



# Recent R and D Trends for CO<sub>2</sub> Capture from Flue Gas of Thermal Power Station

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## Introduction:

Chandrapur is most polluted city in Maharashtra due to thermal power station and coal mines. Today environmental problem i.e. climate change is mainly due to the global warming which is mainly cause by increasing CO<sub>2</sub> % in atmosphere and increasing CO<sub>2</sub> % in atmosphere is due to consumption of fuel. Energy demand in future is satisfied only by consumption of coal. Energy requirement increases day by day in India and unlikely any option for coal consumption in near future. Therefore capture and utilization is only the way we have.

The urgent need strategy to reduce global atmospheric concentration of green house gases has taken a serious action from international government, industries. The capture and sequestration of green house gas is main strategies in these initiatives, as it offer the opportunity to meet increasing demand of fossil fuel energy in short.<sup>1</sup> Carbon capture and storage scheme (CCS) is a group of technology for the capture of CO<sub>2</sub> from power plant followed by compression, transport and permanent storage. A important point is that carbon capture from flue gas technology having a lots of challenge that require a collaborative effort from government, colleges, industries and research institute (Figure. 1).

## Chemical Absorption

Chemical absorption for CO<sub>2</sub> capture technologies have been employed industrially for over 50 years and are based predominantly on the industrially important primary alkanolamine MEA.<sup>2</sup> The process involves the passage of an aqueous amine solution (typically 25–30 wt.%) down the top of an absorption tower, while a gaseous stream of flue gas containing CO<sub>2</sub> is introduced at bottom. A blower is required to pump the gas through the absorber. At a temperature of approximately 40 °C, the reaction of CO<sub>2</sub> with the amine occurs through a zwitterion mechanism to form carbamates, a reaction that has been extensively studied as shown below. The liquid amine CO<sub>2</sub> rich solvent passes from the absorber column to a stripping tower where the mixture is heated with steam to liberate the CO<sub>2</sub>. The regeneration of the chemical solvent is carried out at elevated temperatures (100–140°C) and pressures not much higher than atmospheric pressure.

The high heat of formation associated with carbamate production due to which huge amount of energy is need for regeneration of solvent. Following regeneration, the amine solution is cycled back to the absorption tower for





additional CO<sub>2</sub> absorption. This technology are advantageous in that the technology is commercially mature and can be easily installed into existing power plants, they suffer a number of drawbacks. These include the considerable energy requirements for solvent regeneration and the necessary use of inhibitors to control corrosion and oxidative degradation due to residual oxygen in the flue stream. The sensitivity of the solvents to chemical degradation from other by-products in the flue gas streams, such as SO<sub>x</sub> and NO<sub>x</sub>, also lead to reduced efficiencies and increased costs for electricity production. Improved strategies for flue gas CO<sub>2</sub> capture include the use of liquids with lower heats of adsorption, increasing the concentration of the adsorbent molecules and improving the mass transfer and reaction kinetics. Need of other amine-based molecules with lower regeneration temperatures for best commercial output of chemical absorption technology (Figure. 2)

### **Adsorption Materials**

Solid physical adsorbents possess significant advantages for energy efficiency compared with chemical and physical absorption approaches. Whereas CO<sub>2</sub> molecules dissolve into the bulk of the material in absorption, CO<sub>2</sub> adsorption involves either physisorption (vander Waals) or chemisorptions (covalent bonding) interactions between the gas molecules and the surface of a material. The CO<sub>2</sub> loaded solid is purified in stages using pressure, vacuum, or temperature swing adsorption cycles to remove and concentrate the CO<sub>2</sub>. Several authoritative review articles have discussed characteristics and examples of physical adsorbents.<sup>3,4</sup> A key concern for physical adsorbents is balancing a strong affinity for removing an undesired component from a gas mixture with the energy consumption required for their regeneration. In addition to the adsorption capacity, the selectivity is a principal property relevant to adsorptive gas separation. While both factors are dependent on the operational temperature and pressure, as well as the nature of the adsorbent and the gas adsorbate, the factors which influence selectivity are more complicated. Possible mechanisms of adsorptive separation include: 1) the molecular sieving effect, which is based upon size/shape exclusion of certain components of a gas mixture; 2) the thermodynamic equilibrium effect, due to preferential adsorbate-surface or adsorbate packing interactions; and 3) the kinetic effect, due to differences in the diffusion rates of different components of a gas mixture.<sup>5</sup>

A variety of solid physical adsorbents have been considered for CO<sub>2</sub> capture including microporous and mesoporous materials (carbon-based sorbents such as activated carbon and carbon molecular sieves, zeolites, and chemically modified mesoporous materials), metal oxides, and hydrotalcite like compounds. We discuss some of them mostly studied.

### **Microporous and Mesoporous Zeolite**

Zeolites are most widely reported physical adsorbents for CO<sub>2</sub> capture in the patent and journal literature.<sup>6</sup> they constitute the primary adsorption material for commercial hydrogen production (involving H<sub>2</sub>/CO<sub>2</sub> separation) using pressure swing adsorption, with the most popular of these based on zeolite 13X. Zeolites are typically used at elevated pressures (above 2 bar), and their adsorption capacity





has been shown to be greatly reduced by the presence of moisture in the gas, thereby necessitating very high regeneration temperatures (often in excess of 300°C).<sup>7</sup> these additional recovery costs for their regeneration gives a significant disadvantage. Recently, attention has turned to experimental and computational screening studies to assess CO<sub>2</sub> removal from low pressure flue gas using naturally occurring zeolites, such as X and Y Faujasite systems as well as synthetic zeolites including 5A and 13X. Experimental studies on several synthetic zeolites have shown that the most promising candidates for capture of CO<sub>2</sub> from a simulated flue gas mixture (consisting of CO<sub>2</sub> and N<sub>2</sub>) are characterized by a near linear CO<sub>2</sub> adsorption isotherm. However, a linear isotherm is indicative of weak adsorbent-adsorbate interactions, which is not compatible with a high CO<sub>2</sub>/N<sub>2</sub> selectivity.

The adsorption can be enhanced by a low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and the presence of cations in the zeolite structure which exhibit strong electrostatic interactions with CO<sub>2</sub>.<sup>7</sup> while these potential adsorbents were shown to be adequate for pressure swing adsorption applications, their regeneration required significant energy input. An advantage of porous solid materials is the ability to modify their properties by impregnating active groups such as alkyl-amines onto their internal surfaces. This strategy has often been exploited to improve the gas sorption properties of porous materials for low pressure capture applications, such as those relevant in flue streams and for capture from ambient air. In this regard, numerous amine modified silica materials have been prepared.<sup>6</sup> the surface modification with primary amines facilitates the adsorption of CO<sub>2</sub> through the formation of carbamate species, similar to the amine-CO<sub>2</sub> chemistry used in chemical absorption process. The impregnation of polyethylenimine into periodic MCM-41 mesoporous molecular sieves has also been shown to lead to a significant enhancement in the CO<sub>2</sub> absorption capacity of the solid support using a pressure swing adsorption approach.<sup>8</sup> Increased absorption capacities were also observed in a series of amines immobilized in supports such as poly(methyl methacrylate).<sup>9</sup> However, these materials impregnated with physisorbed amines often suffer from a lack of stability over repeated cycles.

### **Activated Carbon as Adsorbents**

Adsorption studies on activated carbon, charcoal, and virgin coal have focused on high pressure CO<sub>2</sub> capture applications given that the adsorption capacities scale with pressure.<sup>6</sup> While the surface properties of the adsorbents can vary widely, the materials are advantageous in that they are inexpensive relative to other solid adsorbents (such as zeolite 13X), and are insensitive to moisture. The majority of studies on carbon-based sorbents are motivated by the significant industrial potential of enhanced oil recovery schemes.<sup>10</sup> Few studies on carbonaceous adsorbents have investigated their feasibility for low pressure flue gas applications using vacuum or temperature swing regeneration approaches. In a recent study, activated carbon and charcoal were shown to exhibit moderate adsorption selectivity for CO<sub>2</sub> over N<sub>2</sub> (defined as the ratio of the pure-component sorption capacities) at low pressures below 1 atm, while increasing the pressure reduced the selectivity.<sup>4</sup> In general, the selectivity and capacity of carbonaceous adsorbents is too low for CO<sub>2</sub> capture from flue gas.





### **Metal–Organic Frameworks:**

The past 10 years have seen remarkable progress in the design, synthesis, and characterization of metal-organic frameworks (MOFs) due to their enormous structural and chemical diversity and their potential applications in gas storage, ion exchange, molecular separation, and heterogeneous catalysis.<sup>11,12</sup> These microporous crystalline solids are composed of organic bridging ligands coordinated to metal-based nodes to form a three-dimensional network with uniform pore diameters. The nodes generally consist of one or more metal ions (e.g.,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Zn}^{2+}$ ) to which the organic bridging ligands coordinate through a specific functional group (e.g., carboxylate, pyridyl). The intense current research efforts towards industrial applications of MOFs in gas storage, separation, and catalysis is attributed to their unique structural properties, including: robustness, high thermal and chemical stabilities, unprecedented internal surface areas (up to  $5000 \text{ m}^2/\text{g}$ ), high void volumes (55–90%), and low densities (from 0.21 to  $1.00 \text{ g cm}^{-3}$ ), which can be maintained upon evacuation of the guest molecules from the pores.<sup>13</sup> The regular monodisperse nature of the crystalline array of micropores is a key feature that distinguishes these systems from other porous materials (e.g., polymers, mesoporous silicas, carbons, etc.). In addition, the ability to modulate systematically the pore dimensions and surface chemistry within metal–organic frameworks is a feature that was previously largely absent in zeolite materials. The high surface area-to-weight ratio of MOFs is such that they have enhanced capacities for  $\text{CO}_2$  capture at moderate pressures compared with zeolites. The capacities of metal–organic frameworks up to high pressures scale with the amount of active area per unit weight: activated carbon has an active area of  $400\text{--}1000 \text{ m}^2 \text{ g}^{-1}$ , zeolites of up to  $1500 \text{ m}^2 \text{ g}^{-1}$ , and frameworks of  $1500\text{--}4500 \text{ m}^2 \text{ g}^{-1}$ . In addition to the adsorption capacity, the selectivity is a principal property relevant to adsorptive gas separation, and is determined by an interplay of factors including the molecular sieving effect, the thermodynamic equilibrium effect, and the kinetic effect.<sup>5</sup> While the mechanism for  $\text{CO}_2$  capture and separation can often be determined predominantly by one of these factors, it is more often the case that a synergistic combination of effects is operative.

Zeoliticimidazolate frameworks (ZIFs) constitute a subclass of metal–organic frameworks that can adopt zeolite structure types based on the replacement of tetrahedral  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  ions with tetrahedral transition metal ions such as  $\text{Zn}^{2+}$  or  $\text{Co}^{2+}$  and bridging  $\text{O}^{2-}$  ions with bridging imidazolate-based ligands. An extensive review article<sup>14</sup> has highlighted the exceptional selective  $\text{CO}_2$  capture and storage properties. Functionalization of the imidazolate and benzimidazolate linkers was also shown to permit fine-tuning of the interactions between the pore walls and guest molecules, thereby varying the selectivity of adsorption. Importantly, in contrast to many metal–organic frameworks, ZIFs exhibit high thermal stabilities and chemical stability in refluxing aqueous and organic media, which are required for practical separations processes.<sup>15</sup> In particular, the stability of a framework toward long-term exposure to water vapour is a critical issue in determining its suitability for  $\text{CO}_2$  capture from flue gas.





## Membranes

Membrane separation technologies will be a high efficiency for CO<sub>2</sub> capture due to their selective extraction of CO<sub>2</sub> from mixed gas streams, their low energy requirements and the flexibility in their possible configurations in industrial plants relative to conventional amine absorber/desorber columns. The constituent materials are classified in two types.

1-Inorganic: Ceramic, metal oxide, metallic, molecular sieves, porous alumina cylinder as support, metal-organic frameworks.

2-Organic: Cellulose acetate, polymers such as polysulfone, polyamide, polyimide, cross-linked polydimethylphenyleneoxide, hollow fibers with high surface area to volume ratios of 1500-2000 m<sup>2</sup>.

A number of mechanisms for membrane separation have been studied, with the most important is solution diffusion and molecular sieving.<sup>16</sup> The factors which formally defined by the gas permeability (transport factor) and selectivity (separation factor), respectively, and are inversely related. The purpose of membrane studies has thus been to reach this maximum to achieve both high permeability and high selectivity, in addition to adequate robustness and material life time.

The mechanisms for separation in inorganic membranes are typically based upon adsorption selectivity and surface diffusion, which give rise to relatively low separation factors. Commercially available  $\gamma$ -alumina and silica microporous membranes exhibit significantly higher separation factors (up to 40), however, these are dependent on the stability of the membrane pore size, which is adversely affected by steam in the feed streams. Molecular sieves such as zeolites (aluminosilicate compositions) or non-zeolites (aluminophosphates and silica) have been considered as inorganic membranes. In these cases, the separations are based on kinetic size discrimination within the channels of the porous structures.

Clearly, membranes represent a promising technology for gas separation; however, they suffer a number of drawbacks, particularly with regard to CO<sub>2</sub> capture from flue gas. In this case, the low CO<sub>2</sub> partial pressure provides a minimal driving force for gas separation, which creates an energy penalty due to the need for compression of the feed gas. Membrane materials also suffer from a decrease in permeability over time due to particulate deposition on the surface.







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