\mu_3\text{-}O_2C)_4(tpa)$			298	3.96/.899	d/f		[119]

Ligand abbreviation for MOFs: H2abdc = 2-amino-1,4-benzenedicarboxylic acid; H2abtc = 1,1ˊ-azobenzene-3,3',5,5'-tetracarboxylic acid; ad = adinate; adc = 9,10-anthracenedicarboxylate; AM1 = 2-acetamido-1,4-benzenedicarboxylate; H2am2 = 2-

be formed with topologies akin to zeolites but larger pores. ZIF-8 and ZIF-69 are particularly interesting for CO2 capture in industrial settings as they have been demonstrated to maintain their crystal structure in harsh environments such as boiling water, boiling benzene, and supercritical CO2.[121,122] The groups of Long and Yaghi have robotic equipment for the preparation of new ZIF materials.

A key point in assessing the viability of MOFs for CO2 capture is that a given MOF will be much more suited for sorption of a given gas under a given set of conditions. Each gas separation poses its own challenges and no one MOF is better in all regards than all others. This statement is made due to the fact that certain MOF materials are simply more celebrated often based on surface area or pore volume. Unfortunately, the largest surface area MOFs, while they have high capacity, show low uptake for CO2 at the low partial pressures that would be found in flue gas. A relatively small amount of work (<12 papers) has been reported on polymer composite MOFs for gas separations. These materials incorporate the MOF into a polymer matrix and will be discussed later in this report.

By whom?

The majority of research in this area is being conducted in university laboratories. The largest (and most prolific) MOF research groups in the world are (in no particular order): Omar Yaghi (UCLA, USA); Susumu Kitagawa (U. Kyoto, Japan), Gerard Ferey (U. Versailles-San Quentin, France); Jeffrey Long (UC-Berkeley); Joseph Hupp (Northwestern U., USA); Hongcai (Joe) Zhou (Texas A&M U., USA), Matthew Rosseinsky (U. Liverpool, U.K.). Yaghi actually coined the term “MOF” for this family of compounds. Presently, the International Union of Pure and Applied Chemistry (IUPAC) is seeking to formalize the class of compounds that fit this moniker versus “coordination polymer” or “coordination polymer network.” Thomson Reuters, based on citation data, in 2010 predicted Laureates by Nobel Prize category (http://www.prnewswire.com/news-releases/thomson-reuters-predicts-nobel-laureates-103420389.html). Their analysis was that if a Nobel Prize were awarded in MOF science, it would go to Yaghi and Kitagawa. In Canada, the MOF/coordination polymer groups are: George Shimizu (U.Calgary), Daniel Leznoff (Simon Fraser), Stephen Loeb (U. Windsor), James Wuest (U. Montreal), Muralee Muragescu (U. Ottawa) Dmitri Soldatov (U. Guelph) and Richard Puddephatt (U. Western Ontario). Amongst these groups, the Shimizu and Soldatov are the only groups that have studied gas sorption.

Through the Advanced Research Projects Agency (ARPA) of the US government, the program IMPACCT, Innovative Materials & Processes for Advanced Carbon Capture Technologies, funds three carbon capture projects which involve MOFs. These are: High-Throughput Discovery of Robust Metal-Organic Frameworks for CO2 Capture (J. Long, PI); Stimuli-Responsive Metal-Organic Frameworks for Energy-Efficient Post-Combustion Carbon Dioxide Capture (H. Zhou, PI) and; High Performance MOF-polymer Composite Membranes for CO2 Capture (David Sholl, Georgia Tech, PI). In 2006, the US DOE funded ($2M) a project headed by UOP LLC (Richard Willis, PI) in collaboration with the Universities of Michigan, Edinburgh, Vanderbilt, and Northwestern to prepare a lab-scale CO2 capture apparatus with simulated flue gas. In the last year, some results from this project (vide infra) have emerged.

BASF has scaled up MOF synthesis and, under the trade name Basolite, is selling five different MOFs through Aldrich Chemicals. News articles have referred to MOF research ongoing at Shell and Exxon Mobil but specifics are not available. This is likely applying existing MOFs rather than making new materials. The Norwegian company, SINTEF, is very active in CO2 capture including MOF research (Richard Blom). Undoubtedly, based on the number of graduates from MOF groups moving to industry, the trend of MOF research in industry will grow significantly in the next few years. There is also research ongoing on MOFs, largely computational, at the US federal labs, Sandia National Laboratories (Mark Allendorf) and Pacific Northwest Laboratories (Praveen Thallapally).

What development stages and scale of testing are these solid sorbents at?

MOF Adsorbents for PSA/TSA

The sequence of study for a MOF material being developed as a flue gas CO2 capture material would involve the following: 1) Synthesis of the MOF; 2) Structural characterization of the MOF in crystalline form and as a bulk material; 3) Characterization of stability of the MOF/structural retention in the absence of guest molecules; 4) Characterization of porosity via sorption of different pure gases (selectivity inferred from comparisons of pure isotherms); 5) Competitive sorption experiments with gas mixtures including water vapour; 6) Scale up of preparation; 7) Testing of performance on flue gas slip stream.

With respect to the overall state of development of MOFs for CO2 capture from flue gas, ten years ago, it was quite common to have access to the necessary infrastructure to prepare and structurally characterize MOFs but relatively few research teams housed the full suite of infrastructure (powder X-ray diffraction, gas sorption) to assess porosity (i.e. up to step 4 above). In the past 5 years, more and more groups have gained access to gas sorption equipment and the standard for required studies to publish in a good journal has increased. A search for publications on “CO2 adsorption and/or separation in MOFs” per year on the ISI Web of Knowledge, shows as few as 10 publications in 2006, increasing to 42 in 2008 and 90 in 2010.The focus of these studies has largely been showing high pore volumes and high surface areas based on gas sorption as well as making new MOFs with different components. Typical volumetric gas sorption equipment will not allow competitive studies to be undertaken. In these cases, selectivity for sorption is extracted/inferred by taking the ratios of the Henry’s law constants (slope of the isotherm at low P) for different gases, or by applying the Ideal Adsorbed Solution Theory (IAST), to compare single component isotherms. Much of the focus on MOFs, with respect to CO2 and other gases has been on capacity. Millward and Yaghi[16] studied saturated CO2 capacities at room temperature and 42 bar for 10 MOF materials. Their saturated CO2 capacities are generally larger than those of traditional zeolites mainly due to larger surface areas and pore volumes of the MOF materials. Cavenati et al.[123] also reported CO2 adsorption in HKUST-1 from 30 to 100 ˚C and up to about 50 bar and found that the CO2 isotherms for HKUST-1 have only small nonlinearity below 4 bar. In addition, the CO2 adsorption processes in most MOF materials are fully reversible, which is desirable for pressure swing adsorption. However, because the CO2 partial pressures in flue gases are well under 1 bar, it is of greater importance to understand CO2 adsorption in MOF materials at low pressures, in competition with N2 and O2, and in the presence of water vapour and NOx and SOx gases. The past two years have seen more reports of competitive gas sorption experiments and studies done on CO2 sorption as a function of humidity. A summary of the leading recent works follows.

Stemming from the UOP-DOE funded project, in 2009, Snurr et al. reported that the MOF, HKUST-1, showed enhanced CO2 uptake in the presence of 4% water.[124] This MOF possesses sites where water is coordinated to copper centres and, upon activation, the water is removed. Essentially, the work showed that the MOF where water refilled these sites was better for CO2 than the equivalent MOF with the site on copper empty. It was recognized that this did not translate to better uptake of CO2 in the presence of higher degrees of hydration. A more thorough follow-up to this work by LeVan et al. in 2010 examined the Ni-analogue of MOF-74 and HKUST-1 for CO2 sorption in humid atmospheres.[125] Figure 2 shows the results of CO2 sorption experiments performed for both MOFs at ambient temperature and different degrees of hydration. The results clearly show a loss of CO2 sorption ability with increasing moisture content in the MOF but these results require context.

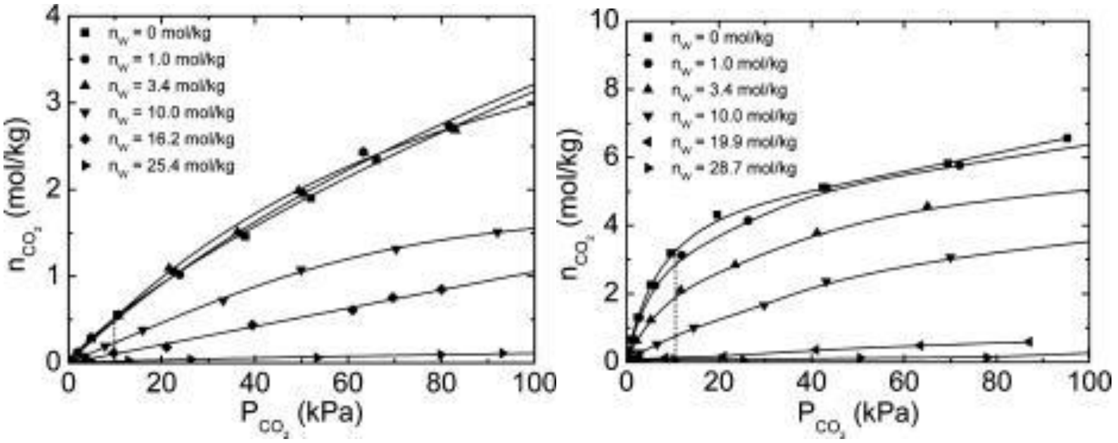

Figure 2. Left CO2 sorption at varying hydration at 25˚C for HKUST-1 (left) and Ni-MOF-74 (right). Both show a trend of decreasing uptake with humidity but the uptake is not lost completely until higher humidity levels.

In terms of their hydration dependent performance relative to zeolite materials, the MOF materials, particularly Ni-MOF-74(aka NiDOBDC) showed promising performance. The two MOFs chosen are both materials with very high surface areas and have reported high heats of adsorption for CO2. Another common feature of the two materials is that they both offer hydrated sites on the metal centres (Ni and Cu) which can be removed to generate the high affinity binding sites. While these sites would be the preferred site of interaction for CO2 molecules, they would have an even stronger affinity for water. Finally, these two materials are among the easiest MOF materials to prepare.

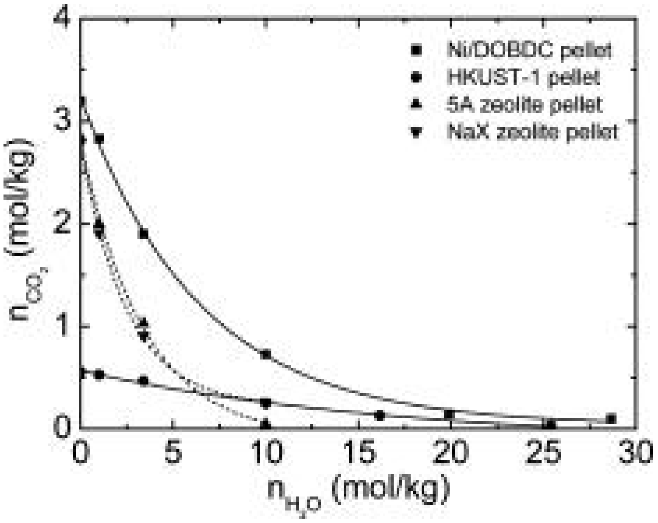

Figure 3. CO2 uptake at 0.1 atm partial pressure of CO2 (comparable to flue gas) at 25˚C and various levels of moisture content in the MOF. The Ni-DOBDC material shows higher capacity than the zeolites at higher humidity.

For the Ni-MOF74 material, high CO2 capacities (3.28mol/ kg) were found at a point of interest for flue gas application (25 ˚C, 0.1 atm CO2 partial pressure). Ni-MOF74 has a higher CO2 capacity than benchmark zeolites (5A and NaX) under these conditions. Adsorbed water vapour impacted CO2 adsorption in the MOFs but not nearly as much as on 5A and NaX zeolites. Importantly, adsorbed water was more easily removed from the MOFs by regeneration than in the zeolites, not surprising given the less hydrophilic nature of the MOFs. Most importantly, Ni/DOBDC was found to retain substantial CO2 capacity with moderate H2O loadings. This team also studied the effect of hydration on the stability of the MOF. The HKUST-1 sample showed increasing degradation over 7 runs but the Ni-MOF74 material showed higher stability over 10 runs (Figure 4).

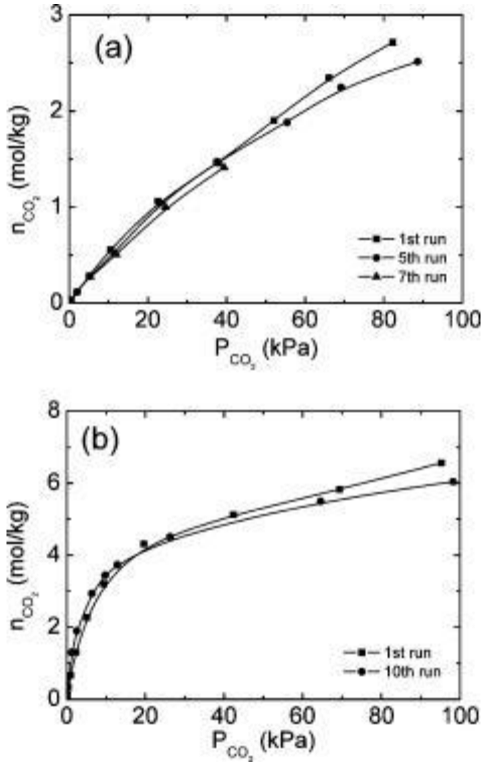

Figure 4. CO2 isotherms at 25 ˚C for MOF samples at different stages: (a) HKUST-1 pellet and (b) Ni-MOF74 pellet.

The authors concluded, “Considering the less intensive regeneration processes compared with benchmark zeolites and its hydrothermal stability, Ni/DOBDC may have a promising future for capturing CO2 from flue gases.” Certainly for low moisture coals or natural gas, there is potential. This report represents the first thorough study of CO2 capture by MOFs with water as a co-adsorbent and it appeared in late 2010. Since most of this research is ongoing in academic labs, the access to the necessary infrastructure is an issue for many researchers. The Sholl review, [1] published in early 2010, in stating future challenges for MOFs for carbon capture stated, “By far the most critical issue is, to paraphrase Coleridge’s Ancient Mariner, *water, water everywhere, but not a drop of data*.” More work is needed and ongoing in respect to CO2 sorption in water vapour but existing data shows promise.

To provide an assessment of the state of the development of MOF science, a fair statement would be that **much more progress has been made in terms of understanding what makes a good flue gas CO2 capture material than has been realized experimentally**. Much of the initial effort on MOF materials was focussed on capacity for storing hydrogen gas for automotive fuel cell applications; the challenges for CO2 capture are dramatically different and many of the CO2 sorption studies are being carried out on materials that were initially conceived for H2 storage. Major advances in modelling the expected sorption properties of MOF materials have been made. This has been established as highly useful for explanatory purposes in understanding why a particular MOF does or does not perform as expected. However, the major advantage will come in the form of predictive potential of computer modelling. The UOP-DOE project led to a publication in 2009 that compared the CO2 uptake at 0.1 bar of 14 MOFs generally touted as amongst the most promising MOFs for CO2 capture.[126] Figure 5 shows the correlation between the observed and simulated CO2 uptake values for the 14 MOFs.

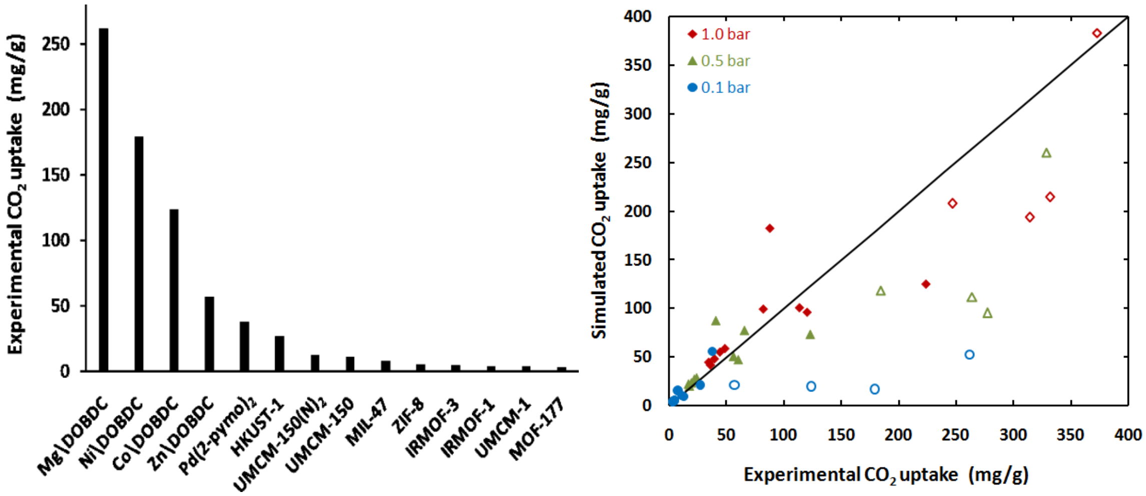

Figure 5. (Left) The experimental CO2 uptake of 14 MOFs and (right) a comparison of the observed CO2 uptake and that from computational simulation.

Beyond the calibration of the computational methods, the authors attempted to draw correlations between the structural features of the MOFs and the low pressure CO2 uptake. These intriguing results are shown in Figure 6.

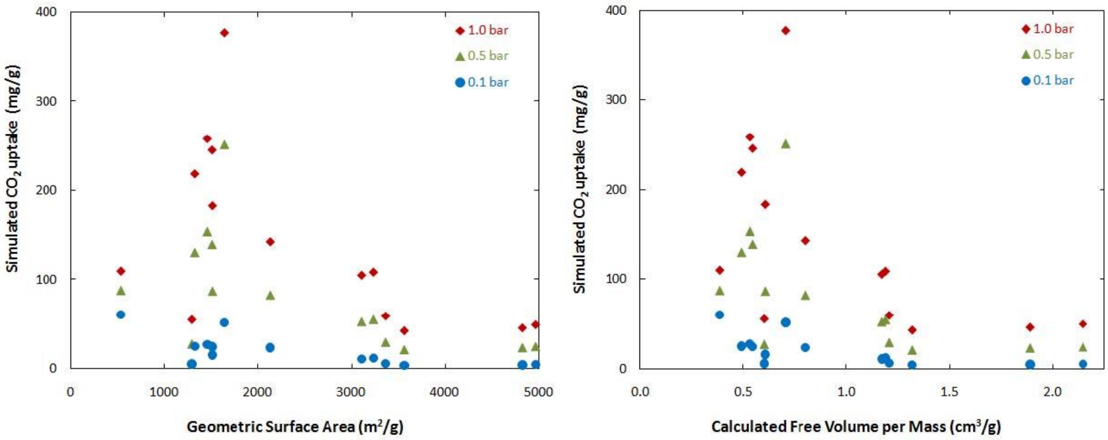

Figure 6. (Left) Geometric surface area and simulated CO2 uptake in screened MOFs and (right) geometric free volume and simulated CO2 uptake in screened MOFs. Both sets of data are shown at 0.1 bar, 0.5 bar and 1 bar. Data were obtained at temperatures that ranged from 293 K to 298 K. No correlation is observed between CO2 uptake and MOF surface area or between CO2 uptake and MOF free volume at these pressures.

From other computational modelling of MOFs, the following trends are observed with respect to targeting a gas sorption process: at low pressures, uptake in different MOFs correlates with the heat of adsorption; at intermediate pressures, uptake correlates with the MOF surface area; and at the highest pressures, uptake correlates with the free volume available within the MOFs.[127] Therefore, one key factor for CO2 uptake at low pressure is a reasonably high heat of adsorption. At the San Francisco American Chemical Society Meeting in 2010, Omar Yaghi stated that the ideal range for this value was 38-40 kJ/mol in that this value would enable good capture but also not be excessively high such that release of the CO2 is energy intensive. This statement apparently stemmed from a computational collaboration. **An important point is that the heats of adsorption reported in Table 1 are for the heat of adsorption at zero-loading (i.e. the value for interaction of CO2 with the most favoured sites). For efficient capture, the heat of adsorption should be sustained over the range of CO2 loading**.

In a recent work by Vaidhyanathan et al. [128] the exact locations of CO2 binding in a MOF with amine lined pores were determined via X-ray crystallography. This MOF showed a sustained heat of adsorption near 40 kJ/mol over the range of loading but it demonstrated modest capacity. This data served to validate a suite of computational methods, specifically the REPEAT method for assigning partial atomic charges to atoms in a MOF, developed by Woo et al. [129] Beyond simulating isotherms, this work showed, with high precision that the Grand Canonical Monte Carlo methods typically employed, when applied to highly accurate potential model, can extract the exact binding locations of CO2 molecules. The authors went one level further and extracted the contributions to the binding energy of CO2 of each individual contact that surrounded the CO2 molecules. While, at this stage, the findings do represent an academic result, the implications for understanding the binding of CO2 are profound. Asides from the validation of the computational methods, perhaps the most significant result from this work was the finding that the fact that the MOF in question bound CO2 as T-shaped dimers (an orientation that optimizes the quadrupole moments between the CO2 molecules) was as significant as the electrostatic contribution of the amines to CO2 binding. This joint experimental and modelling study confirmed that the cooperative binding interaction between the CO2 molecules was the reason for the high heat of adsorption over the full loading range. Capacity for CO2 and high heat of adsorption over the entire range of loading are often incompatible as only the CO2 binding sites immediately adjacent the pore wall (first monolayer), experience the full polarizing effect of the surface.

Given the fact that some of the most critical questions have only just begun to be addressed experimentally, it is perhaps not surprising that no accounts of any large scale testing of MOFs for CO2 capture from flue gas were found including the patent literature. Inventys Technologies in Burnaby, BC, builds new prototypes for gas separation apparatus. They do not develop sorbents but more energy efficient configurations for the use of good sorbents. They also model gas separations based on the sorption isotherms of pure gases with the known sorbents in virtual configurations. The Shimizu group has signed a non-disclosure agreement with Inventys and Shimizu will be visiting in February.

Apart from the potential MOFs mentioned above, MOFs offer some extraordinary prospects for gas separation distinct from any metal oxide solid sorbent. Some MOFs can shift structure, and hence gas storage properties, in response to external stimuli such as pressure[130] or temperature. [131,132] There are stimuli-responsive MOFs whose structures, thereby properties, change reversibly upon external stimuli such as temperature[130,131] and gas adsorption.[132] This offers unique opportunities for gas separation including CO2 capture by controlling gas diffusion/adsorption properties. For flue gas capture, the "pressure gating" options are likely not so viable but a MOF that changes structure with temperature could translate to a significant energy savings in a pressure/temperature swing adsorption process if the two forms of the MOF had substantially different sorption properties. This is a field of study in relative infancy.

MOF Membranes and Polymer Composite Membranes

Another aspect of MOF research that is also in its infancy is the field of polymer composites. This area of research is more amenable to membrane separations. As discussed, adsorption and adsorptive separation processes for CO2 capture, are based on differences in the affinities of gases for the surfaces (heat of adsorption, an exclusively thermodynamic quantity. Membrane separation relies on not thermodynamics but also of differences in diffusivity (kinetics), thereby potentially achieving higher selectivity for a given separation. Other advantages for membrane-based gas separation are that it involves no moving parts, making it energy efficient, it is a continuous process, making membrane modules a more attractive option for plant retrofitting.[133]

Polymer membranes for CO2 separation have a few distinct advantages over other materials (low cost, high diffusivity and flux) however, they also suffer from low CO2/N2 selectivity (less than 100). For membrane-based separation to be economically viable, the CO2/N2 selectivity has to be in the range of 200 .[134] Zeolites have also been studied and despite the potential of these materials for molecular sieve membranes, zeolites are limited for use in CO2/N2 separation due to the similarity of the kinetic diameters of CO2 (3.3 Å) and N2 (3.6 Å) and the limited pore sizes available for zeolites.[135] Mixed matrix membranes (MMMs) consist of a continuous phase (polymer) and a homogeneously distributed discrete phase (typically inorganic particles). The purpose of including inorganic particles is to marry the strengths of two different materials (e.g. the flexibility and low cost of the polymer phase with the high selectivity of the filler phase). Despite the progress made with traditional materials as membranes for CO2 capture, challenges such as insufficient CO2/N2 selectivity and low CO2 permeability remain and MOFs have been examined only to a small extent in this regard.

Pure MOF-based membrane for gas separation is an emerging field with only a few reports that include gas permeation data available to date,[136-148] only one of which specifically discusses the membrane's potential for CO2 capture.[143] As a pure MOF membrane, recent results have only examined CO2/N2 selectivities in non-competitive experiments. With ZIF-7 [142] and ZIF-22[145] but in neither of these cases was any selectivity for CO2 shown. When contemplating potential MOFs to investigate for CO2 capture membranes, many properties in addition to CO2 adsorption affinity must be considered, such as pore size, pore structure, stability in humid environments, and thermal stability. Choosing a MOF with the appropriate pore size to differentiate gases is not as straightforward as it may seem since the framework structure of MOFs used in MOF membranes has been observed to be rather flexible. The results with ZIF-7 and ZIF-22, (both with pore aperture size of 3.0 Å) indicated that even relatively large molecules, such as CH4 (3.8 Å) can still appreciably permeate through the membrane, implying that it may be worthwhile to pursue MOFs with even smaller apertures.

With respect to MOF polymer composites, challenges associated with MOF membrane fabrication such as poor substrate-MOF interaction, moisture instability, and easy microscopic crack formation present hurdles. These challenges can mainly be attributed to the weakness of the coordination bond in the MOF structure and so more robust MOFs are desirable. MOF composite membranes can be prepared by either growing the MOF crystallites in the polymer matrix or embedding the pre-grown MOF into the polymer. Mixed matrix membranes using MOFs as the filler material is also a new area of research and there are also only a very few reports available.[148-153] Koros and coworkers [150] reported a composite membrane comprised of poly(vinyl acetate) (PVAc) and a MOF composed of copper and terephthalic acid (Cu-TPA). This membrane exhibited increased selectivity for many gases, including CO2 upon inclusion of the MOF compared to the pure PVAc membrane. The ideal selectivity of pure PVAc for CO2/N2 is ~32 and for 15% CuTPA-PVAc is ~35. Musselman and coworkers[151] reported the first ZIF-based polymer composite using ZIF-8 as the filler phase and Matrimid as the polymer phase. Inclusion of the ZIF phase had substantial impact on the membrane selectivity. Pure Matrimid exhibited an ideal selectivity for CO2/CH4 of ~43, and at 50% loading of ZIF crystals the ideal selectivity increased to ~124.

What are the key requirements of a MOFs system for post-combustion CO_2 at a scale of 1000 t/CO_2/day?

The following approximation is highly dependent on the cycling time for a pressure swing adsorption cycle. Much research is ongoing to optimize configurations (e.g. hollow fibres where flue gas flows into the fibre and CO2 passes through to the outside of the cylinders-AITF in past work in this area) and cycling times as short as 20 seconds are reported. For this ensuing calculation, a 1 minute cycle time is assumed.

To process 1000 metric tonnes of CO2 each day, if a MOF could capture 4 mol CO2/kg in the flue gas stream then, for 1440 cycles a day, ~4 (3.95) metric tonnes of MOF would be required.

The above number takes a very attainable value of 4 mol/kg of MOF in a flue gas stream (cf. Mg-MOF74 at 1 atm takes up 8 mol CO2/kg). NiDOBDC takes up 3.2 mol CO2/kg at 0.1 atm when loaded with 1 mol/kg of water and 2.1 mol/kg when loaded with 3.4 mol/kg of water. **The best MOF sorbent has yet to be made**.

For 200 tCO_2/d for natural gas turbine flue gas streams, the challenge would be slightly different in that the CO2 concentration would be even lower increasing the challenge. However, the moisture content of the flue gas stream would also be lower making capture easier. As a direct comparison to the calculation above, to capture 200 tCO2/d would require 0.8 t of the same MOF with a capacity of 4 mol CO2/kg. The target of 4 mol CO2/kg will be easier to reach in the case of the natural gas stream owing to humidity levels roughly 1/3 of that in a coal-fired flue gas stream. Exact numbers based on simultaneous capture from a humidified CO2 stream are not yet available for any MOF system. Liu et al. [125] presents data based on pre-humidified MOF samples but gives important benchmark numbers.

Based on the available literature and my personal expertise, the key features required in a MOF for efficient CO2 capture from flue gas are:

1) A three-dimensionally porous structure to allow facile diffusion of CO2 into and out of the solid's interior.
2) A heat of adsorption in the range of 35-45 kJ/mol importantly sustained over the entire range of CO2 loading.
3) Pores in the range of the 10-15 angstroms would allow a compromise between capacity and cooperative CO2 interactions enabling a high heat of adsorption. The shape of the pores will be critical and ideal if they can fit higher aggregates of CO2.
4) Related to point 3, the isotherm would ideally be linear on the diagonal as this would be a good compromise between uptake and facile release.
5) The MOF must have high hydrolytic stability. In this regard, it is very unlikely that any of the Zn4O carboxylate cluster based MOFs will be suitable. Phosphonate groups can form more stable MOFs but these also tend to be less crystalline. The Shimizu group has recently filed a technology disclosure on a new family of linkers that give much greater water stability
6) The MOF must show CO2 uptake in the presence of 15% water vapour for coal flue gas and 5-8% for natural gas flue gas.
7) The MOF should have a preparation and cost amenable to large scale production. The range of cost of organic linkers in MOFs is not at all prohibitive as many are, even at lab-scale purchase prices, very cheap.

Does any MOFs currently being developed have the potential to meet the requirements?

The answer to this question is highly dependent on the PSA configuration and what cycling times are possible as well as simply how much MOF material as sorbent is considered acceptable. With present numbers and a 1 minute PSA cycle (based on the limited testing under anything resembling flue gas conditions) the best present candidate would be Ni-MOF74 and it would require 5 t of sorbent to capture 1000 t CO2/day. For a commercial configuration, its CO2 uptake in the presence of water vapour would need to be improved and possibly its durability. A key point is that MOFs exist that address all the criteria above. Presently though, a single material that merges all features does not exist.

Will a MOFs sorbents separator be competitive to amine-based processes for post-combustion CO_2 capture? In an ideal case, what could the improvement be over the amine-based processes in terms of capital cost, operation cost, and parasitic energy requirement?

The answer to this is a strong yes. The 40 kJ/mol range of physisorption of CO2 in a MOF is much less than the ~100kJ/mol bond strength of the CO2 interaction in an amine solution. To release the CO2 would require under half the energy. Moreover, a key difference with a solid sorbent versus amine scrubbing is that with amine scrubbing, in addition to a more strongly bound CO2 molecule, the entire aqueous solution of the amine must also be heated (water has a very high specific heat capacity). As mentioned above, much research is ongoing into new configurations for PSA processes that are faster and more energy efficient. This is Inventys Inc.'s core business. From my personal experience, it seems much of the generalizations on solid sorbents taking up water and having high energies of regeneration are based exclusively on zeolites. Virtually all MOFs release guests more easily than zeolites.

What are the gaps from the best available MOFs absorbent today to the "ideal" solid absorbent?

As mentioned above, based on available testing, Ni-MOF74 probably is the best MOF for flue gas capture right now. This MOF has "bare" metal sites which act as high affinity sites for CO2. However, the heat of adsorption drops after the first layer of CO2 is adsorbed. No MOF has been designed to load higher aggregates of CO2 and exploit cooperative CO2-CO2 interactions. Thus, the most important gap is still in the advances that can be made in basic research. A second prominent gap is between the lab scale study of a promising material and the ability to study the MOF for capture from a flue gas stream. As mentioned, the only work with thorough studies appeared late in 2010[125] from a consortium of industry and four universities. The breakthrough to be made is still with regards to better materials.

What needs to be done to close the gap? Time required to close the gap?

Given that rapid progress is being made in making better MOFs and in engineering new PSA configurations, continued forward progress requires facilitating means of doing the most critical experiments with the most promising materials. Present research is not at the stage where investments in scale-up are a pressing need. More important are funds to enable the necessary infrastructure for primary researchers and funds to enable/encourage industrial collaborations (from both sides). The time required to close the gap I would project as three years to have the "best" material in hand and another two years to have it scaled up and tested in different pressure swing adsorption configurations.

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Appendix II. Post Combustion CO2 Capture Using Amines

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1. Introduction

The post combustion flue gas streams typically contain 3 – 15% CO_2, for example.

- The composition of the exhaust stream from a gas turbine – 3.3% CO_2, 76.4% N_2, 14.3% O_2, 6% H_2O, 10 ppm NO_x at 130°C and 120 kPa;
- Flue gas from a coal fired power plant burning Alberta Plain coal and no desulfurization – 13.34% CO_2, 71.36% N_2, 4.27% O_2, 11.03%H_2O, 230 ppm SO_2, 1.1 ppm SO_3, 350 ppm NO_x, 5.2 g/m^3 particulates at 162°C and 101 kPa.

Since the flue gas stream is low in CO_2 and under low pressure, the capture options are limited. Chemical absorption is the preferred option.

Alkanolamines have long been accepted in North America as the solvent of choice for the removal of H_2S and CO_2 from process gas streams. Aqueous solutions of monoethanolamine (MEA) and diethanolamine (DEA) have been used extensively due to their reactivity, availability and low cost.

In this report, four solvent based processes, Fluor Econamine FG Plus ^{SM}, Kansai Mitsubishi Carbon Dioxide Recovery process (KM-CDR), Cansolv Technologies SO_2 and CO_2 Scrubbing Systems and HTC Purenergy CO_2 Capture System, will be reviewed. The review is based on the following considerations:

- Potential performance
- Challenges related to operation
- Technology maturity
- Safety and environmental impacts

2. The Amine Absorption Process

Alkanolamines can be divided into three groups:

(1) Primary amines
  - include monoethanol amine (MEA), diglycolamine (DGA);

(2) Secondary amines
  - include diethanolamine (DEA), di-isopropylamine (DIPA); and

(3) Tertiary amines

- include triethanolamine (TEA) and methyl-diethanolamine (MDEA).

Among the alkanolamines, MEA is the least expensive and has the lowest molecular weight. It possesses the highest theoretical absorption capacity for CO_2.This theoretical upper absorption capacity of MEA, however, is not realized in practice due to corrosion problems. In addition, MEA has the highest vapor pressure of any of the alkanolamines and high solvent carryover can occur during CO_2 removal from the gas stream and in the regeneration step. To reduce solvent losses, a water wash of the purified gas stream is usually required. In addition, MEA reacts irreversibly with minor impurities such as COS and CS_2 resulting in solvent degradation. Foaming of the absorbing liquid MEA due to the build-up of impurities can also be a concern.

The principal reaction between CO_2 and primary and secondary amines is the formation of carbamates.

Carbamate Formation: $2\ RNH_2 + CO_2 = RNHCOO^- + NH_3R^+$

Thus the CO_2 loading is 0.5 mole of CO_2 / mole of amine via carbamate formation.

The reaction mechanisms of CO_2 absorption by amines are fairly complex and the relative importance of the various reaction pathways depends on the specific amine and details of the reaction conditions. Contrary to primary and secondary amines, tertiary amines absorb CO_2 via the bicarbonate mechanism. So the theoretical CO_2 loading for tertiary amines would be 1:1 via the bicarbonate/carbonate route; however, the slow reaction kinetic of this route hinders the removal of CO_2.

Bicarbonate Mechanism: $RNH_2 + CO_2 + H_2O = HCO_3^- + NH_3R^+$

For the current MEA absorber systems, the absorption and desorption rates are reasonably high. However, the column packing represents a significant cost. Energy consumption is also significant for flue gas treatment.

Table 1 displays data for the heat of reaction between the three amines and carbon dioxide.

Table 1 Heat of Reaction between Amines and CO_2

	Primary	Secondary	Tertiary
Amine	MEA	DEA	MDEA
ΔH_r for carbon dioxide in BTU/lb	820	650	517
in kJ/kg	1900	1500	1200

Therefore, from an energy consumption point of view,

Primary Amines > Secondary Amines > Tertiary Amines.

Tertiary amines react slower with CO_2 than primary and secondary amines thus require higher circulation rate of liquid to remove CO_2 compared to primary and secondary amines.

Tertiary amines show a lower tendency to form degradation products than primary and secondary amines, and are more easily regenerated. In addition, tertiary amines have lower corrosion rates compared to primary and secondary amines.

It may be pointed out that corrosion has been a serious issue in amine processes. In general, alkanolamines themselves are not corrosive to carbon steel; the dissolved CO_2 is the primary corroding agent. As such, the alkanolamines indirectly influence corrosion rate due to their absorption of CO_2. The observed corrosiveness of alkanolamines to carbon steel is generally in the order

Primary Amines > Secondary Amines > Tertiary Amines.

The major issues in chemical absorption include:

- Solvent life
    - Process requires very low SO_x (<10 ppm) and NO_2 (<20 ppm); some polishing beyond conventional desulfurization is usually needed
    - Inhibitors may be added to mitigate the impact of oxygen on the solvent
    - Reduces solvent losses as solvent can be expensive to replace and its release can cause environmental impact
- Corrosion
    - Stainless steel versus carbon steel
- Energy consumption
    - Regeneration of the solvent consumes large amount of energy
- Environmental impacts
    - Some degradation products are known and regulated; others are not
    - Inhibitors can contain heavy metals

3. Reference MEA Absorption Process

A typical amine absorption unit is shown in Figure 1. The gas stream and liquid amine solution are contacted by a counter-current flow in an absorption tower. Conventionally, the gas to be scrubbed enters the absorber at the bottom, flows up, and leaves at the top, whereas the solvent enters the top of the absorber, flows down (contacting the gas), and emerges at the bottom. The absorber typically operates at 40 – 60°C. The liquid amine solution containing the absorbed gas then flows to a regeneration unit where it is heated and the acid gases liberated. The temperature at the regenerator typically ranges from 100 – 120°C. The solvent regeneration can be carried out at low pressures to enhance desorption of CO_2 from the liquid. Some amine solution is typically carried over in the acid gas stream from the regeneration step and the amine solution is recovered using a condenser. The hot lean amine solution then flows through a heat exchanger where it is contacted with the rich amine solution from the contact tower and from there the lean amine solution is returned to the gas contact tower.

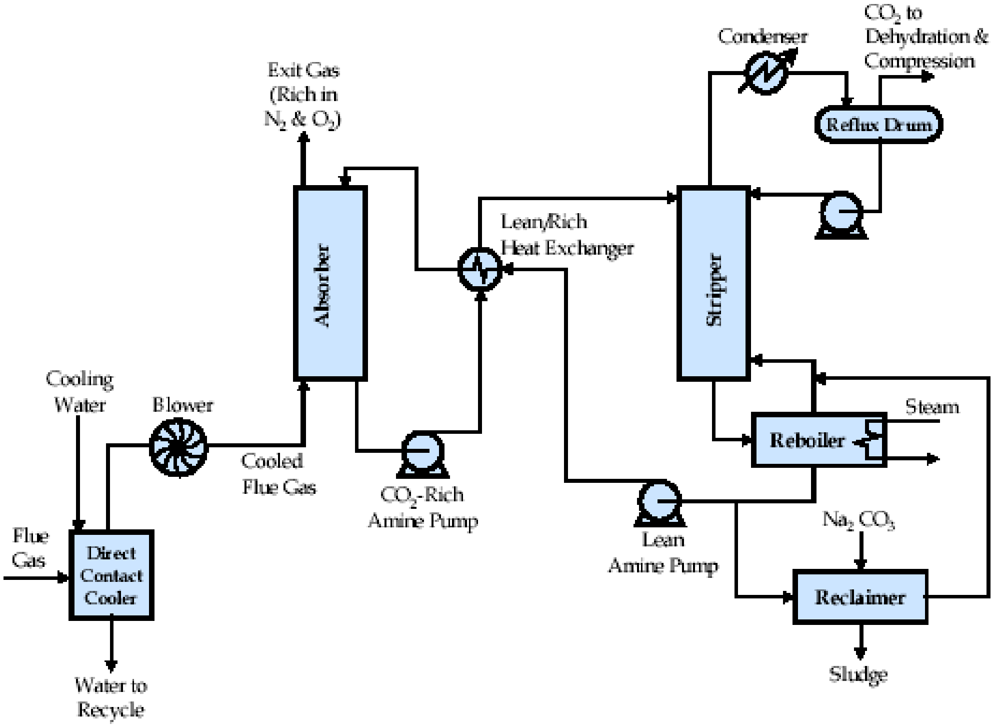
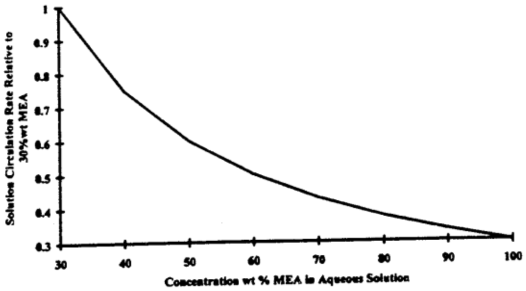


Figure 1: Typical Amine Absorption Unit for CO_2 Recovery from Flue Gas

It is more common now to use inhibitors with the MEA. The application of inhibitors is to mitigate the impact of O_2 and reduce corrosion of the MEA, thus allowing a higher concentration of MEA to be used (30 wt % versus 15-20 wt %). The increased concentration or loading of the amine in the solution is an area where energy savings can occur. Leci (1997) showed that increasing the MEA concentrations in the MEA aqueous solution will significantly reduce the solvent circulation rate, hence the pumping power (see Figure 2). However, at concentration above 30 wt %, corrosion remains an issue.



. Decrease in circulation rate with increasing concentration

Figure 2: Circulation Rate and MEA Concentration (Leci, 1997)

The 30 wt % MEA with inhibitors, for example the Flour Econamine FG (different from the FG PLUS) has been well documented (Chapel et al. 1999). Additional information can be found in Kothandaraman et al. (2008) via process simulation using the ASPEN RateSep framework. This would be our reference MEA absorption process.

A comprehensive methodology for assessing the performance (technical with implication to economics as well) of a chemical absorption process is provided in Ciferno (2010). The chemical absorption process is treated as a two-step separation process requiring 5 energy inputs:

Energy = Q (sensible) + Q (reaction) + Q (stripping) + W (process) + W (compression)

First, the CO_2 rich solvent temperature must be raised to the stripper temperature by sensible heat transfer. The amount of heat required for this process depends on the specific heat capacity of the solvent which does not vary much among the various solvents. The cross heat exchanger which heats up the in-coming CO_2 rich solvent with the hot out-going lean solvent, helps to reduce the sensible heat requirement. Cooling may also be required to bring the lean solvent to the operating temperature of the absorber.

Second, sufficient heat must be provided to break up the CO_2-solvent complex formed during the absorption process and this is accounted for by the heat of reaction. This is solvent dependent.

The third term is the latent heat for the vaporization of the water and of the solvent. The latent heat of vaporization of water is the same for all solvent systems; however, the energy required for this step depends on the portion of water present in the solvent. Obviously the latent heat of vaporization of the solvent is a property of the solvent itself.

The fourth term is the work energy required for the operation of the process. This includes:

- The energy required for the blower to bring the flue gas to the absorber. This is a function of the flue gas flow rate (in a way, also a function of the CO_2 concentration in the flue gas stream) and the pressure differential for operation of the absorber.
- The energy required for pumping the lean and rich solvent stream. The circulation rate depends on the CO_2 loading of the solvent and the water in the solvent.

The fifth term is the energy required for dehydrating the CO_2 and bringing the CO_2 to a dense phase for pipeline transport, typically in the 1,500-2,000 psi range. This would be common to all amine systems.

Performance of the amine systems are summarized in Table 2. Data for the reference MEA are sourced from Chapel et al. (1999) and Kothandaraman et al. (2008).

Table 2: Performance of MEA-based Absorption Processes:

Solvent	**MEA**	**Econamine FG PLUS^{SM}**
- Concentration	30wt% + inhibitor	>35 wt% + inhibitor
- Specific heat	2.55 kJ/kg-^{o}C	
- Latent heat of vaporization	826 kJ/kg	
- Heat of formation	1,900 kJ/kg	
- Corrosiveness	9 mils per year	Same??
- Absorption rate (kinetics)		(+) Higher MEA conc. (+) Absorber intercooling
Absorber		
- Absorber temperature (^{o}C)	45 – 60	
Regenerator		
- Regeneration temperature (^{o}C)	115 – 125	
- Regeneration pressure (atm)	1 – 2	
Capture efficiency	90%	90%
Solvent circulation rate (m^3/h)	0.71 x (t/d CO_2)	(-) Higher MEA conc. (+) Split flow (-) Absorber intercooling (-) Condensate flash steam
CO_2 lean loading (mol CO_2/mol Solvent)	0.22	(+) Split flow
CO_2 rich loading (mol CO_2/mol Solvent)	0.50	
Make-up solvent (kg/t CO_2)	1.6 + A[*]	
Vapor emission	Solvent loss via Absorber vent	(-) Advanced scrubbing - solvent release < 0.2 ppm
Solid discharge	Reclaimer waste and SO_2 scrubber waste [**]	(-) Low temperature reclaiming
Major Energy Inputs		
Steam consumption (MJ/t CO_2)	4.2	2.8 – 3.2
- Sensible heat	23%	(-) Higher MEA conc. (-) Split flow (-) Condensate flash steam (-) Absorber intercooling (-) Lean vapor comp.
- Heat of formation	51%	
- Heat of vaporization	26%	(-) Higher MEA conc. (-) Split Flow (-) Condensate flash steam (-) Absorber intercooling (-) Lean vapor comp.
Cooling load	6.8 m^3/h per (t/d CO_2)[***]	(-) Lean vapor comp.
Blower	B[****]	
Circulation pumps	B[****]	(-) because low recirculation
CO_2 compressor		
Equivalent parasitic load	33%	

Notes:

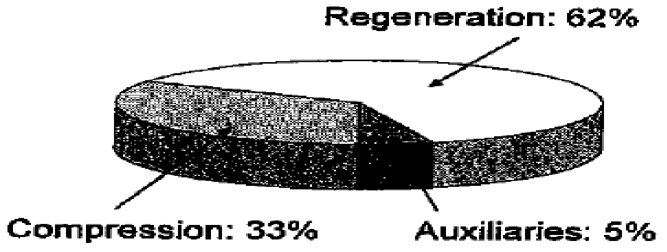
[*] A = 0.5 * (ppmv SO_x entering the absorber /% CO_2) in kg MEA/t CO_2

[**] Reclaimer waste about 0.003 m^3/t CO_2;
SO_2 scrubber waste@10 wt% salts m^3/h = (t/d CO_2) x (ppm SO_x absorbed)/(8900 x (% CO_2))

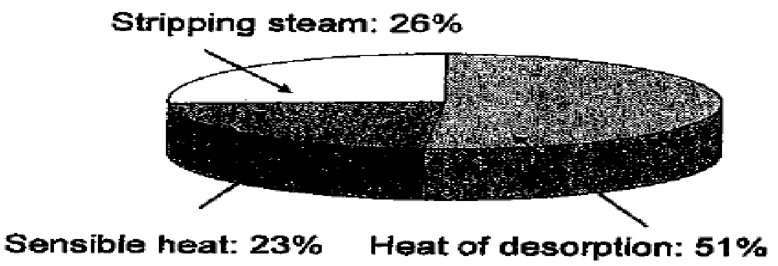
[***] based on 8 vol% CO_2

[****] B = (0.4+16.4/(%CO_2))*(t/d CO_2) in kw, includes blower, circulation pump and absorber water pump

Kothandaraman et al. (2008) stated that the work lost in the MEA system due to CO_2 capture and compression was calculated to be 0.013 KWh/gmol CO_2 (295 kWh/t CO_2) for coal fired power plants for 85% capture. The amounted to an efficiency decrease of 25% in the power plant. The breakdown of energy consumption is given in Figure 3. Kothandaraman et al. (2008) suggested that the main opportunity for energy recuperation in the MEA system is in the reduction of sensible heat requirements. This will however require a larger heat exchanger and will come with the attendant trade-off of capital cost.



Breakdown of energy consumption in MEA absorption



: Breakdown of regeneration energy for MEA

Figure 3: Breakdown of Energy Consumption in MEA Reference Case (Kothandaraman et al. 2008)

4. Fluor Econamine FG PLUS^{SM}

Dow Chemical and Union Carbide initially developed the GAS/SPEC FT-1 process in the 1970s to capture CO_2 primarily for the EOR market. In 1989, Fluor Daniel purchased the technology and renamed it the Econamine FG^{SM} process. The process is based on an inhibited 30 wt% MEA solution. The inhibitor not only tolerates oxygen and NO_x containing flue gas but also required oxygen to maintain its activity. The Econamine FG^{SM} is our reference MEA case; its performance was described in the last section.

To date Fluor has 25 plant/licenses for Econamine FG worldwide. These plants process flue gases with CO_2 concentrations range from 3% to 20% v/v and O_2 concentrations from 1 to 15% v/v. Econamine FG is the only process that has commercially demonstrated CO_2 recovery from a gas turbine exhaust. The plant is located in Bellingham, MA, with a capacity of 330 t/d of CO_2. The plant produces food grade CO_2 from a flue gas stream with 3.5% CO_2 and 13-14% O_2, v/v.

In 2003, Fluor came up with a new improved process, called Econamine FG PLUS^{SM}, by incorporating these new features (Reddy et al. 2003):

- Enhanced solvent formulation – Econamine FG+ has improved solvent designed with MEA concentration > 35 wt% (versus 30 wt% for Econamine FG and 18-20 wt% for generic MEA). Higher MEA concentration increases reaction rates (less absorber packing required, allowing a smaller absorber) and solvent carrying capacity (lower solvent circulation rates and steam requirements).
- Split flow configuration – The first portion of the rich solvent is regenerated in the stripper. The second portion of the rich solvent is preheated against the lean solvent stream and then regenerated by flashing in a flash drum. The CO_2 is made without any additional steam requirement, as the energy required for the regeneration is provided by the heat remaining in the lean solvent stream after it leaves the stripper boiler. However, it should be noted that since the solvent entering the absorber has a higher loading with this configuration, a higher recirculation is required.
- Stripping with condensate flash steam – this feature is an extension of the split flow configuration. The addition of steam to the semi-lean flash drum reduces the semi- lean loading, thereby decreasing the overall solvent circulation rate. The end effect is a decrease in re-boiler heat requirement.
- Absorber intercooling – heat is released in absorber due to heat of reaction. Intercooling produces a lower temperature at the bottom of the absorber which increases the solvent carrying capacity (decreasing solvent circulation rate which resulted in a lower re-boiler heat requirement) and CO_2 absorption rate (decreasing the absorber size).
- Heat integration with the power plant – three potential strategies for power plant integration, flue gas re-boiler, vacuum condensate heating and supplemental duct firing in natural gas combined cycle power plants.

Reddy et al. (2003) reported an energy consumption of 1395 BTU/lb CO_2 (about 3.2 GJ/tonne of CO_2) and a solvent replacement cost of US $ 2.30/tonne of CO_2).

Fluor is continuously improving the Econamine process to lower energy consumption and solvent losses. In 2008, Fluor reported adding additional features like lean vapor compression and low temperature reclaiming to Econamine FG PLUS ^{SM} (Satish Reddy et al. 2008).

- Lean vapor compression at the regeneration column – Hot lean solvent from the stripper is flashed at low pressure in a flash drum. The resulting flash vapor consists mostly of steam with small amounts of CO_2 and solvent. The flashed vapor is compressed in a thermo-compressor and returned to the bottom of the stripper where it flows upwards while stripping CO_2 from the rich solvent. The result is lower steam consumption and lower cooling water requirement.

- Advanced reclaiming technology – new processes for low temperature reclaiming have dramatically reduced solvent losses. One of the technologies used is based on ion-exchange. Ion-exchange reclaiming efficiently regenerates the solvent from heat stable salts with very little solvent losses.

It is claiming a steam consumption of 2.8 GJ/ton CO_2 removed. It is not clear that this has been demonstrated in CO_2 capture plants or is estimated value.

Fluor is involved with E.NO Energie of a coal-fired power plant demonstration in Germany. In July 2010, Fluor announced that Tenaska has chosen Econamine FG PLUS^{SM} for use at the company's proposed Tenaska Trailblazer Energy Center being developed near Sweetwater, Texas.

Over the last two years, there has been an increased level of concern regarding amine emissions. A theoretical modelling study done in Norway has hypothesized that amines react with atmospheric NO_x in the presence of ultra violet light to form nitrosamines which is considered harmful to the environment. Atmospheric chemistry testing with amines is also being conducted in Valencia, Spain. The results of the tests are yet to be announced. In general, Fluor's goal is to lower solvent concentration in the absorber vent to less than 1 ppm (Satish Reddy, 2010). It is reported that Fluor has developed an advanced scrubbing system where the solvent concentration is greatly reduced to around 0.1 - 0.2 ppm level.

The performance of Econamine FG PLUS ^{SM} is compared to the reference MEA, as shown in Table 2. The higher MEA concentration improves the absorption rate, lowers the recirculation rate and hence the re-boiler heat duty and pumping power. All the process flow-sheet enhancements target to lower the recirculation rate and re-boiler heat duty. The fact remains that the process has to work within the limitations of MEA.

5. Kansai – Mitsubishi Carbon Dioxide Recovery (KM-CDR) Process

Mitsubishi Heavy Industries (MHI) has been involved in R&D related to CO_2 capture from flue gas since 1990. It has developed a proprietary, advanced solvent called KS-1 which is believed to be a sterically hindered amine. The KS-1 solvent has many good properties – high rate of CO_2 absorption, lower solvent degradation, low corrosion and no requirement for a corrosion inhibitor. The heat consumption for the conventional KM-CDR process ranges from 730 – 830 kcal/kg CO_2 (3.05 – 3.47 GJ/t CO_2). Figure 4 shows a comparison of the efficiency of MEA and SK- solvents developed by Kansai Electric Power Co. (KEPCO) and MHI. Typically KS-1 is having an energy saving of 20 -25% compared to MEA

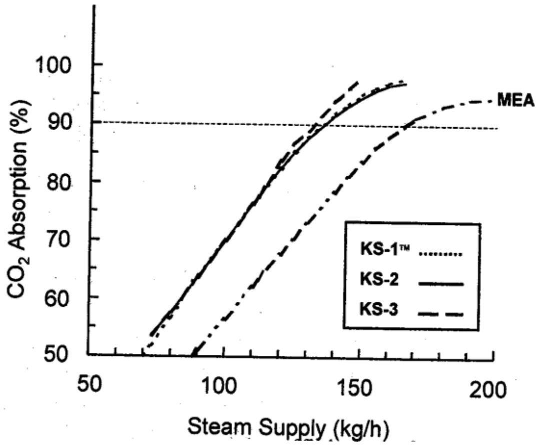


Figure 4: Comparison of Steam Rate between KS-1 and MEA (Tatsumi et al. 2010)

MHI has developed an "Improved Process", which results in a reduction in steam requirement of 15% over the conventional KM-CDR process. The process incorporates additional plate heat exchangers which utilize lean solvent and steam condensate heat for regeneration inside the stripper. This improved process has been applied to a commercial project in Abu Dhabi. This improvement means steam consumption reduces to 660 kcal/kg CO_2, i.e. 2.76 GJ/t CO_2 or 1.3 t steam / t CO_2 (Mitchell and Iijima, 2008).

As significant energy is consumed in the low pressure steam, MHI has made progress in heat integration by recovering waste energy more efficiently. One area that shows great potential is recovering energy from the condenser of the low pressure turbine (see Figure 5) and using it in the regenerator.

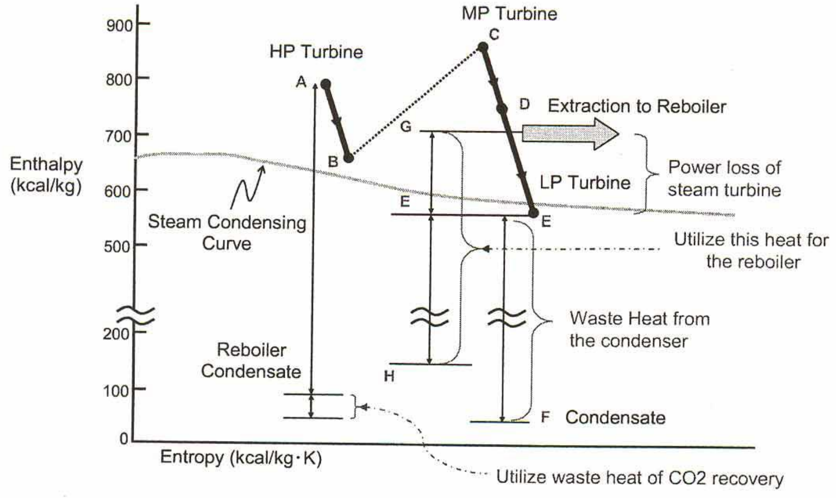


Figure 5: Options for heat integration based on the power plant steam cycle (Mitchell and Iijima, 2008)

MHI identified a number of process improvements, called “Energy Saving Process”, which include:

- Increased CO_2 loading of rich amine by reduced absorber temperature
- Reduced absorbent heat loss by decreasing absorbent recirculation rate
- Reduced CO_2 reflux cooler heat loss by lowering the temperature at the top of the regenerator

As a result, regeneration energy requirement of 603 kcal/kg CO_2 (2.53 GJ/t CO_2) was achieved by demonstrating the “Energy Saving Process” at the Nanko CO_2 capture pilot using the KS-1 solvent (Tatsumi et al. 2010).

The first commercial plant using KS-1 is the Kedah urea plant at Kedah, Malaysia. It started operation in 1999. The feed gas is a natural gas reformer flue gas with a CO_2 concentration of 8%. The capacity is 200 tonnes per day. Plant performance so far has been good. The low pressure steam consumption is 1.5 t / t CO_2 recovered; solvent degradation is low. To date, there are seven commercial operations (the largest capacity being 450t/d) and two more are under construction and will be operational by the end of 2010. The KM-CDR process has been applied commercially to natural gas based boiler and reformer flue gases. For natural gas fired flue gas, the regeneration energy can be guaranteed at 700 kcal/kg of CO_2 (2.94 GJ/t CO_2).

Hence, the absorption/desorption process of KM-CDR is well understood and for it to be applied to coal-fired power plant flue gases, the impurities in the gas stream must be treated properly before entering the absorber.

Currently, there is no commercial KM-CDR process to capture CO_2 from power plant flue gas. There is a 10t/d pilot plant at the Matsushima Power station operational since 2006. A 500t/d demonstration plant is to be deployed at Southern Company’s Plant Barry Power Station in Alabama. Commissioning of the plant will take place Q2-2011 (Endo et al. 2010). A FEED order has been received from E.ON UK to design CO_2 capture for the 1,600 MW supercritical coal fired power plant at the proposed new Kingsnorth Power Station in Kent.

The pilot unit has demonstrated that SO_x concentration of ~ 100 ppm and dust of ~ 10mg/Nm^3 can be fed to the deep desulphurization unit which will take it down to < 0.1 ppm before entering the absorber. Then the process performance will be similar to that of natural gas based flue gases.

The KM-CDR process includes a SO_2 polishing section in the Quench (cooling) Tower that is based on MHI’s Double Contact Flow Scrubber (DCFS) technology. MHI has tested increased SO_2 level at the 10 t/d Matsushima pilot plant by taking a slip stream from the FGD. Currently, a SO_x level of 250-300 ppm and a NO_x level up to 200 ppm would be an acceptable feed to the SO_2 polisher, which would be able to reduce SO_2 to < 0.1 ppm level before entering the absorber. For SO_2 level > 300 ppm, alternative methods to reduce SO_2 level would have to be included.

The typical kind of emissions and solid waste streams from coal-fired flue gas CO_2 capture with KM-CDR are:

- Treated gas containing trace amount of degraded solvent from the CO_2 absorber
- Blow down from the limestone based $deSo_x$ process
- Reclaimed waste which can be disposed of off-site or can be incinerated on site as currently practiced in some of the commercial plants

It is expected that the quantities of the waste streams would be much less than the MEA-based process.

A comparison of the KM-CDR performance with the Reference MEA is shown in Table 3. This is difficult to predict as the properties of the KS-1 solvent are not known.

Table 3: Performance of KM-CDR compared to the MEA-based Reference Absorption Processes:

Solvent	**MEA**	**KM-CDR – KS-1**
- Concentration	30wt% + inhibitor	
- Specific heat	2.55 kJ/kg-°C	
- Latent heat of vaporization	826 kJ/kg	
- Heat of formation	1,900 kJ/kg	1,200 kJ/kg ??
- Corrosiveness	9 mils per year	3.5 mils per year
- Absorption rate		Lower
Absorber		
- Absorber temperature (°C)	45 – 60	40 – 50
Regenerator		
- Regeneration temperature (°C)	115 – 125	120
- Regeneration pressure (atm)	1 – 2	
Capture efficiency	90%	90%
Solvent circulation rate (m^3/h)	0.71 x (t/d CO_2)	Lower
CO_2 lean loading (mol CO_2/mol Solvent)	0.22	0.08
CO_2 rich loading (mol CO_2/mol Solvent)	0.50	0.55
Make-up solvent (kg/t CO_2)	1.6 + A[*]	Lower
Vapor emission	Solvent loss via Absorber vent	Lower solvent loss
Solid discharge	Reclaimer waste and SO_2 scrubber waste [**]	Lower quantities
Major Energy Inputs		
Steam consumption (MJ/t CO_2)	4.2	2.53 – 2.94
- Sensible heat	23%	
- Heat of formation	51%	
- Heat of vaporization	26%	
Cooling load	6.8 m^3/h per (t/d CO_2)[***]	
Blower	B[****]	
Circulation pumps	B[****]	
CO_2 compressor		
Equivalent parasitic load	33%	Lower

Notes:

[*] A = 0.5 * (ppmv SO_x entering the absorber /% CO_2) in kg MEA/t CO_2

[**] Reclaimer waste about 0.003 m^3/t CO_2;
SO_2 scrubber waste@10 wt% salts m^3/h = (t/d CO_2) x (ppm SO_x absorbed)/(8900 x (% CO_2))

[***] based on 8 vol% CO_2

[****] B = $(0.4+16.4/(\%CO_2))*(t/d\ CO_2)$ in kw, includes blower, circulation pump and absorber water pump

MHI has assessed the scale-up issues and technically it can achieve a 3,000 t/d commercial size to day. However, due to the permitting process and the time allocated for the FEED study (6 months) and EPC (36 months), the earliest time frame for a commercial CO_2 capture unit would be 2015. It is not the technology but rather the physical time required to complete a project.

MHI has completed a 4,067 t/d FEED package and is currently working on another 4,318 t/d FEED study. Hopefully this would lead to a FEED study of a full-scale commercial coal-fired application which would be in the order of 2 x 8,000 t/d trains. The Quench and Absorber vessels would be rectangular in section. With the absorber vessels, MHI has a standard preferred modular size and then dependent on the amount of flue gas/CO_2, additional modules can be added. If space is limited, some of the equipment can be located separately, however, it is preferred that the equipment stays together.

6. Cansolv Technologies SO_2 and CO_2 Scrubbing Systems

Cansolv Technologies is a Canadian company founded in 1997 (spin-off of the Union Carbide Canada SO_2 program). The company's main business is its commercially proven SO_x removal technology. It has 14 SO_2 plants in operation worldwide. They now offer an amine based CO_2 capture process as well as an integrated process for simultaneous capture of CO_2 and SO_2.

Two Cansolv CO_2 capture demonstration plants have been built – one in Montreal (for flue gas of natural gas fired boiler) and the other one in Virginia, USA (flue gas of a coal fired boiler). No commercial plants have yet been built. In 2008, Cansolv Technologies was bought by Shell Global Solutions.

The main features of the Cansolv process are the proprietary solvent and the possibility of integrating the SO_2 and CO_2 capture units.

The proprietary solvent is called Absorbent DC101, which is claimed to have these characteristics:

- Low oxidative degradation of the amine
- Low volatility of the amine
- Low energy consumption in the process

No constituents of DC101have been offered, but it is believed that it contains a blend of various types of amines (mostly secondary amines) and at least one type of tertiary amine and an oxidation inhibitor. Primarily the secondary amines act as an activator to the tertiary amine to increase its mass transfer rate for capturing the CO_2.

The second feature of the Cansolv process is the possibility of combining SO_2 and CO_2 capture with the same solvent and the same absorber column although in different sections of the column and with two different solvent cycles.

The process flow sheet for integrated SO_2 and CO_2 capture is shown in Figure 6. The feed gas containing SO_2 and CO_2 is first washed with a spray of water and cooled to the adiabatic saturation temperature. The pre-treated gas then flows through a chimney tray to the SO_2 removal section counter-currently to the DC101 solvent, where it is in so-called "half salt" form. As such, the buffering pH is kept in the right range of 3-6 for SO_2 capture. The majority of the SO_2 is removed and leaves the tower in a SO_2 rich stream. This SO_2 is regenerated by indirect steam stripping in the SO_2 regenerator. Approximately 80% of the heat used for the SO_2 regeneration is used for the CO_2 regeneration. The regenerated SO_2 overhead steam is led to one of two re-boilers for the CO_2 regeneration. The remaining heat for the CO_2 regeneration is provided by indirect steam fed to the second re-boiler. The SO_2 lean stream from the SO_2 absorber section flows through a chimney tray before it is treated in a CO_2 scrubbing loop with an amine stream to obtain the CO_2 rich stream. The amine stream is the same DC101 but in free base form, which means a pH range of 6-9 suitable for CO_2 capture. Most of the remaining SO_2 is also removed in this section. The CO_2 rich stream is regenerated in the CO_2 regeneration column. Both a slip stream from the SO_2 loop and the CO_2 loop is treated separately to avoid accumulation of heat stable salts in the system.

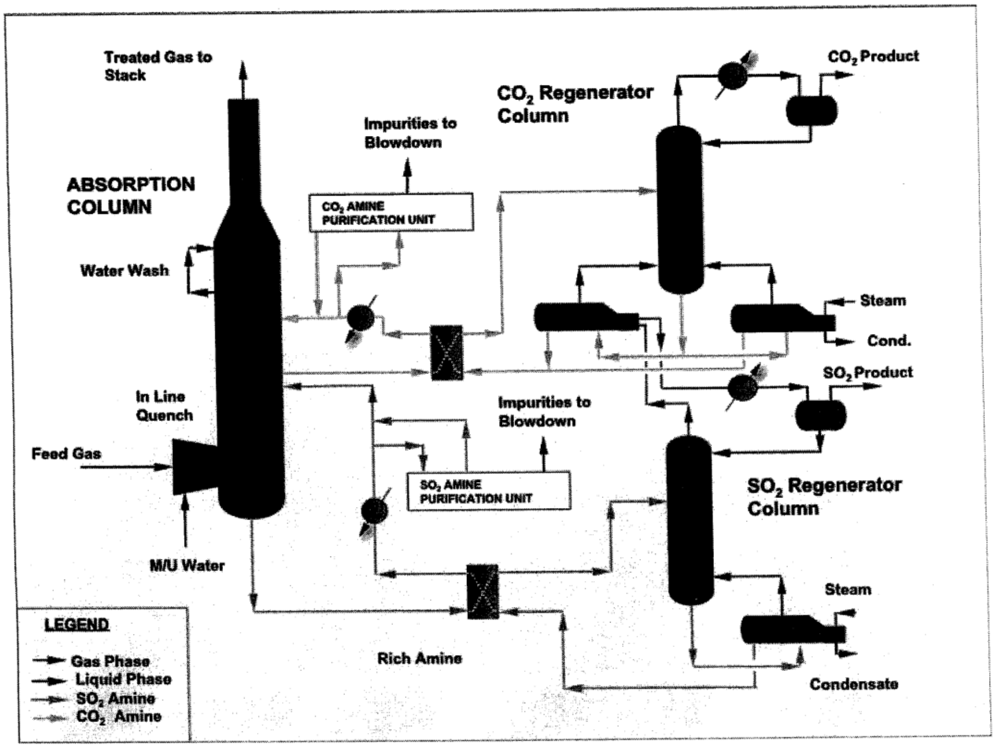


Figure 6: Process Flow-sheet of Cansolv Integrated SO_2 and CO_2 Capture Process (Birnbaum, 2007)

Obviously, integrated plant means significant reduced capital cost as one absorber can be used for both SO_2 and CO_2 capture. However, the integrated process is very integrated both in heat and process streams. This implies generally a more complex and challenging operation than MEA as it needs strict requirements for pH control and salt concentration control in two separate but still integrated solvent loops.

It is claimed that the DC101 solvent reduces steam consumption by 40% compared to MEA. Cansolv reported a designed steam consumption of 1.18 t / t CO_2 or about 2.4 GJ/t (Just et al. 2009). There is no confirmation of this number from pilot plant data. It is also not clear whether this steam consumption number applies to CO_2 capture process alone or including the integrated SO_2 removal process as well.

It is also claimed that the degradation of DC101 is very low compared to MEA and that the kinetics is comparable to primary amines.

There is no data on the extent of emissions to air and the amount of degradation products or reclaimer waste formed in the Cansolv process. Therefore its environmental impact cannot be assessed.

Cansolv indicated that a SO_2/CO_2 capture demonstration plant (50 t/d CO_2) is currently in detailed engineering and procurement phase, with start-up beginning in 2011. The objectives are: to confirm specific heat consumption; to evaluate scale-up effects and to prove SO_2 compatibility of CO_2 solvent. Cansolv is expected to participate in the SaskPower CCS activity in Saskatchewan where they are requested to provide a proposal for the 1050 MW unit with 90% CO_2 capture for the Boundary Dam Power Station near Estevan, Saskatchewan. Additionally, there are plans for a 100 t/d CO_2 capture pilot in collaboration with E.ON Energie at the Heyden power station, Germany.

7. HTC Purenergy CO_2 Capture System

HTC Purenergy is a Canadian company founded in 1997, backed by extensive R&D work by the University of Regina and the International Test Center. The IP includes unique customized solvents, proprietary modelling/simulation and process engineering. It also aligns with Doosan Power Systems.

In a September 4, 2008 news release, HTC Purenergy and Doosan Babcock of the UK signed a Global Technology Licensing Agreement which includes the right to utilize products and technologies developed by HTC and the University of Regina/International Test Center. In conjunction with the Licensing Agreement, Doosan Babcock and its parent Doosan Heavy Industries will subscribe to a Private Placement for an approximate 15% equity share ownership in HTC with an investment of CDN $10 million.

HTC offers the world's first pre-engineered modularly constructed CO_2 capture unit that can be retrofitted to existing or new-build coal and gas fired power plants. The system is said to be capable of capturing up to 3,000 t/d of CO_2. Presently it has no commercial or demonstration installations. It reported an emission reduction test facility in Glasgow, Scotland and a 2 t/d pilot plant at Boundary Dam Power Station, Saskatchewan.

There are a couple of commercial developments of note regarding HTC Purenergy. In December 2009, Basin Electric selected HTC Purenergy to replace PowerSpan to operate the CO_2 capture plant at

Antelope Valley Station at Beulah, ND. However, in December 2010, Basin Electric announced that it was shelving Antelope Valley indefinitely due to cost and timing difficulties. In August 2010, Doosan Power Systems (HTC's EPC partner) was awarded a CO_2 capture project by Scottish and Southern Energy. Construction has started at Scottish and Southern Energy's Ferrybridge Power Station. The plant will capture 110 tons per day of CO_2 from Ferrybridge's coal-fired power plant. The capture plant is scheduled to be completed by the end of 2012.

The Purenergy CCS system features the RS-2 formulated solvent, with these characteristics:

- Enhanced rate of absorption/kinetics of reaction
- Superior capture capacity, solubility of CO_2 in solvent
- Improved mass transfer coefficient
- Corrosion and fouling resistant
- Minimize degradation via O_2, SO_x, NO_x
- Low regeneration energy

There is no data on the constituents of RS-2. Figure 7 shows the process design performance of RS-2. Its re-boiler duty is about 70% of 30wt% MEA. If the 30 wt% MEA baseline steam consumption is 4.2 GJ/t CO_2, then the RS-2 solvent would command a re-boiler heat duty of about 2.9 GJ/t CO_2. It is not known if this number is based on simulation results or supported by pilot plant data.

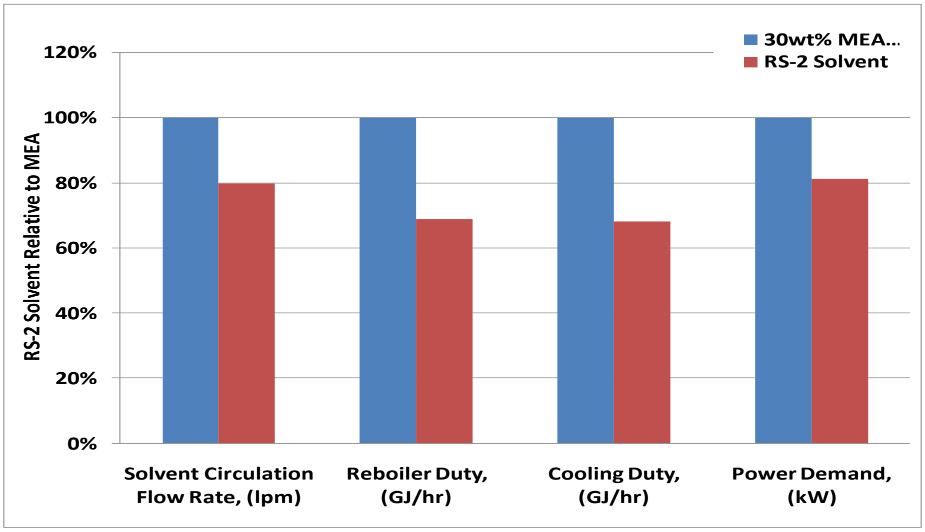


Figure 7: Design Performance of RS-2 Compared to 30 wt% MEA (Osborne, 2011)

8. Conclusions

- Of the four chemical absorption processes evaluated, the Econamine FG PLUS^{SM} and the KM-CDR process are the most matured and technically advanced for commercial application to capture CO_2 from coal-fired boiler flue gases.
- Econamine FG PLUS ^{SM} is MEA-based. As MEA is a primary amine, it is limited by its higher volatility, corrosiveness and regeneration energy. The corrosiveness of the MEA would limit the maximum concentration that can be applied. Process enhancements are targeting to lower the recirculation rates and hence the re-boiler heat duty and pump power requirements. The best performance we have noted for steam consumption is 2.8 GJ/ t CO_2.
- Fluor's approach to emissions and wastes reduction is to use advanced technologies such as an advanced scrubbing system for solvent recovery at the absorber vent and a low temperature reclaiming system to treat the heat stable salts and recover the solvent from the reclaimer. As environmental regulations are becoming more stringent, this will add to the cost of the capture process.
- The KM-CDR process uses KS-1, a sterically hindered amine. It has far better characteristics than MEA in terms of volatility, corrosiveness and regeneration energy. However, its reaction rate (kinetics) is lower. Better packing in the absorber vessel would improve the mass transfer rate. The best performance we have noted for steam consumption is 2.54 GJ/t CO_2.
- MHI's approach to emissions and waste reduction is to reduce the impurities in the flue gases to very low level before entering the absorber. This is driven by the fact that KS-1 is an expensive solvent and its loss would be minimized. This reduces the quantities of the waste streams to be treated. MHI seems to be making great progress in treating the impurities of the flue gas stream and configuring them into the flow-sheet.
- MHI indicated it is ready to apply the KM-CDR process on a 3,000 t/d scale to capture CO_2 from coal-fired boiler flue gases. If a decision is made today, the earliest time the plant can be on-stream is 2015.
- Cansolv and HTC Purenergy are working with amine blends of tertiary amine/sterically hindered amine with primary/secondary amines to optimize their properties for capturing CO_2. At this stage, they are less matured than either the Econamine FG PLUS ^{SM} or the KM-CDR in terms of commercial application.

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