Kinetics and Engineering of Carbon Capture by Chemical Looping Process

THESIS

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by

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CERTIFICATE

This is to certify that the thesis entitled “**Kinetics and Engineering of Carbon Capture by Chemical Looping Process**” submitted by **Bolisetty Sreenivasulu** ID. No. **2012PHXF0526H** for the award of **Ph.D** Degree of the Institute embodies original work done by him under my supervision.

Signature in full of the Supervisor------------------------------------

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Dedication

This Ph.D work is dedicated to Prof Dr.K.V.Raghavan who passed away on 12th Oct 2017. He has been my source of inspiration throughout this Ph.D work. Thought provoking discussions and valuable suggestions from him helped immensely in this work.

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ABSTRACT

Global warming due to greenhouse gas emissions leading to the climate change has become a serious concern worldwide. Among the greenhouse gases, carbon dioxide is the major contributor to global warming. This trend continues in the near future too as fossil fuels would continue to be used in power generation sector, a major emission source of CO_2. Hence extensive research efforts have been directed to mitigate the climate change due to global warming like demand side conservation, supply side improvement of efficiency and more importantly carbon capture. Carbon capture solutions in both pre and post combustion modes have been identified viz., adsorption, absorption, membrane separation, cryogenic separation and chemical looping combustion with and without oxygen uncoupling.

In this work, adsorption based carbon capture studies have been done using wide variety of adsorbents viz., CaO, MgO, Zeolites H-Beta, H-ZSM 5, mixed metal oxides, coal flyash doped sorbents mostly focusing on high temperatures. After initial screening of around twenty candidates, five best performing adsorbents and their combinations have been identified that gave high carbon capture for further rigorous standardization. Chemical looping process has been employed in the studies where the sorbent CaO is carbonated and regenerated in alternate cycles to complete the loop. Various process parameters like adsorbent composition, synthesis protocol, morphology, amount of sorbent, temperature, carbonation time, feed gas composition and flow rate have been taken for process standardization. Optimal set of parameters of sorbent composition of CaO-50%, MgO-10%, FA-C-40%, sorbent amount of 20g in powder form, carbonation time of 1hour, temperature of 650^{o}C, feed gas composition of 100% CO_2 (though 40 % CO_2 and 60 %N_2 was close to typical flue gas), feed gas flow rate of 250 cc/min have been identified that gave the highest carbon capture of around 11mmol of CO_2/g_{ads}. Cyclic stability and regenerability studies too have been conducted upto 15cycles to reinforce the long term utility of the sorbent. Thermodynamic studies have been done not only to test the feasibility of the process but also to understand the positive role played by the coal fly ash (CFA) doped sorbents in reducing the regeneration temperature and thereby the energy penalty. Kinetic studies have been done to identify the best suited model that fit the experimental data. It was found that first order model was best suited with kinetic controlled regime during the initial stages and diffusion controlled regime for the rest of the process. The rate constant and activation energies for the reaction and diffusion regimes respectively are found to be 2.5min^{-1}, 23kJ/mol and 0.8min^{-1}, 30kJ/mol). Calcination kinetics also was found to follow the 2nd order model with kinetic rate constant and activation energies in the kinetic regimes estimated respectively as 1.6 $m^3.kmol^{-1}.min^{-1}$ and 36 kJ/mol. Our studies proved that high temperature carbon capture could be effectively done using appropriate sorbents doped with CFA that would facilitate the integration of carbon capture process with power generation systems thereby making it commercially viable. Characterization tools viz., SEM, XRD, EDX and XRF, have been employed to understand the physico-chemical changes during the CC process.

Keywords: High temperature carbon capture, synthesis of adsorbent, coal flyash doped sorbents, Adsorption, process standardization, cyclic stability, regenerability, thermokinetic investigations, kinetic model and validation

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LIST OF SYMBOLS

f_{calc} : The fraction of $CaCO_3$ calcined to CaO sorbent with reference to moles of $CaCO_3$ sorbent from former carbonation and ranges from 0 to 1 in every cycle.

X: sorbent conversion and is the ratio of $\Delta M/\Delta M_\infty$

M_∞: final mass of sorbent after 60 minutes carbonation cycle period.

ΔM : the mass loss of sorbent due to regeneration at time (t)

ΔM_∞ : the mass loss of all the sorbent assumed to have completely regenerated.

X_{calc} : final $CaCO_3$ contents of calciner (moles of $CaCO_3$ per mole of CaO)

X_{carb} : initial $CaCO_3$ contents of calciner (moles of $CaCO_3$ per mole of CaO)

$X_{carb} – X_{calc}$: the $CaCO_3$ sorbent in the sorbent calcined per mole of CaO in the sorbent.

k_c is the kinetic constant of $CaCO_3$ calcination ($m^3.kmol^{-1}.s^{-1}$)

E_{ac} is the activation energy of the kinetic constant of $CaCO_3$ calcination.

k_{c0} is the pre-exponential factor of the kinetic constant of $CaCO_3$ calcination.

$C_{CO_2}$is the concentration of CO_2 in the gas phase ($kmol/m^3$).

C_{eq} is the equilibrium concentration of CO_2 in the gas phase ($kmol/m^3$).

P_{CO_2}, is the partial pressure of CO_2

$P_{CO_2,eq}$ is the equilibrium partial pressure of CO_2

ABBREVIATIONS/ACRONYMS

AAP: Agglomeration and Attrition of particles
AR: Air Reactor
BESs: Bio Electrochemical Systems
BJH: Barrel-Joyner-Halenda
BR-MPBR: Biomass Retention-Membrane Photo Bioreactor
CaLP: Calcium Looping Process
CC: Carbon (or) CO_2 Capture
CLC: Chemical Looping Combustion
CLP: Chemical Looping Process
C-MPBR: Carbonation-Membrane Photo Bioreactor
CP: Co-precipitation
CPT: Cryogenic Packed-bed Technology
CRS: Condensed Rotational Separation
D-IMP: Dry Impregnation
DM: Dispersion Method
FA-C: Fly Ash (C-type)
FA-F: Fly Ash (F-type)
FG: Freeze Granulation
FPSC: Free Piston Stirling Cooler
FR: Fuel Reactor
FzB: Fluidized-Bed
GLS: Gas, Liquid and Solid fuels
GtC: Giga tons of CO_2
Max. CC: Maximum Carbon Capture
MECs: Microbial Electrolysis Cells
MEDC: Microbial Electro Dialysis Cell
MM: Mixing of solids with water and then sintered
OC: Oxygen Carrier
OFC-1: 1st Generation Oxy Fuel Combustion (OFC)
OFC-II: 2nd generation OFC
OFC-III: 3rd generation OFC
PCC: precipitate calcium carbonate
PC-P: Pulsed current processing.
PKB: Packed-bed
SCS: Stirling Cooler System for cryogenic CO_2 capture
SD: Spray Drying
SESR: Sorbent enhanced Steam Reforming
SG: Sol-Gel method
TRL: Technology Readiness Level
W-IMP: Wet Impregnation

1 INTRODUCTION

1.1 GLOBAL WARMING NECESSITATES CO_2 CAPTURE

Global warming is the sustained increase in the average temperature of earth's atmosphere due to accumulation of greenhouse gases (GHG's), especially CO_2. Ever-increasing anthropogenic emissions of CO_2 due to deforestation and industrialization lead to this undesired global warming phenomenon. The first meeting of United Nations Framework Convention on Climate Change (UNFCCC) held in 1992, had triggered global interactions on climate change due to GHG emissions. **Figure 1.1**, shows the global trends in industrial CO_2 emissions [1]. In the last 100 years, atmospheric temperatures have increased by 0.5°C. Also during this time, anthropogenic emissions from fossil fuels led to the release of CO_2 and other GHG's including CH_4, SOx and NOx [2].

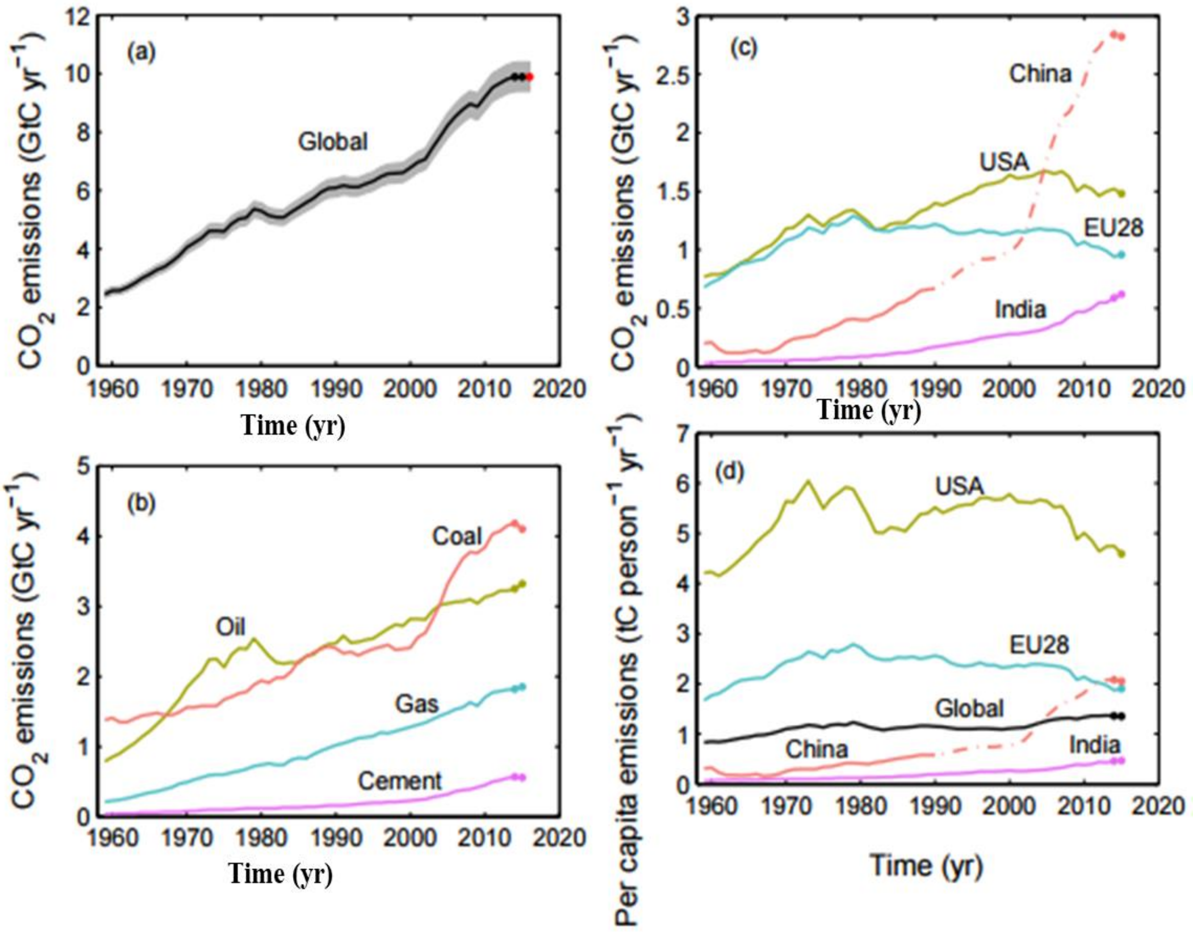

Figure 1.1 (a) Global CO_2 emission trends, (b) Fuel-wise CO_2 emission trends, (c) Region with CO_2 emission trends, (d) Region with per capita CO_2 emission trends

According to the Intergovernmental Panel on Climate Change (IPCC), GHG emissions must be reduced by 50 to 80 percent by the year 2050 to avoid dramatic consequences of global warming. The implications of global warming include ecological imbalance leading to natural disasters, melting of polar ice sheets, increased sea levels, ocean acidification, extinction of natural water resources, acid rains, draughts, etc. **Figure 1.2**, shows the impact of global warming on average land temperature and annual sea level rise [3].

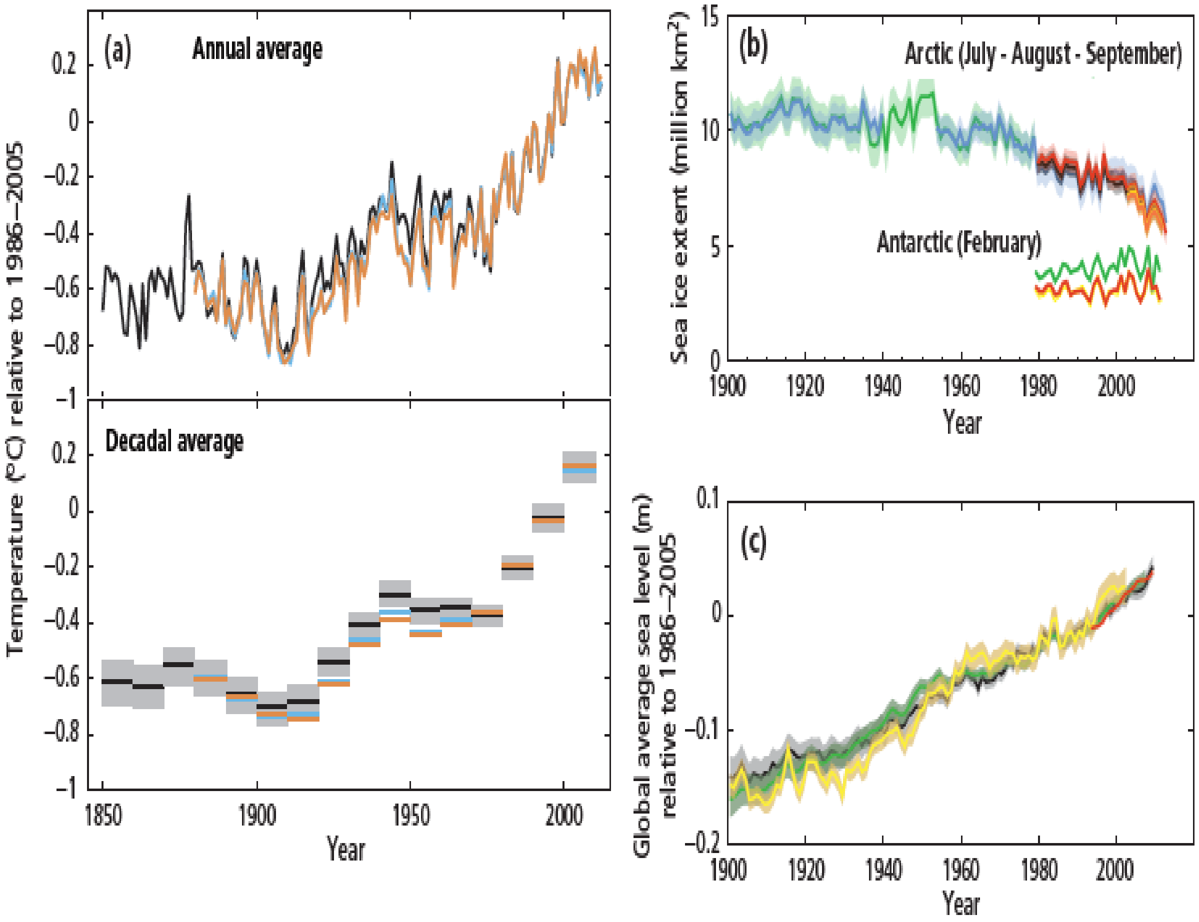

Figure 1.2 (a) Annual and decadal temperature rise trends, (b) Region wise sea ice depletion, (c) Sea level rise with temperature rise trends

Worldwide coal based thermal power stations and cement, iron and steel industries are the major emission sources of CO_2 [4]. Coal is India's primary source of energy and is the 4th largest energy consumer after United States of America, China and Russia [5]. Hence there is an urgent need to implement CO_2 capture (CC) as a mitigation tool to the global warming. Capturing CO_2 at the source of emission is called carbon capture (CC). It could be implemented in two ways viz., pre-combustion (before fuel combustion when CO_2 gas concentrations of >15%) and post combustion (after fuel combustion when CO_2 gas concentrations of 3-15%) of solid, liquid and gaseous fuels. CC could be achieved using technical options of absorption, adsorption, membrane and cryogenic separations. The captured CO_2 is stored in natural or artificial reservoirs (carbon sinks) for an indefinite period to off-set emissions into atmosphere with physical and biological mechanisms. The atmospheric CO_2 capture process through carbon sink option is known as carbon (CO_2) sequestration.

1.2 CO_2 CAPTURE OPTIONS AND THEIR MERITS / DEMERITS

The Carbon Capture and Sequestration (CCS) provide a family of technologies and techniques that enable CO_2 capture for enhancing the sustainability of fuel combustion processes. They could be viewed as a portfolio of solutions with potential to enhance their sustainability levels by introducing new technological solutions, renewable options and enhanced energy utilization efficiencies. The current CC options could achieve only 20-30% of the possible enhancements. The CCS technologies have to be so designed that they deliver consistent environmental and social benefits which outweigh their cost of capital, energy and operation. The first level of CCS technologies focused on the basic requirement of environment viz., minimization of GHG emission for human health and safety with inherent economic tradeoffs [6]. The second and third generation technologies adopted more sustainable retrofits which could readily curtail the use of fossil fuels and capture agents and phase out techno-economically inefficient process options.

There are various technical options of CC viz., CLC, OFC, absorption, adsorption, membrane separation and cryogenic separation. **Table 1.1**, compares them under specified process parameters. The CC options if used in conjunction with CO_2 utilization processes their sustainability levels. The CO_2 utilization technologies for synthesis of urea, precipitated $CaCO_3$, CO and methanol would significantly nullify the associated energy penalties of CC processes. The use of environment friendly materials in CC would further enhance their sustainability levels. For example, CLC option with reusable metal oxides derived from unutilized ores, industrial or agro wastes is a better sustainable option than Oxy fuel combustion (OFC) using O_2 either in pure form or from air.

Table 1.1 Overview of CC Technologies

Parameter	**Post combustion CC**			**Pre and Post combustion CC**			
	OFC	**CLP**	**CLOU**	**Absorption**	**Adsorption**	**Membrane separation**	**Cryogenic separation**
Definition	Pure O_2	O_2 transported via a OC.	O_2 released from OC	CC using liquid solvent	CC using solid sorbent	Selective separation	Cryogenic Temperatures
Principle	O_2 : CO_2 in 1:2 ratio.	*CLP(Type-I)*: Oxidation-Reduction Loop. *CLP(Type-II)*: Carbonation-Regeneration Loop.	Auto reduction of OC to release O_2	Selective absorption	Selective adsorbent.	Diffusivity and pressure difference across the membrane.	Temperature difference
Merits	100%CO_2 capture is possible.	100%CO_2 capture is possible.	Large scale CO_2 capture possible	Retrofitting possible	Easily tunable pore characteristics.	Compact design, low capital costs [7].	ASU and 100% Liquid CO_2 (SCS) are possible[8].
Demerits	Higher cost	scale-up issue	scale-up issue	Scale-up issues with <15% CO_2 conc.	Low CO_2 selectivity.	flue gas impurities, temperature must be >100^oC [7].	High cost and energy consumption [8].
Equipment	Cryogenic ASU and combustion furnace.	PKB or FzB	PKB or FzB	PKB	PKB	PKB	Cryogenic Distillation column
Process intensification	CLOU unit for O_2 supply to the OFC-I unit.	Rotating PKB reactor.	IGCC unit to capture N_2, H_2 and CO_2.	IGCC unit and CC with absorption.	IGCC unit and CC with adsorption.	PKB columns connected in parallel.	ASU with Cryogenic CO_2 capture.
Scale	Commercial	Pilot scale	Pilot scale	Commercial.	Pilot scale.	Commercial.	Commercial.
Max. CC	75-80%	100%	100%	>80%CO_2 [9]	0.088 – 0.176 g CO_2/g_{ads}	100%	93%[7]
Applications	30-70% CO_2 in flue gases.	GLS fuels can be used for >90% CO_2 in flue gases.	GLS fuels used for >90% CO_2 in flue gases.	Industrial Flue gases.	Industrial Flue gases.	>20%CO_2 flue gases.	For a flue gas of 15%CO_2.

Note: CLP (type-I): OC used for fuel combustion; CLP(type-II): OC used for CO_2 capture

Post-Combustion CC processes are well suited for retrofitting into coal / gas fired thermal power plants for CO_2 removal from the flue gases. They generally contain less than 15% of CO_2 with other concentrations of nitrogen, water vapor, SO_x and NO_x. **Figure 1.3**, shows a variety of CC options based on gas-liquid absorption, gas-solid adsorption and solid membrane facilitated separations.

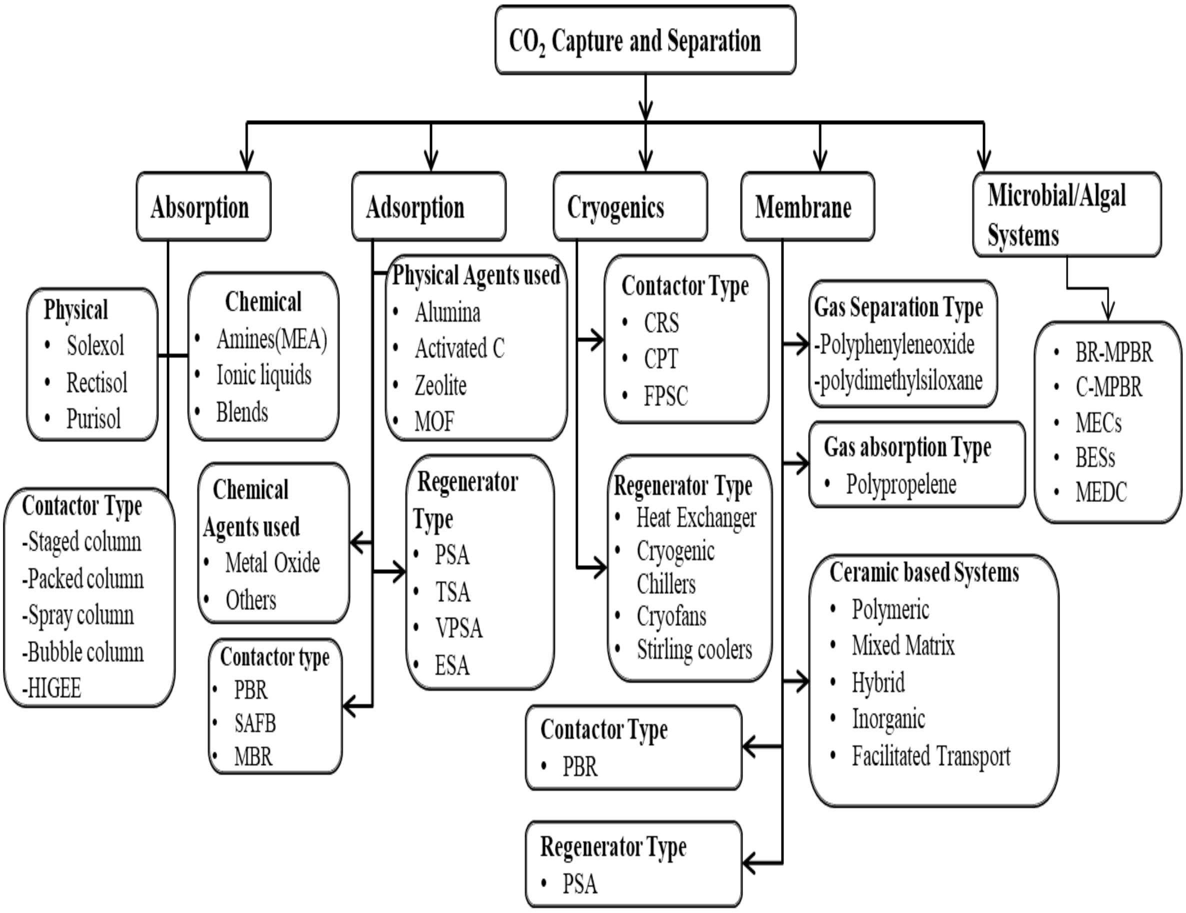

Figure 1.3 Technical options for CCS.

The major factors that were found to influence CC efficiencies are composition, flue gas temperature and energy penalties associated with regeneration. **Table 1.2**, shows a comparison of various contactors based on critical process and design parameters.

Table 1.2 Comparison of various contactors used for CC

S.No	Parameter	Significance	Fluidized-bed	Moving-bed	Packed-bed	Rotary – bed
1.	**Gas-solid Contact**	Perfect contact between phases	Limited	Fair	Good	Excellent
2.	**Thermal Control**	Uniform temperature profile.	Excellent	Good	Limited	Excellent
3.	**Regenerability**	Number of cycles	Good	Good	Limited	Excellent
4.	**Scale-up**	Performance repeatability at larger scale.	Good	Fair	Fair	Excellent
5.	**Pressure Drop**	Lower pressure drop	Good	Good	Fair	Excellent
6.	**Agglomeration and Attrition**	Agglomeration and Attrition losses.	Very high	medium	Limited	Limited
7.	**Oxygen Carrier Circulation**	Circulation rate	Very high	medium	Limited	Limited
8.	**Fuel Conversion**	Maximization	Good	Fair	Excellent	Excellent
9.	**Gas leakage**	Impact on CO_2 separation cost.	Fair	Fair	Limited	Very high
10.	**CO_2 separation**	separation from flue gases	CLC, CLOU, SAFB	CLC, CLOU	Membrane, adsorption, absorption, TSA,PSA,ESA, Cryogenic CO_2 separation	CLC, CLOU
11.	**Insitu CO_2 separation**	Fuel Combustion	Post-CCC,OFC	Post-CCC	Post-CCC &pre-CCC	Post-CCC,CLP, CLOU

1.2.1 Absorption

CC by absorption is the most widely employed technical option among various post-combustion CC options. It is a well-established process which could be easily integrated / retrofitted to any power generation system as an end of the pipe technology. Moreover, it is highly selective with very high CC efficiency. Most of the absorbents are very economical and could be easily regenerated. They have been widely used in coal gasification, petroleum refining, syn-gas production, natural gas (sweetening) and hydrogen manufacture. The energy penalty for CO_2 absorption- desorption lies in the range of 0.37-0.5 MWh/ton of CO_2. By employing more novel solvents and their blends, the energy penalty could be brought down to 0.19-0.2MWh/ton of CO_2. The disadvantage of absorption are noticeable in scale-up, the need for large amount of solvent, toxic nature of solvents and large energy penalties involved in their regeneration and quality improvement.

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1.2.1.1 Absorbent selection

An absorbent should have high reactivity and absorptivity with respect to CO_2, low vapor pressure, easy regenerability, high thermal and chemical degradation stability, low environmental impact (green) and low cost. Among various absorbents used for CC, the earliest and most commonly employed solvent has been monoethanolamine (MEA). It was relatively cheap, has high reactivity and higher absorption rate. It, however, degrades in oxidizing atmosphere, becomes energy intensive during regeneration, has limited CO_2 loading capacity and corrosive with foaming and fouling characteristics on contactors [6]. Other alkanolamines similar to DEA have also been used for absorption but they also suffer from similar drawbacks. MDEA (Methyldiethanolamine) has been employed because of its improved CO_2 loading capacity, corrosion resistance, minimum degradation and reduced regeneration costs but with lower absorption rates [10]. Di-isopropanolamine (DIPA) has also been used due to its high corrosion resistances and lower regeneration costs though with similar drawbacks [11]. Sterically hindered amines acting as AMP (2-amino-2-methyl-1-propanol) have been attempted in CC, since they have high absorption capacity, high selectivity, easy regenerability, corrosion and degradation resistances [12].

Piperazine(PZ)/cyclic diamines have been employed due to their high loading capacity, low regeneration costs and high resistance to corrosion and oxidative and thermal degradation. PZ was more successful as a promoter due to its rapid formation of carbamates with CO_2. Potassium carbonate supported on MgO was reported to achieve an efficiency of 99.4% CO_2 [13]. Studies have also been conducted on CC in a tray absorption tower with >95% CC efficiency [14]. In the recent past, imidazolium ion based ionic liquids (ILs) have been employed due to their unique properties viz., non-explosivity and non-inflammability, high chemical and thermal stability, higher selectivity, higher reaction velocity and negligible vapor pressure [6]. They were also economical, efficient and were compatible with membrane technology due to their non-wettability.

1.2.1.2 Contactors and Process Engineering Aspects

From operation angle, the precooled power plant flue gases enter the absorption system at near atmospheric pressure. The CO_2 lean absorbent from the stripper is pumped into the absorber in a countercurrent fashion. The CO_2 was absorbed to form carbonate or bicarbonate and allied compounds. Since, it is an exothermic reaction, interstage cooling in contact towers is desirable to maintain high absorption efficiency. The CO_2 rich absorbent exiting at the bottom of the contactor is pumped to the top of the stripper operating at 100-150^oC under the influence of a thermal swing operation. The reboiler at the bottom generates stripping steam which meets CO_2 rich absorbent as it flows down the stripper. The temperature swing reverses the CO_2 absorption reaction and returns the same to the gas phase. The CO_2 released from the stripper is compressed and sent for storage [15]. Extensive literature has been reported in the development of efficient gas-liquid contactor configurations, solvent systems and stripper configurations. The main focus of energy investigations was to achieve high capture efficiency with minimal energy penalty [6,16].

Various contactor configurations are employed for CO_2 absorption viz., packed bed, bubble column, rotating packed bed and tray towers. Process flow-sheet modifications have to be made to achieve optimal CO_2 absorption to make it more energy efficient. This could be achieved by employing multiple columns in the pre-treatment stage and in inter-stage temperature control to meet desired temperature range of 40-60^oC [17]. Heat integrated stripping was used to reduce energy requirement (by half or one third) in the regeneration process and the split flow process was used to achieve reduction in energy requirements by 50%. The major factors affecting CO_2 absorption in a packed column are physical properties of the solvent, liquid and gas flow rates, CO_2 partial pressure/total pressure of the system, temperature, absorbent concentration, nature of packing and CO_2 loading on the solvent [18]. Among the physical properties, the surface tension of the solvent has a great influence on mass transfer and effective packing area [19]. The CO_2 partial pressure has a direct influence on the CC efficiency due to the increase in the driving force for the mass transfer [20].

1.2.2 Adsorption

Though a variety of adsorbents have been employed for Post-Combustion CC, no adsorption based technology could be brought to the commercial scale. However, there is a large potential in future for the commercialization since it has significant energy savings as compared to liquid absorption. Their major challenges lie in enhancing the thermal efficiency of the sorbent materials, minimizing the physical attrition problems, improving their time on stream performance and selection of appropriate contactors. It is found that no adsorbent is ideal with no technical demerits eventhough several potential candidates are endowed with regeneration energies significantly lower than the global bench marks. Pressure, temperature and electro-thermal swings have been employed for carrying adsorption – desorption processes driven by physi or chemisorption. Their rate and effectiveness are dictated by the polarity, surface area, pore size and spacing of the selected adsorbents.

1.2.2.1 Adsorbent selection

An ideal adsorbent should have high CO_2 capture capacity, easy regenerability, stability, large pore dimensions and recyclability. Carbon fibre monoliths obtained from poly acrylo nitrile (PAN) and Viscose Rayon fibres and activated carbons are reported for electric swing adsorption (ESA) and pressure swing adsorption (PSA). The efficiencies of various sorbents have been reported for CO_2 capture [6]. High temperature adsorbents similar to calcium chabazite, 13X zeolites and K_2CO_3 based HTC zeolite, hydrotalcite-like (clay minerals) compounds containing nickel and iron cations with and without boehmite alumina have been employed as adsorbents. Pilot test results have been reported for hundred adsorbents in a fixed bed contactor [21]. Amine and carbon based adsorbents have also been tried successfully in CC. The former exhibited high adsorption capacity while the latter had shown higher cyclic stability though with low CC capacity [22]. Future research efforts need to be directed towards the development of novel and cost effective synthesis protocols followed by scale-up [23]. Industrial wastes acting as slags, fly ash, filter cakes, foundry sands, dusts from cyclone, furnace and cement kiln have been reported as low cost adsorbents. Among these, fly ash derived adsorbents have shown a great potential for enhanced and sustained CC at high temperatures [24,25]. Porous silica sand was found to perform better than the silica gel as adsorbent in clathrate hydrate process in achieving higher conversions to hydrates [26].

Various carbon based materials have been employed as adsorbents with appropriate modifications. PEI loaded mesoporous carbons with 65% loading have shown a sorption capacity of 4.82mmol-CO_2/g-sorbent [27]. Of late, the novel biomass based carbon adsorbents have been developed as a greener option with advantages of low cost, high selectivity, easy regenerability and high stability in humid conditions. Olive stones and almond shells have been reported as carbon adsorbents with high adsorption capacity

(4.8mmol/g at 101kPa and 0^oC) [28]. Bio-char from sugarcane bagasse modified by hickory wood with an adsorption capacity of 73.55mgCO_2/g at 600^oC was reported [29]. To summarize, the microporous and mesoporous solid adsorbents possess huge potential for large scale CO_2 capture.

1.2.2.2 Contactors and Process Engineering Aspects

Fixed bed (single or multiple columns), normal, bubbling and ultra sound assisted fluidized beds and moving bed contactors have been reported for adsorption due to their relatively simple operation and design. The critical parameters that affect the functioning of the fixed bed contactors are CO_2 concentration in the feed, temperature, feed flow rate and the amount of the adsorbent used. An optimal CO_2 exists at which adsorption capacity is maximum (52mm/g at 15%) since the available active sites would become a limiting factor beyond certain concentration of adsorbate molecules [30]. Adsorption capacity decreases with temperature and low feed flow rate has a negative influence on adsorption capacity due to long residence times. The fixed bed contactors have been employed for clathrate hydrate process for precombustion CC due to lower power requirement and larger surface area available [26]. Moving bed adsorption (MBA) with heat integration has been used for postcombustion CC with one adsorption and two desorption beds [31]. An efficient heat integration between adsorption and desorption beds contributes to energy savings. A CO_2 purity of 97%, recovery of 80% with degree of heat integration of 57% has been achieved. The N_2 was employed as stripping gas which could be replaced with steam. The regeneration heat was estimated to be 2360kJ/mol which is significantly lower than that of MEA scrubbing process. Multi-stage fluidized bed process with inter-stage heat integration for improved energy efficacy using sorbents of K_2CO_3, Na_2CO_3 modified MgO and Li_4SiO_4 was reported [32]. Each stage contains an adsorber, a regenerator and heat exchanger for intra stage heat recovery. Between adjacent stages, an absorber at high temperature was thermally integrated with a regenerator at lower temperature for necessary thermal balance. It was estimated that for a three stage process, a net electrical efficiency of 32.8% was achieved in power plant of 500MW capacity.

1.2.3 Membrane Separation

Membrane separation of CO_2 employs permeability and selectivity of a suitable membrane to separate CO_2 from flue gas mixture. Membrane separation has advantages of the absence of operational problems viz., foaming, flooding, entrainment and channeling [7]. Membrane separation is also reported as a process intensification tool for reactive absorption processes. Ceramic membrane contactors were employed in cases where significant absorption could not be achieved with conventional absorbers [6]. They have been reported to encounter difficulties in scale-up and retrofitting. They also have higher energy penalties. The absorption processes for CC require contacting towers of large diameter (18-20 meters) and length (25 – 30 meters). Membranes with as much as 1000 times more surface area per unit volume were much more effective in minimizing the size of contact towers. CO_2 permeation increased when there was a chemical affinity with specific molecular groups present in the membrane. Cost savings of 35% have been reported in a coal fired power plant operated under vacuum conditions [33]. They offer various advantages viz., no flooding at high flow rates, no unloading at low flow rates, high surface area per unit contact volume, independent control of gas and liquid flow rates, compactness and scalability [34]. The advantages outweigh their fouling issues [6]. From operational point of view, they offer low maintenance cost, relatively low capital cost and small physical footprint which makes it favorable for platform and less energy intensive operations.

Liquid membrane process has been used for the separation of hexane from heptane [35]. Material selection, membrane synthesis, modular concepts are major factors in scale-up and system characterization. The use of catalytic inorganic membrane contactors used for refinery products and CO_2 separation from membrane reformed synthesis have also been reported [6]. The major material development challenges in membrane processes are due to the maintenance of membrane porosity and thickness, in achieving non-wetting characteristics, hydrophobicity and non-polar characteristics and pore size distribution.

1.2.3.1 Membrane Selection

Inorganic membranes and facilitated transport membranes fall under microporous membranes [36]. The membrane support has an asymmetric porous structure (except palladium-based membranes) to minimize flow resistance [37]. They could be configured as modules of hollow-fibres or flat plates. The different types of membranes employed in CC have been widely reported in published literature [6]. Gas absorption occurs in the gas filled membrane pores. The membrane support plays a key role in enhancing the system performance with marginal influence on selectivity. Hyper cross-linked networks consisting of aromatic rings connected to polymeric matrices have been reported to form porous networks. Modification of the network surface could be achieved through functionalization of hyper cross-linked layers [38]. Porous inorganic membranes were used in high temperature CC processes. The mechanisms of CO_2 separation in inorganic membranes are based on surface diffusion and adsorption selectivity with relatively low separation factors. The CO_2 capture could also be achieved with molecular sieve membranes in which CO_2 separation occurs on account of suitably selected and sized channels of its porous structure.

Oxygen permeation involves selective passage of gas molecules through a dense membrane (generally polymeric). Its permeability and selectivity would be critical parameters in the process optimization. A solution-diffusion or a molecular sieving mechanism explains the process. Dense polymeric membranes are successfully used in CC due to their high permeability and flux achieved [39]. Mixed matrix membranes of polyvinyl alcohol containing amines with multi walled carbon nano-tubes (MWCNTs) dispersed as mechanical reinforcing fillers demonstrated high stability. This has been used for gas separation at high pressures upto 1.5MPa. A novel hybrid membrane system based on potassium carbonate doped hydrotalcite-catalyst was used for precombustion CC and H_2 production [40].

In Supported Liquid membranes (SLM), the liquid is dispersed on a porous or non-porous support. The CO_2 in the flue gas is physically or chemically absorbed into the liquid and passes through the membrane support. Viscosity of the liquid plays a key role in the system design and the performance. Ionic liquids have been used to eliminate the solvent evaporation step to achieve higher stability. Selection of the support was found to have marginal influence on the selectivity but it was found to be crucial in determining the stability of the system.

1.2.3.2 Contactors and Process Engineering Aspects

Packed columns have been the most commonly employed contactors for membrane based CC. The critical design parameters for scale-up are pressure drop, temperature, solvents, dispersion effects of gas mixture, mechanical stability, water condensation effects, and flow rates. An average volumetric CO_2 absorption capacity of 1mol/m^3.s could be taken as a baseline performance of packed columns to assess the intensification effects of membrane contactors [41]. For a hollow fiber configuration, the external diameter and thickness of membrane material are 0.001m and 100 microns respectively for a module length between 0.1 to 1m. The potential of N_2 selective membrane for postcombustion CC has been examined for optimization of membrane surface area and energy consumption [6,38].

1.2.4 Chemical Looping Process (CLP) with OFC and CLOU

Chemical Looping Process (CLP) is classified into three types (**Figure 2.4**) and is the 2nd generation of OFC. Chemical Looping Process (type-I) with an oxidation-reduction cycle of an oxygen carrier sorbent in fuel combustion called Chemical Looping Combustion (CLC). CLP (type-II) with carbonation and de-carbonation or reduction cycle of a metal oxide or sorbent for CO_2 capture is called Chemical Looping CO_2 Capture process (CLCC). When calcium based sorbent was used then it is generally referred to as Calcium Looping Process (CaLP). Oxy-fuel combustion is proposed mainly for industrial production of pure CO_2 used in Enhanced Oil Recovery [42]. Sorbent Enhanced Steam Reforming (SESR) or Chemical Loop Reforming (CLR) is the CLP(type-III), in which sorbent is used for in-situ CO_2 capture and separate H_2 production from fuel mainly methane. It was reported that CaO and NiO based sorbents could save 50% energy over conventional steam methane reforming for CO_2 capture at 650^{o}C and enhanced pure H_2 gas production using CH_4 as fuel[43]. OFC (1st generation OFC or OFC-I) is the fuel combustion with pure O_2 gas to avoid NO_x emission and for easy separation of CO_2 from flue gases. Pure O_2 gas is supplied by an air separation unit (ASU). Due to the deployment of very high temperatures (>1500^{o}C) involved with pure O_2 gas used for fuel combustion, thermal stability of materials in furnace construction is a major engineering challenge. Temperature control is achieved by mixing O_2 gas with recycled flue gas of CO_2 in the ratio of 1:2. The third generation of CLC is referred to as CLOU (OFC-III). In this oxygen carrier releases O_2 gas due to auto reduction in the CLC process but with same working principle.

1.2.4.1 Oxygen Carrier (sorbent) Selection

Sorbents are important in CLP system made of active sorbents and inert or supporting sorbents. The sorbents that are used for fuel combustion called oxygen carriers (metal oxides) while the other type of sorbents were used only for CO_2 capture. If fuel combustion involves high temperature and the Ni based metal oxides are found to be better than other metal oxides in terms of reduction capacity but exhibited low strength [6]. Apart from pure metal oxides, mixed metal oxides have been employed to derive synergistic effect from Cu-Ni and Ni-Co metal combinations [44]. In high temperature CLP, the sorbents made of metal oxides for CO_2 capture need to possess substantial mechanical strength and stability for multi-cycle CO_2 capture capacity. These are enhanced with active metal oxides (mainly limestone mineral due to natural abundant availability) supported by inert metal oxides of Al_2O_3, TiO_2, ZrO_2, SiO_2, coal fly ash, etc. They are prepared by mechanical mixing, co-precipitation, freeze-granulation, spray drying and impregnation methods. Perovskites and mixed metal oxides of NiO, Fe_2O_3, Mn_3O_4 are best suited for CLR while mixed oxides were suited for CLP.

1.2.4.2 Contactors and Process Engineering Aspects

Fixed, moving and fluidized bed contactors with single/dual circulating bubbling and spouting facilities have been used for CLP in batch and continuous modes. The typical components for CO_2 capture in CLP are carbonator reactor, regenerator reactor, loop seal, cold traps, hydrogen generator and other auxiliary facilities [6,45]. CC performance of rotary bed reactors employed for CLP was comparatively better than that of fixed and fluid contactors [46,47]. The superior performance of fixed bed contactor is established as far as fuel conversion and CO_2 concentration are concerned. However, oxygen carrier particles have been found to undergo undesirable structural transformations. The commonly employed reactor configurations viz., Packed-bed, fluidized-bed and rotating packed-bed reactors used in CLP were reported in our published paper [6].

1.2.5 Cryogenic Separation

Cryogenic separation of air was known from the early 19th century. The cryogenic separation occurs due to decrease in internal energy with an increase in exergy and its low critical temperature acts as an efficient medium to recover heat [48]. The Cryogenic Society of America defines cryogenic temperatures as temperatures below -153°C [49]. Oxygen is produced commercially either by cryogenic distillation process or by adsorption based processes such as vapor pressure swing adsorption. Cryogenic separations suitable for high

CO_2/H_2S gases in natural gas were mostly employed for off-shore applications. Cryogenic separation of air and cryogenic distillation of carbon dioxide (-73.3^{o}C, at 1 atm.) has got immense industrial importance in CC. Membrane separation, adsorption and cryogenic distillation were among the novel methodologies for CO_2 separation. It separates CO_2 (100% pure) in liquid form with an energy requirement of 1 MJ/Kg CO_2 from other flue gases [50].

1.2.5.1 Coolant or Refrigerant Selection

Cryogenic technologies operate at high pressures and low temperatures (<120K). Helium (He) gas is used as coolant in cryogenic CO_2 capture at -269^{o}C (boiling point). The normal boiling points of permanent gases (helium, hydrogen, neon, nitrogen, oxygen and normal air) are all below -180^{o}C to be used as cryogenic coolants or refrigerants [49]. Cryogenic Stirling Cooler (CSC) uses helium (He) gas as coolant in CO_2 recovery due to its superior thermal performance as compared to the conventional refrigerants [51]. This has an advantage of being small in size and efficient. At the same time the disadvantages are long pre-chilling time and limitation on cooling area. The cryogenic coolants of Liquefied Natural Gas (LNG) and liquid Nitrogen (LN) possess good liquidity with rapid freezing. CSC cryogenic temperature of -140^{o}C can be achieved easily with its cryogenic temperatures at -164^{o}C and -196^{o}C respectively. But, the coolant LNG has high capital cost of installation and flammability [52]. The LN as coolant also has disadvantage of high capital cost of Installation and high production cost as well [53]. Desired temperature would be reached in 240 minutes to pre-chill the system in Stirling Cooler [51]. These systems are preferable to other conventional CC methods due to their small system size, low energy requirement, separation of acid gases in liquid form at high pressure which could be readily pumped to a reservoir. The cryogenic capture process can reach 99% CO_2 capture efficiency (at 1 atmosphere) at -135^{o}C asnd 90% at -120^{o}C [6]. In cryogenic separation of CO_2, the moisture in feed gas should be removed in order to avoid plugging in the system. But, the major limitations of these methodologies are their high capital and operating costs.

1.2.5.2 Contactors and Process Engineering Aspects

Various contactors for cryogenic CC with their kinetic parameters have been reported by us [6]. In condensed rotational separation (CRS), a maximum compression ratio of 4 per stage with heat exchanger effectiveness of 82% is employed to achieve 70-90% CO_2 recovery. The energy penalty has been reported as 9-12% for an inlet CO_2 concentration of 40-70% and for CRS combined with oxygen enriched coal, combustion is reported to be 16%-19% [6]. Cryogenic CO_2 separation is a single process of sequestration and compression. CRS separates CO_2 in liquid form with energy penalty slightly higher than gas compression alone. The inlet conditions of feed and exit conditions of product are maintained at 1bar and 40^oC in CRS. It is capable of producing waste stream purity of $\geq 95\% CO_2$ liquid at 100 bar pressure. Cryogenic combined cycles integrated with molten carbonate fuel cells (MCFC) have been reported with an electrical efficiency similar to that of the original combined cycle (58.7% LHV).

A techno-economic comparison between cryogenic CO_2 capture for cooled packed beds, amine based absorption and membrane separation has been reported [54]. It is found that the availability and the cost of LNG for cryogenic process and the steam for absorption process determines the decision making process. The initial bed temperature, feed flow rates and CO_2 concentration in the feed are critical parameters affecting the process economics. The cryogenic capture would be the best candidate for low pressure drop and simultaneous removal of various impurities in a single process. A novel Stirling Cooler system was employed for cryogenic CC achieving the CO_2 separation from flue gas of 85% with 3.4MJ/kg CO_2 [51]. This was found to be advantageous as the CC could be achieved at atmospheric pressure to avoid the regeneration of solvent and energy penalty due to pressure drop. The long idle times and higher heat transfer resistances limiting the overall efficiency were the challenges to overcome in future research. Besides packed beds and Stirling Coolers, dynamically operated low cost fiber beds (with high area-volume ratio and lower sweep gas pressure drop) have been successfully employed for the enhanced cryogenic CC [51]. Two types of fiber materials have been tested viz., hollow cellulose acetate and monofilament Nylon in a two stage process achieving CO_2 purities between 28 mol% and 99.5 mol%. This would be a potential method to reduce capital costs of the cryogenic method and to increase the CO_2 loading per chilling cycle at larger scales [51]. Cryogenic separation of CO_2 can be done at cryogenic temperatures of CO_2 from other flue gas impurities with disadvantage of higher energy penalty, scale-up and retrofit.

1.3 SCOPE OF PRESENT WORK

Carbon capture has been found to be an effective solution to global warming in mitigating climate change and its consequential effects. This can be done using various technical options like absorption, adsorption, membrane separations, cryogenic separation, chemical looping combustion etc. In the present work, adsorption process has been chosen as it is economical and simple operation and has great scope of improvement in terms of identifying novel, cost effective sorbents and their combinations that can sustain high temperatures and thereby improve its commercial viability by integrating with power sector. The focus of our work is more on high temperature carbon capture which has been a major challenge in any technical option. The role of coal fly ash, an industrial waste which is thermally inert as a doping agent also would be studied in detail with its thermodynamic implications. Chemical looping process where the sorbent material could be employed for longer times using alternate carbonation-calcination cycles would be used in the present study. The study would broadly comprise of sorbent synthesis and characterization, process standardization at two levels and thermokinetic investigations.

The overall objectives of the present study are:

- To design a suitable reactor system that can sustain high temperature for carbon capture studies.
- To identify novel and cost effective sorbents and their compatible combinations for the carbon capture studies.
- To compare various protocols for the synthesis of the sorbent combinations with reference to the morphology and physico-chemical properties achieved.
- To make an experimental design using Taguchi method for process standardization at two levels after identifying the critical process parameters.
- To determine optimal set of process parameters that would give highest carbon capture capacity viz., sorbent composition and morphology, sorbent loading or amount, temperature, carbonation time, feed gas composition and flow rate.
- To conduct cyclic stability and regenerability studies upto 20cycles to confirm the long term usage of the sorbents.
- To do characterization studies using various tools like SEM, XRD, EDX, BET, XRF Optical spectroscopy, etc., to estimate the properties and understand the physico-chemical changes that occur during the capture process.

- To conduct thermodynamic studies to understand the feasibility and spontaneity of the carbon capture process and also to see the possible influence of coal flyash in reducing the energy penalty during regeneration.
- To identify the kinetic model that fits well with the experimental data and thereby estimate the kinetic parameters like rate, order, Arrhenius parameters besides controlling regimes and the influencing factors for both carbonation and calcination
- To identify the future challenges in the research problem identified.

Chapter 1, mainly describes about the anthropogenic emissions of CO_2 into atmosphere which are responsible for global warming and the necessity of CC. It also describes about the technical options of CO_2 capture processes with appropriate remarks. A detailed discussion on absorption, adsorption, membrane separation, chemical looping combustion (CLC) process and cryogenic separation have been undertaken. In each of these technical options sorbent selection and contactors with process engineering aspects are briefly discussed. Analysis of Contactors and process engineering aspects of CLC and cryogenic separation has also been reported.

Chapter 2 describes the advances made in the chemical looping process (CLP) with reference to postcombustion and precombustion CO_2 capture options. Screening of doped sorbents has been analyzed based on morphology of powder and pellet forms. Compressed monolith pelletizer and screen printable monolith pelletizers were used for various synthesized pellet sizes. Special attention has been given on sorbent selection for high temperature CC applications in IGCC (Integrated Gasification Combined Cycle) to separate H_2 gas. This is followed by detailed analysis of CaO or limestone doped sorbents for high temperature carbonation. Cost effective and ecofriendly sorbents from industrial waste are discussed. Sorbent synthesis methods and analytical instruments used for analysis of CC capacities of sorbents are also discussed.

In Chapter 3, First level screening of sorbents has been undertaken with reference to their cost effectiveness, ecofriendly disposability, CO_2 capture capacity, abundant availability and simplicity of sorbent synthesis. In the second level, sorbent screening has been made to ascertain the suitability of double metal oxides doped with fly ash of various compositions. The screening of fly ash compositions has been undertaken to ascertain their suitability as an inert supporting sorbent. Later, the better performing sorbents, their stability studies (using XRD, SEM, EDX and TGA) have been made for multiple carbonation-regeneration cycles.

In Chapter 4, discussion is centered around the evaluation of the thermodynamic feasibility, heat of reaction, equilibrium constants and the equilibrium conversion of the doped sorbent. The Gibbs free energy variation with temperature has been analyzed using HSC chemistry software for alkaline metal silicates carbonation. Mathematical calculation of heat of reaction, equilibrium constant, Gibbs free energy and entropy have been undertaken.

Chapter 5, Sorbent kinetics parameters were calculated for both carbonation and regeneration. Kinetic models adopted for carbonation and regeneration are discussed. Comparison of experimental and model based results analysis was undertaken for both carbonation and calcination cycles.

Finally, Chapter 6 and Chapter 7 highlight the overall conclusions, recommendations for future work and limitations of research study respectively.

2 CHEMICAL LOOPING PROCESS AND SORBENT SYNTHESIS

This chapter describes screening of sorbents based on synthesis protocols, crushing strength and morphological forms of sorbents. The carbon capture through chemical looping process (CLP) with working principle while employing suitable sorbents of mesoporous and micro porous have been discussed. Detailed discussion is presented on applicability of coal fly ash doped sorbents due to their rich alkaline mineral contents contributes as an accelerator to achieve increased CO_2 capture capacity.

2.1 INTRODUCTION

Significant developments in CLP have taken place in terms of sorbents, fuels and reactor configurations during the past two decades [6]. Solid, liquid and gaseous fuels have been used most extensively. The gaseous fuels in the form of syngas, natural gas, refinery gas, biogas etc., have been employed in CLP. The critical issues of gaseous fuels are due to the presence of sulfur and light hydrocarbon impurities. They are also responsible for the reduction of metal oxides reactivity and CO_2 concentration in the exit stream. The selection of appropriate thermodynamically suitable metal oxides and the reactor configuration are crucial for effective operation [55]. CLP using solid fuels (coal, petroleum coke, solid wastes, biomass etc.) have been widely being used in the recent past and fossil fuels acting as coal will remain as the main energy source in future. The sulfur content in the fuel is a critical factor for solid fuels too. It can be tackled by integrating a desulfurizing unit along with CLP reactor system besides selecting robust oxygen carriers that are sulfur resistant [56].

Adsorbents can be classified as microporous (<2nm size), mesoporous (2nm-50nm size) and macro porous (>50nm size). They exist in carbonaceous and non-carbonaceous forms. Adsorption is gaining industrial importance due to the limitations of absorption with respect to stability, corrosion and energy penalty issues [57]. Traditional applications of porous materials are in ion-exchange, catalysis, physical and chemical adsorption. Their effectiveness is governed by their composition and the structural attributes like poresize, shape, void space, volume and surface area. The macroporous materials are larger than the mean free path length of typical fluid molecules which are controlled by viscous flow and bulk diffusion. Their porosity is achieved due to cavities, channels, interstices and the pores that are deeper than wider. The mesoporous materials are still smaller than their mean free path but are controlled by Knudsen diffusion (KDif), surface diffusion (SDif), multilayer adsorption and capillary condensation. Porous materials are used for controlling combustion flames and in solar and thermal energy storage applications [57]. Various types of adsorbents with transport mechanisms viz., viscous flow, bulk diffusion, KDif, SDif and capillary condensation have been reported [58].

Figure 2.1, lists all the three types of adsorbents. Micro porous materials are classified as ultra-micro porous (<0.7nm) and supra micro porous (0.7nm-2nm)[58]. They have higher surface area than mesoporous materials. Their surface area is dependent on particle size, morphology, surface texture and porosity. The internal structures of micro porous materials depend on pore size, shape and pore distribution. In recent years, an attempt was made to understand the surface heterogeneity and pore size assessment of disordered micro and mesoporous carbons by employing statistical mechanics. The underlying mechanisms associated with adsorption, pore condensation, hysteresis behavior in micro and mesoporous carbons with reference to density and quenched solid density functional theories were reported [58].

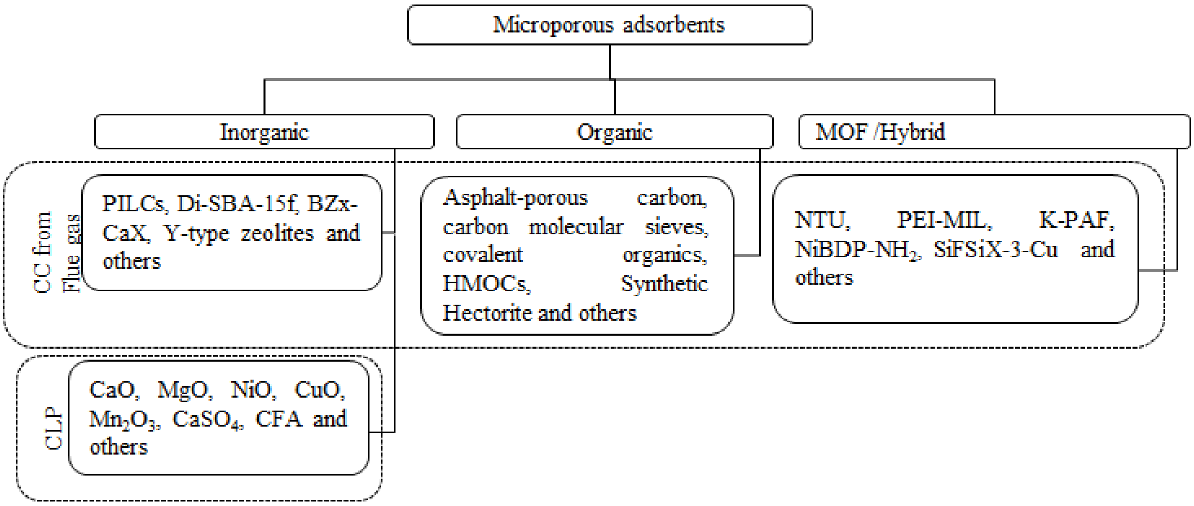


Figure 2.1 Microporous adsorbents in CC

The mesoporous inorganics, organics and metal organic frameworks were examined for CC mainly at ambient pressure and temperatures as in **Figure 2.2**[58]. The CO_2 capture and fuel combustions demand high temperature stability and resistance to contamination. The mesoporous adsorbents cover inorganics, organics and MOFs or their hybrids as adsorbents for CC from flue gases and for fuel combustion in CLP. The characterization of micro and mesoporous carbons, metal organic frameworks, template mesoporous solids and hybrid inorganic- organic structures with disordered pore structures is highly challenging. Their characterization is quite complicated since they neither possess a well-defined pore shape nor a narrow pore size distribution. Well defined 3D models of mesoporous networks are still lacking. Even characterization techniques like inverse size exclusion chromatography (ISEC) in combination with mercury porosimetry and physisorption with N_2/argon have definite limitations. In recent years, the physisorption results of mesoporous materials are explained in combination with other techniques [6,58]. For example, small angle x-ray scattering (SAXS) data of the mesoporous structure over length scales of several orders of magnitude could be interpreted with the help of chord length distribution (CLD) methodology of physisorption [57].

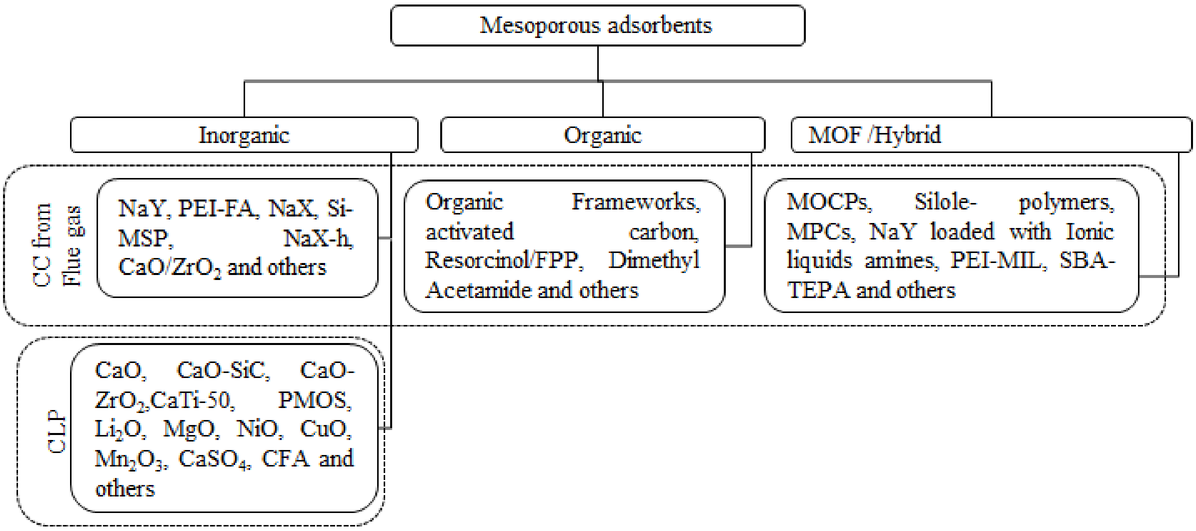


Figure 2.2 Mesoporous adsorbents in CC

Different types of adsorbents synthesized through various protocols could be assessed on their performance in carbon capture employing suitable characterization tools. Further development on adsorbents could only be done based on the results in these tests. The XRD studies on fresh and reused adsorbents give the stability of the adsorbent in terms of crystallinity and the presence of pore blockages, if any, caused during the course of carbon capture. GC or volumetric adsorption apparatus of Micromeritics ASAP 2010 could be employed for estimating carbon capture capacities, adsorption isotherms and isosteric heats. These parameters could be estimated by analyzing the influence of pressure and temperature on the capture capacity using Clausius-Clayperon equation. Various aspects of sorbent materials could be understood by different tools viz., surface morphological changes by SEM studies; functional group changes and their symmetric/asymmetric stretches by FTIR; thermal stability and the effect of temperature of capture capacity using TG/DTA studies, surface area and pore volume and thereby availability of space for further new additives that may be incorporated by impregnation/doping/grafting methods to further foster the adsorbents' performance using BET; elemental analysis and the presence of various chemicals/metals in the adsorbent by EDX tool. All these analytical studies if properly planned, analyzed for fresh and used sorbents shall give a great insight into the mechanism of adsorption based carbon capture. These studies could be used to rank the performance of various adsorbents in terms of carbon capture efficiency, their stability to regenerability, cyclic stability, thermal, mechanical and structural changes. From these interpretations, the synthesis protocols for different materials could be reviewed and new avenues for further process and product development could be formulated.

Inorganic adsorbents used for fuel combustion at >1000 ^{o}C were sintered to evaporate the unburnt carbon particles. Fly-ash with 50% binder material are subjected to deposition-precipitation method with nickel, copper and iron oxides as OC in CLP [57,58]. Sol-gel process coupled with reverse micro emulsion was employed for iso-octane and a surfactant mixture. Ethylene oxide, propylene oxide with 1-pentanol, Aluminium isopropoxide and barium isopropoxide polymers were also synthesized. They were later subjected to temperature induced phase separation and the resulting mixture is washed with acetone and freeze dried to remove volatiles.

The CC studies include technical options and its advances to minimize energy penalty with value added byproducts. **Figure 2.3**, shows the critical unit processes and operations involved in pre and post-combustion CC technologies and their downstream applications in thermal power and fertilizer sectors[6]. It shows that both pre and post-combustion options can be employed for coal and biomass. Gasification and reforming of fuels can be used for achieving enhanced combustion rate and hydrogen production [6].

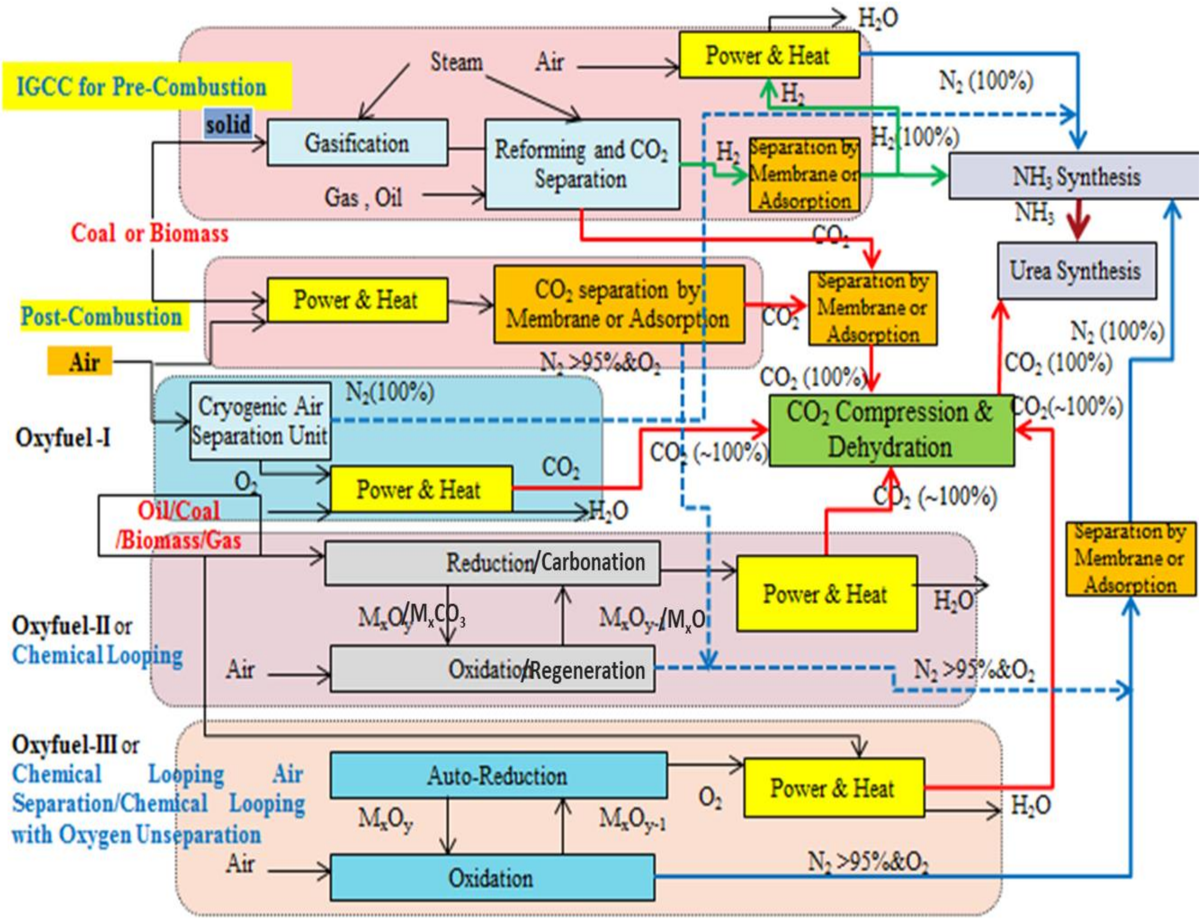


Figure 2.3 CO_2 capture pathways

Insitu ammonia and urea production as value added products will minimize the energy penalties associated with CC [59]. The Oxy-fuel combustion can be implemented in three modes out of which two of them facilitate fuel combustion through a looping process. The current status of the above technologies has been summarized as follows.

- In pre-combustion technologies, upto 90% of carbon in the fuel is converted into synthesis gas through gasification or reforming processes. Employing integrated coal gasification combined cycle (IGCC) concept, the resulting gas can be further converted into a stream of H_2 and CO_2 through a shift reaction. The pre-combustion technologies can be applied to new power plants. Their technologies are yet to reach commercial maturity levels and they require high capital investments due to major changes to retrofit them into boiler and flue gas systems.
- In post-combustion technologies, CO_2 is separated from combustion flue gases by employing absorption, adsorption, membrane separation and other options of fossil fuel based thermal power plants by retrofitting. They are yet to be commercially established except in the case of absorption. The CO_2 in flue gases

with fairly diluted concentrations (10 to 15%) need high recovery, capital costs and 25 to 30% additional energy penalty for plant operation.

- Oxyfuel, chemical looping and Clatherate hydrate processes can be employed in pre and post-combustion modes. The former employs pure or enriched oxygen for combustion of fuel or flue gases to obtain CO_2 in higher concentration. The Clatherate process forms hydrate crystals from water and CO_2, N_2, O_2, H_2 and natural gas components. The process enables maximum CO_2 recovery of 42.5% at 8.5 Mpa [60].

In all above options for CO_2 capture and recovery, pilot experimentation, modeling, validation tests and field scale demonstrations are essential to establish their commercial viability.

2.1.1 Chemical Looping Process

There are three types of Chemical Looping Processes available till date. All the three types of the CLP's were shown in **Figure 2.4**. CLC (type-II) process with selective OC undergoes carbonation with flue gas and releases CO_2 through reduction (or calcination) upon heating to high temperature.

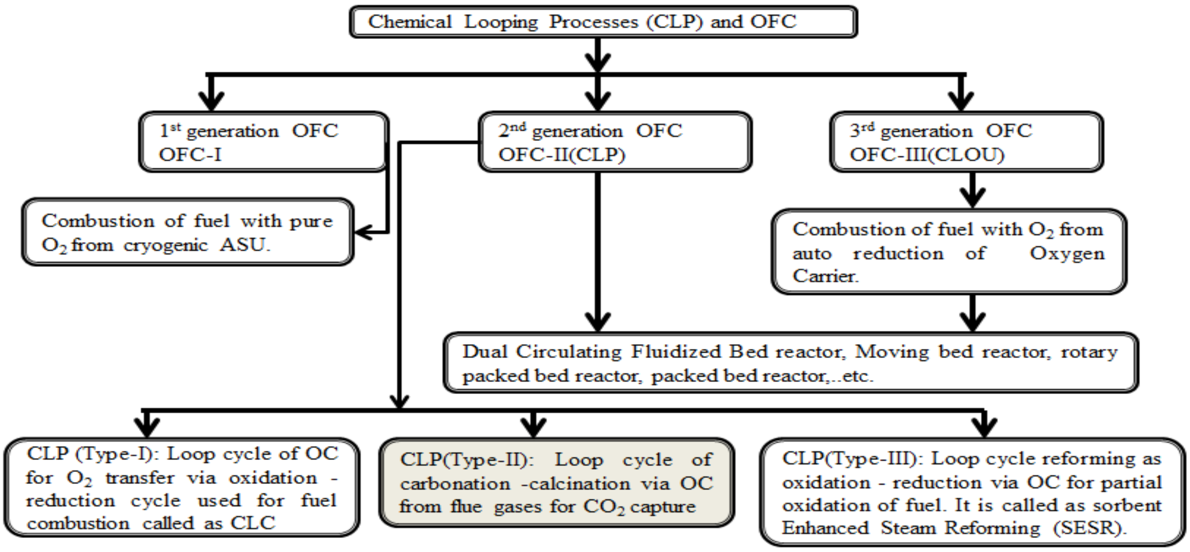


Figure 2.4 Advances in Chemical Looping Process

Power generation is poised to be based on fossil fuels acting as coal for next two to three decades. Using industrial wastes generated from the power sector functioning as coal fly ash would be welcome. This contains many inert alumino-silicates that are stable even at high temperatures [61]. The mechanism of solid fuel combustion follows a two-step process of gasification of solid fuel to form CO and H_2 which then undergo combustion. Another approach is the direct combustion of solid fuel with *in-situ* gasification by CO_2/H_2O [44].

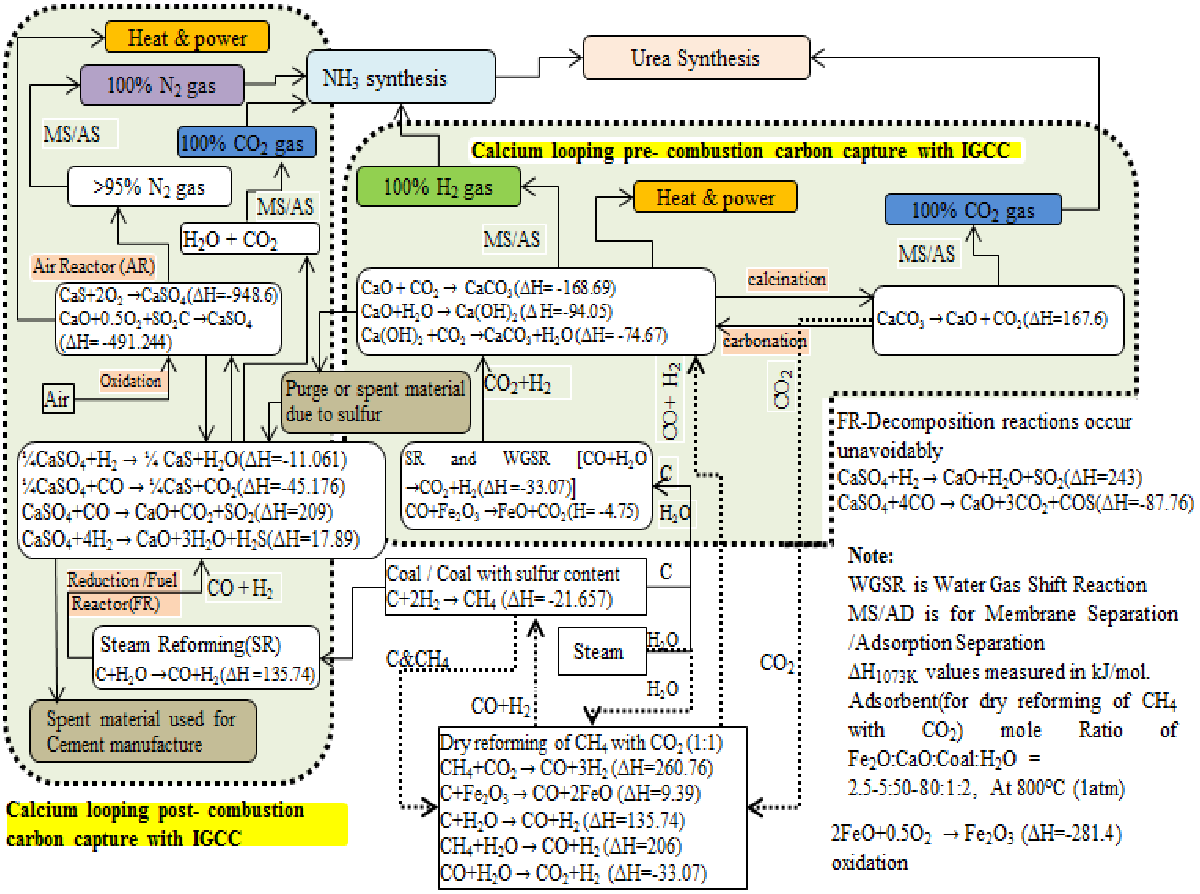


Figure 2.5 Calcium based Chemical Looping.

The CC technology could be commercialized only if it could be successfully integrated with power generation industries that demand thermally stable sorbents. These sorbents should possess the desired attributes functioning with high sorption capacity, selectivity to CO_2, low regeneration energy and easy synthesis protocols [58]. CO_2 capture (CC) and separation from industrial process during coal gasification has got industrial importance due to its high temperature (>400°C) capture from H_2+CO_2 gas mixture as shown in **Figure 2.5** [4]. Limestone doped on Flyash (FA) based porous adsorbents is an ecofriendly and possess resistance to moisture and other contaminants. The spent adsorbent could be used in cement manufacture [58]. Various mixed metal oxide combinations, their synthesis protocols, operating temperatures and enthalpy values are associated with CLP were reported [62]. The CLP technology has the potential to significantly reduce the residence time, reactor size and the complexity in CC. **Figure 2.6** show the working principle of CLP in carbonation-regeneration process cycle using solid sorbents of limestone, MgO, Li_2O etc.

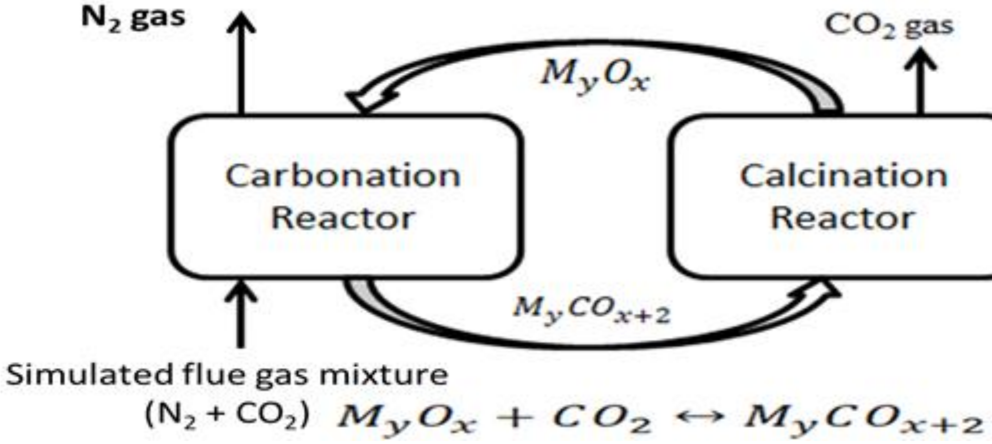


Figure 2.6 Working principle of Chemical Looping Process

Significant research efforts are being made in recent times in the development of novel metal oxides, wide variety of fuels, reactor configurations with various energy integration options. This enables us to understand the kinetics, reactor design and hydrodynamics aspects. Recent reports indicate the use of adsorbents based on limestone, agricultural and industrial wastes for CC. Various type of contactors used for calcium looping process (CLP) were similar to other CLP contactors viz., packed and fluidized beds. These contactor types were discussed in our published paper [58]. But CaO or limestone being cheap, abundantly available and being ecofriendly makes it as a promising alternative to implement in CC applications with minimum energy penalty. High temperature (>400^{o}C) inorganic adsorbents for CC that could be used for CLP were reported with atmospheric pressure [4]. Various adsorbents have been reported in literature with their capture capacity for the single-bed cycle configuration with CO_2 recovery which follows the order as ESA < TSA < PSA < VSA < VTSA [4]. Scale-up of these materials at higher hydrothermal stability towards impurities need to be addressed for commercialization. So far, the best adsorbent process reported is PTSA with highest CC (90% recovery) and CO_2 purity of 99% [6,58].

2.1.2 Role of Inorganic Additives with Coal Fly Ash

The development of a sustainable CC technology is limited by its high energy penalty in pre-combustion, post- combustion and oxy-fuel combustion (OFC) methodologies. A detailed study on various types of sorbents with their CC capacities were reported in our previous paper [63]. Adsorption could be employed for CC in both pre-combustion and post combustion applications and was preferred over absorption, membrane separation and cryogenic separation [6,64]. A significant number of research studies were reported on sorption based CC which was limited by its cost and environmental disposability issues [63]. Various methods of adsorption have been reported for CC employing liquids as well as porous solids. They include porous solid adsorbent (PSaD) materials, zeolites, ZIF, PPN, MOFs, activated carbons, amine containing mesoporous materials, fly ash based porous polymer adsorbents, metal oxide carbonates, perovskites, hydrotalcites and clathrate hydrates listed in **Figure 2.1** and **Figure 2.2** [58]. CaO and its mineral limestone were one of the promising high temperature sorbents among various metal oxides with contactor advances and technological readiness levels (TRL) reported for CC [65].

Limestone and dolomite are two minerals available at a very low cost and the spent material can be used in cement industry. But, its pore blocking nature is the main obstacle for complete carbonation. To avoid this we need to make this adsorbent porous by using industrial waste inert support like CFA. It also contains calcium and magnesium silicates to further enhance CC capacity of adsorbent. The alkaline metal silicates in CFA act as an inert supporting sorbent at high temperature carbon capture. The thermodynamic aspects with feasibility metal silicates carbonation at high temperature (>500^{o}C) has been discussed in 4th chapter. The CO_2 adsorption depends on availability of active sites on surface of a sorbent with basic sites (MgO, CaO) > amphoteric sites (Al_2O_3,) > acidic sites (SiO_2) [4]. Among the CC technologies, adsorption has been the most simple and economical method for CC from flue gases.

2.2 SYNTHESIS PROTOCOLS FOR VARIOUS MORPHOLOGIES

Different types of sorbents synthesized with MM, FZ and DM protocols have been assessed for morphologies based on their structural attributes and performance in CC. The study on sorbent morphology has been done with pelletizer, pellet hardness tester (SISCO - Monsanto type) and surface area analyzer. Further development on adsorbents could only be done based on the results in these CC tests. These morphological parameters of monolithic pellet form and powder form of sorbents were estimated for further analysis. The selected morphological form of sorbents used for carbon capture in chemical looping process (CLP). This has been discussed in 3rd chapter with experimental setup. Solid adsorbents of limestone doped fly ash in the form of monolithic pellets and powder form of sorbents could be tested for CC in packed bed quartz reactor. All the sorbents synthesized initially were made into monolithic pellets using compressed monolithic pelletizer (**Figure 2.7**) and screen printable monolithic pelletizers (**Figure 2.9**) of various granule sizes. The sorbent morphological screening could be done with crushing strength tester as shown in **Figure 2.8** [4]**.**

Figure 2.7 Compressed monolith pelletizer (10mm dia. Size)

Figure 2.8 SISCO- Monsanto type - pellet hardness tester

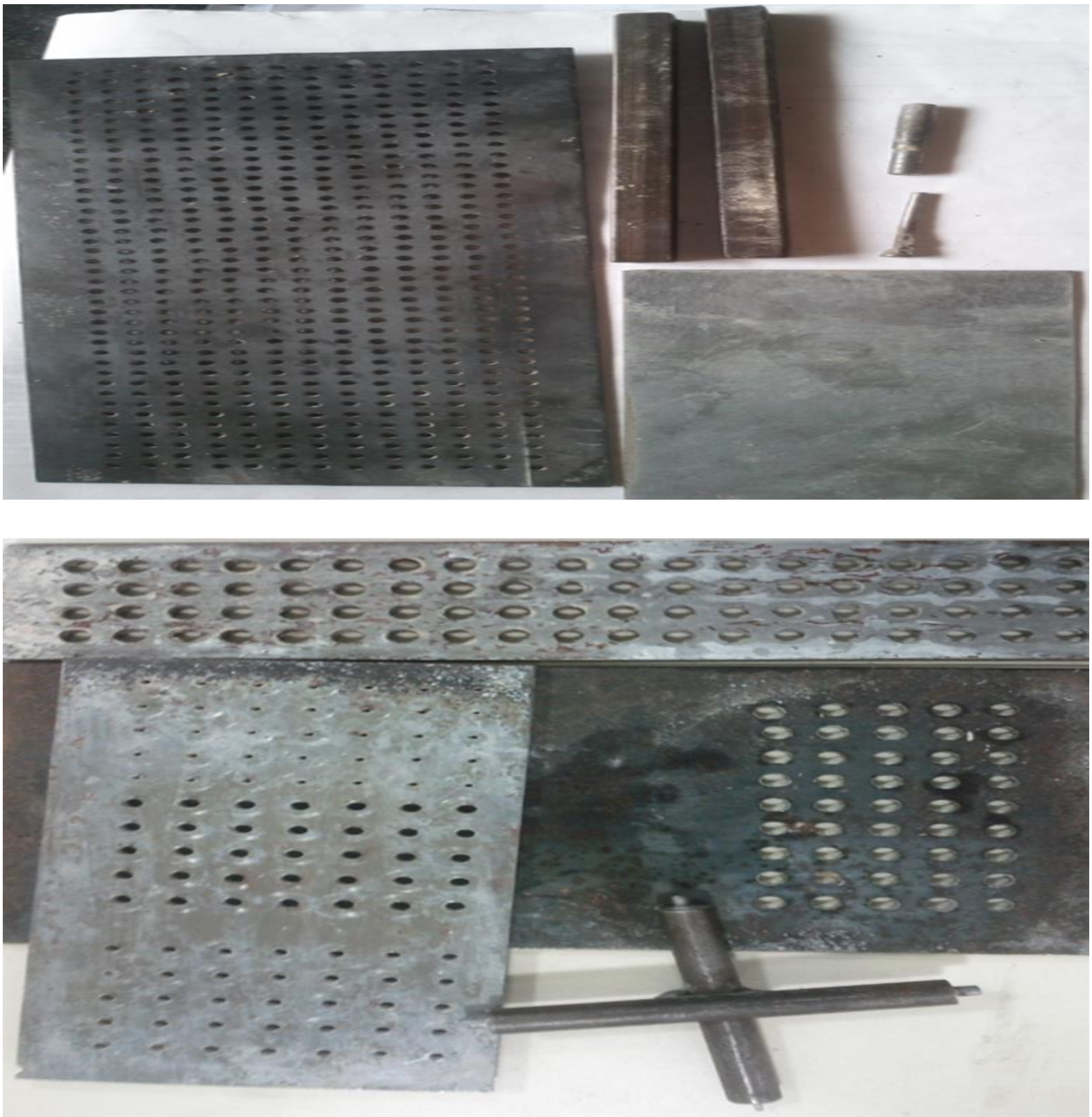


Figure 2.9 Screen printable monolith pelletizers of various sizes

Various aspects could be understood by different tools viz., surface morphological changes by SEM studies; functional group changes and their symmetric/asymmetric stretches by FTIR; thermal stability and the effect of temperature of capture capacity using TG/DTA studies, surface area and pore volume and thereby availability of space for further new additives that may be incorporated by impregnation/doping/grafting methods to further foster the adsorbents performance using BET; elemental analysis and the presence of various chemicals/metals in the adsorbent by EDX tool. All these analytical studies if properly planned, analyzed for fresh and used sorbents shall give a great insight into the mechanism of adsorption based carbon capture. These studies could be used to rank the performance of various adsorbents in terms of carbon capture efficiency, their stability to regenerability, cyclic stability, thermal, mechanical and structural changes. From these interpretations, the synthesis protocols for different materials could be reviewed and new avenues for further process and product development could be formulated.

2.2.1 Powder Morphology

2.2.1.1 Mechanical mixing method of sorbents

In this method, metal oxide and binder material are mixed with water and crushed in specified rotation to form a homogeneous sorbent mixture with suitable viscosity. This mixture is then slowly dried and shaped to the desired shape. Oxygen carrier has been sintered at 1050^oC to increase mechanical strength. Advantages of this MM method include eco-friendly process and there have been no chemical wastes as byproducts with this method. The disadvantages include less strength, Energy penalty due to ball mill and sintering process. Advantages include easy making porous solid adsorbents and surfactants used as templates.

2.2.1.2 Freeze granulation method of sorbents

In this method, the slurry has been prepared by ball milling of solids mixture and additives (dispersant and binder) with deionized water. This homogeneous mixture (slurry) was pumped into the spray nozzle of the freeze granulator into liquid nitrogen container. But, the pelletizer has been used for adjusting size of pellets that were dropped into the liquid nitrogen container. This results in the form of frozen pellet particles. The surface area and porosity of sorbent particles could be adjusted by changing the water content in the slurries. Advantages include size of spheres varied with the variation of air pressure, feed rate and composition of slurry. Disadvantages include emission from sintering and an expensive large scale granulation.

2.2.1.3 Dispersion method of sorbents

The adsorbent composition with binder is mixed and then dispersed in surfactant of poly ethylene glycol polymer (400m.wt). Nitrate of metal oxide and inert/binder material could be dissolved into the solution. A homogeneous solution has been formed after mixing. This sorbent has been dried at different temperatures gradient and sintered at desired high temperature. The oxygen carriers can be produced in the same way as mechanical mixing.

2.2.2 Comparison of synthesis protocols for powder morphology

The synthesized sorbents with powder morphology in MM and FZ methods have been observed to have lower surface area than that of sorbent made of DM. This is due to surfactant being used as binder material in DM than those of MM and FZ. The binder material in MM and FZ that has been used was water causing negligible surface area enhancement. The various powder form morphological sorbents synthesized with dispersion method (DM) are shown in **Table 2.1**. CO_2 adsorption on sorbent is mainly due to Chemical adsorption and forms carbonates from metal oxides. CC depends not only on surface area but also depend on grain boundary diffusion, pore size, temperature and pressure.

Table 2.1 Comparison of sintered sorbents in powdered morphology

Sorbent Code	Raw Material Cost (Rs./gm)	Morphology	Strength (N/cm^2)	S.A (m^2/g)	P.V (cm^3/g)	Pore size (Å)
CaO(30)FA-F(70)	0.277	Powder	-	4.2	0.0057	54.29
CaO	0.39	Powder	-	3.1	0.00316	40.8
MgO	1.04	Powder	-	18.6	0.02843	61.14
CaO(50)MgO(50)	0.715	Powder	-	3.3	0.00671	81.3
CaO(33)MgO(33)Al_2O_3(33)	1.2144	Powder	-	6.8	0.0095	55.9
CaO(33)MgO(33)FA-F(33)	0.4719	Powder	-	3.4	0.0054	63.53
CaO(33)MgO(33)FA-C(33)	0.4719	Powder	-	2.9	0.00423	58.4
CaO(50)H-Beta(50)	5.5445	Powder	-	2.33	0.0047	80.7
CaO(50)H-ZSM-5(50)	5.5445	Powder	-	62.09	0.1892	121.9

2.2.3 Monolithic pellet morphologies

2.2.3.1 Mechanical mixing method (MM)

The sorbent synthesis procedure has been followed similar to the powder form morphology of sorbent. This has been discussed in previous section. Water has been used as binder. Pellets were made using MM synthesis with ethylene glycol-400 as binder material.

2.2.3.2 Freeze granulation method (FZ)

This synthesis method has been discussed in sorbent powder morphological section. The pellets were made with compressed monolithic pelletizer and screen printable pelletizer. Sorbents were made with ethylene glycol-400 and also water as binder material.

2.2.3.3 Dispersion method (DM)

This synthesis method is similar to the DM discussed in earlier section for powder form morphological sorbent. In this we used ethylene glycol-400 as binder material for monolithic pellets.

2.2.4 Process optimization of pellet synthesis

The synthesized monolithic pellet sizes (3mm, 4mm and 5mm) with an aspect ratio (ratio of thickness to diameter) must always be equal to one. This is to avoid the non-uniformity of reaction (aspect ratio of one is selected for pellet to avoid unreacted core at the center of the pellet from its surface) from surface to the center of the pellet. **Figure 2.7** and **Figure 2.9** show the monolithic pellets made with pelletizers [4]. Various sizes of the screen printable monolithic pellets are shown in **Figure 2.10** [4].

4mm(dia.)x4mm (length)

3mm(dia.)x5mm(length)

3mm(dia.)x3mm(length)

5mmx5mm

3mmx5mm sintered

4mmx4mm sintered

5mmx5mm sintered

3mmx3mm-after 15th cycle of carbonation

3mmx3mm-after 10th cycle of carbonation

3mmx3mm-after 5th cycle of carbonation

Figure 2.10 Monolithic granule sizes of sorbents synthesized

The sorbent doped with three compounds made of $CaO:Mg(NO_3)_2:NaHCO_3:FA$ have been considered for further studies in this experiment. Various weight ratios were used to find optimal morphological parameters. The effect of attrition may be negligible in packed bed reactor has been used in this experiment. Packed bed reactor, immediate usage of synthesized and sintered particles could be used to prevent disintegration of particles. They should possess optimal strength of pellet for minimal attrition loss during the cyclic process of carbonation and calcination in the packed bed reactor. The design of experiment has been discussed in **Table 2.2** for monolithic morphological studies. The best performing compositions from design of experiments were further optimized with parameters of temperature, flow rate, cycle time and flue gas concentrations. The sample composition ($CaO:Mg(NO_3)_2:NaHCO_3:FA$) weight % ratios were named as A1 for 40:10:20:30; A2 for 30:10:30:30; A3 for 40:20:10:30; A4 for 30:10:40:20.

Table 2.2 Design of Experiments by Taguchi method

Run No.	Sample name	Synthesis method	Binders	Granule size (mm)
1.	A1	FZ	Acetic Acid	3
2.	A1	MM	Acetone	4
3.	A1	DM	Nitric Acid	5
4.	A2	FZ	Acetone	4
5.	A2	MM	Acetic Acid	5
6.	A2	DM	Nitric acid	3
7.	A3	FZ	Nitric Acid	5
8.	A3	MM	Acetone	4
9.	A3	DM	Acetic Acid	3
10.	A4	FZ	Nitric Acid	3
11.	A4	DM	Acetone	5
12.	A4	MM	Acetic Acid	4

2.2.4.1 Effect of synthesis methods

Mechanical methods and freeze granulation has lower level of atomic level mixing and atomic interaction in synthesis to have sufficient active sites for carbonation-calcination process. But, In dispersion method the adsorbent is dispersed polymer makes adsorbent get better mixing as well as atomic level interaction due to Nitric acid. This nitric acid is relatively stronger acidic in nature than that of acetone and acetic acid. Dispersion method of synthesis with nitric acid based synthesis of solid adsorbent gave higher CO_2 capture due to higher alkalinity at the standard optimal operating conditions. It is reported that addition of alkaline metals and fly ash enhances the carbonation and also alkaline silicates decomposition also contributes for enhancement along with synthesis methods for accelerated carbonation [4,66].

2.2.4.2 Effect of composition

The fresh sample compositions of $CaO:Mg(NO_3)_2:NaHCO_3:FA$ in combination of dispersion method and nitric acid binders were shown better CO_2 captures than remaining combinations of binders and synthesis methods. Further improvement of cyclic carbonation and calcinations adsorbents were shown better capture capacities upto three cycles. Beyond third cycle the CC values remains constant and stable.

2.2.4.3 Effect of crushing strength

The adsorbent, CaO:$Mg(NO_3)_2$:$NaHCO_3$:FA, compositions with weight ratios of 30:10:30:30 and 30:10:40:20 performed better strengths with a value of 15N/cm^2 and 20N/cm^2 respectively. The strength could be enhanced by sintering longer times of >10hr at 1050^{o}C. But, Surface area and porosity may affect. The strength is retained upto 3rd cycle for A2 and A4 sample. Decrease in crushing strengths due to calcium and magnesium silicates present in fly ash decompose into alkaline carbonates while sintering the carbonated adsorbent of sample A2 and A4. Emitted CO_2 from $CaCO_3$ decomposition would accelerates the decomposition of Ca and Mg silicates into carbonates and then to alkaline oxides and silicon dioxides [67].

2.2.4.4 Effect of binder

Both acetic acid and acetone are weak acids than nitric acid, which is responsible for atomic level interactions with CaO. During sintering process (at 1050^{o}C) these nitrates decomposes into active sites of metal oxides giving a better sorption capacity towards CO_2. The carbonation at this high temperature is due to chemical adsorption made of covalent bonding of carbon dioxide with sorbents made of metal oxide compound [61]. Presence of calcium and magnesium in fly ash makes the sorbent towards agglomeration resistant.

2.2.4.5 Effect of surface area

Calcined adsorbent is meso porous and the carbonated adsorbent has higher surface area with decreased pore volume by becoming microporous carbonated. Effect of surface area on CC for sample A1 (1mm pellet size) increased for 1st (from 3.2 to 11.5m^2/g) to 3rd cycle (from 1st cycle to 3rd cycle) of carbonation. The surface areas (S.A) for A1 sample after 3rd cycle for 1mm, 3mm and 5mm pellet size are 11.5, 10.8 and 10.4 m^2/g$_{ads}$ respectively. The surface areas (S.A) for A3 sample after 3rd cycle for 1mm, 3mm and 5mm pellet size are 11.3, 11.1 and 11.5 m^2/g$_{ads}$ respectively. The surface areas of A1 and A3 sample (with pellet size of 1mm) increased from 3.2 - 11.5m^2/g and 4.6 - 11.3 m^2/g for 1st to 3rd cycle respectively. The S.A's increased from 1st cycle to 3rd cycle for the pellet sizes of 5mm samples of A1 and A3, are from 3.2-10.4 and 4.8-11.5m^2/g respectively.

2.2.5 Comparison of synthesis methods for pellet morphology

FZ method with ethylene glycol-400 as binder has been used for synthesis of sorbent. In this method, pellet loses strength due to expansion of metal oxides present in it after removing from cryogenic temperature of liquid nitrogen and allowing sorbent to reach room temperature. The DM comparably possesses better pellet strength than MM and FZ methods of sorbent synthesis. Various metal oxide sorbents were synthesized using dispersion synthesis method. Compressed monolithic pellets (10mm dia size) were made before sintering the sorbent for testing morphological form and then crushing strength etc. Various sorbents combinations made of one, two, three and four metal oxides were used to test the morphological variations as shown in **Table 2.3**. It describes about the pellet morphological variations with crushing strengths and pore sizes. All the synthesized sorbents were of mesoporous in nature after sintering.

Table 2.3 Comparison of sintered sorbents in pellet morphology.

Sorbent Code	Raw Material Cost (Rs./gm)	Morphology	Strength (N/cm^2)	S.A (m^2/g)	P.V (cm^3/g)	Pore size (Å)
CaO(50)Clay(50)	0.545	Monolith	10	8.1	0.0158	78.3
CaO(33)FA-C(33)NaOH(33)	0.3372	Monoliths	15	8.5	0.0056	26.3
CaO(50)K_2CO_3(10)FA-F(40)	0.252	Monolith	10BC/30AC	12.8	0.0273	85.313
CaO(50)K_2CO_3(10)FA-F(30)NaOH(10)	0.4267	Monoliths	10BC/40AC	8.6	0.014	65.12
CaO(50)K_2CO_3(10)FA-F(30)$NaHCO_3$(10)	0.422	Monolith	10BC/20AC	9.1	0.0203	89.23
CaO(50)$NaHCO_3$(20)FA-F(30)(0.5g-qurtz wool)	0.315	Monoliths	40BC/50AC	4.6	0.0056	48.7
FA-C	-	Monolith	60BC/50AC	1.62	0.0024	59.26
CaO(50)FA-C(50)	0.195	Monolith	15	12.91	0.023	71
CaO(33)MgO(33)K_2CO_3(33)	0.66	Monolith	35	14.68	0.0316	86.1
CaO(30)FA-C(40)$NaHCO_3$(30)	0.147	Monolith	25BC/40AC	7.41	0.0145	78.27
CaO(40)FA-C(40)$NaHCO_3$(20)	0.176	Monolith	15BC/25AC	7.1	0.0132	74.37

Note: BC: before calcination; AC: after calcination

Figure 2.11 shows the compressed monolithic pellets with random length because of the material cyclic carbonation and regeneration [4]. This causes the particle size variation inside pellet resulting expansion due to carbonation of particle and contraction in particle size due to regeneration. Due to decreased strength, the pellet surface morphology leads to cracks and ends with powder form. Sorbent undergoes stress across grain boundaries from inside of pellet to surface during cyclic carbonation and regeneration reaction.

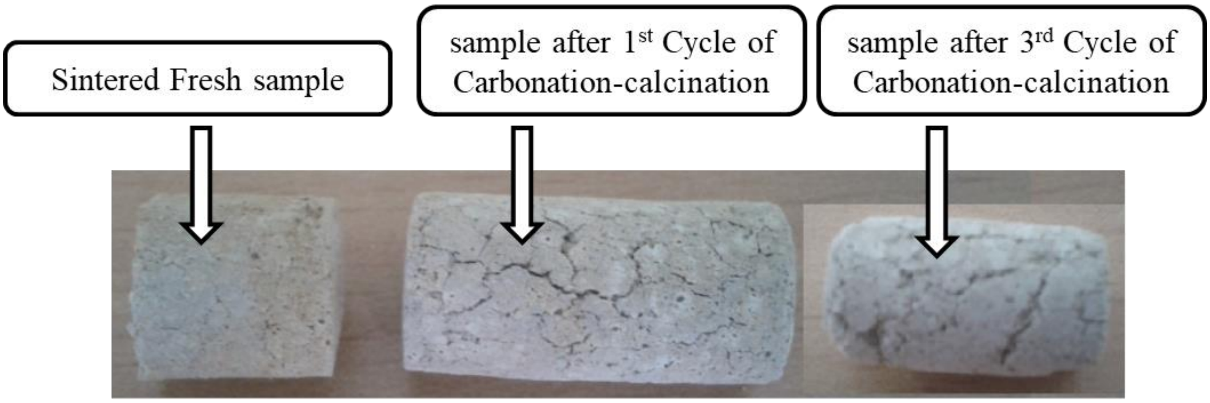


Figure 2.11 Morphological changes in pellets

2.3 CONCLUSIONS

All the tested monolithic pellet sorbents are mesoporous in nature. Sintered (at 1050^{o}C) monoliths of F-type FA (>190N/cm^{2}) have higher crushing strength than C-type-FA (>150N/cm^{2}). Also they have high durability for multiple cycles (calcination – carbonation in packed bed reactor). The doped sorbents of F-type FA (three and four component sorbents) crushing strength ranged from 10N/cm2 to 50N/cm2. Whereas the doped sorbents of C-type FA (single, two and three component sorbents) synthesized pellet crushing strength performance ranged from 10N/cm2 to 60N/cm2. But, the tested monolithic sorbents possess significantly decreased surface area with increased crushing strength which may be due to pore blocking nature of sorbent. These sorbents offer higher resistance to carbonation through diffusion limiting reaction. Granule sizes of higher particle size are needed rather than powder form to minimize pressure drop across bed at higher temperatures. It has been observed that the pelletized granule carbonated until the depth of 2.5 mm from its surface after a prolonged carbonation of two hours(or more). Variation of visual appearance of carbonated material with that of noncarbonated or unreacted core has been observed. The compressed monolithic pellets (**Figure 2.11**) were observed with surface morphological changes in the form of cracks causing pellet to crumble into powder due to cyclic carbonation-regeneration in packed-bed reactor (experimental details of cyclic carbonation-regeneration are described in 3rd chapter). The powdered morhological form of sorbent does not possess agglomeration of sorbent material and is comparatively free from pore blocking nature. These morphological materials possess negligible heat and mass transfer resistance offered towards carbonation reaction. This is applicable only when particles sizes are < 50µm. Hence, the powder forms of sorbents were considered for further studies on screening of sorbents along with its dopants in CC.

Most of the high temperature (>400°C) adsorbents exhibited physical adsorption mechanism. For an adsorbent to be highly effective for carbon capture, the major criteria to be met are high adsorption capacity, selectivity, chemical/mechanical stability, ability to be regenerated with minimum energy penalty, cost effectiveness, minimum heat and mass transfer resistances. From the comparison of performance of different adsorbents, weight percent of adsorbed gas to the total weight of the system is the most important factor. Their CO_2 storage capacity was to be measured at different temperatures and pressures. It is also necessary to evaluate the relationship between their surface area and CO_2 capacity. For assessing the separation capacity of an adsorbent, breakthrough experiments in fixed bed columns employing mixed gas streams will be the best option. It is also important to assess the relative H_2O effects on adsorbent performance. H_2O has both positive effect at low concentrations making it better sorbent regenerator and negative effects at high concentration by decreasing CC capacity. Determining the CO_2 adsorption sites and study of its binding mechanisms would be of great help in designing new carbon capture adsorbents.

The effective CO_2 capture could be achieved for flue gases from thermal power plants as well as water gas-shift reaction (high) temperatures for fossil fuels with limestone doped coal fly ash (CFA) or industrial waste. CaO or limestone based adsorbents with CFA as support could be used for CC in calcination-carbonation cycle and $CaSO_4$ for oxidation - reduction cycle of coal combustion. Around 25% CFA is utilized (in manufacture of cement and fly ash bricks, etc.) from 750 million tons of CFA produced globally and it has adverse environmental impact in terms of polluting ground water with nano sized heavy metal particles [58]. The main drawback of CaO (limestone) based adsorbents in CC is their poor recyclability. The spent CaO in combination with CFA could be reused in cement manufacture to minimize its environmental hazard. The energy penalty, economic viability and its commercialization potential were critical parameters in CC. The profitability depends on CO_2 concentration in flue gas, its pressure and temperature, flue gas type, possible value added products and byproducts that could be derived along with CC. Sorbent modification involving most complex methods appear to be prohibitively expensive and the major challenge is the scalability in sorbent synthesis processes for CCS applications [68]. There is a strong need to evaluate a strategy for the enhancement of CO_2 adsorptions after a first level screening process. It should be aimed at incorporation of unsaturated active centers or doping of metal or nonmetal constituents or chemical functionalization or combinations of them. Incorporation of unsaturated active centers will enhance CO_2 binding capacity and the selectivity. Incorporation of high valency metal ions can enhance chemical and thermal stability of adsorbents. The energy consumption during adsorption / desorption has to be necessarily addressed in carbon capture investigations. CO_2 release and adsorbent regenerations is normally achieved through temperature or pressure (in some cases vacuum) swing methods, all of which require significant energy input. There may be a need to look at more novel strategies to release adsorbed CO_2. In the pursuit of development of cost effective and highly efficient process adsorbents for CC, study of above options are very important. A critical review on the role of micro and mesoporous adsorbents for CC and CLP has shown the superior performance of specific microporous and mesoporous sorbent materials.

The analysis presented highlights the need to evolve a hierarchical approach for screening the powdered adsorbents for CC in Chemical Looping Process (CLP). The factors of adsorbent composition, loading of active materials onto the adsorbents, influence of porous structural attributes and adsorption conditions have to be given due recognition. For large scale CC in CLP applications, environmentally sustainable and cost effective raw material sources have to be identified. Adequate attention has to be given on cycle life time and stability aspects while optimizing the adsorbent composition. The modern tools of process intensification need to be applied wherever needed in adsorbent synthesis and its utilization. Tremendous research opportunities exist in the development of mesoporous adsorbents in the coming years.

3 CARBON CAPTURE USING DOPED SORBENTS

Global warming due to the greenhouse gas (GHG) emissions, mainly CO_2, into the atmosphere has become a serious concern worldwide. There are various technical options available for CC viz., adsorption, absorption, membrane separation, chemical looping process and cryogenic separation in pre- or post-combustion modes. Though absorption technology has been commercialized with few solvents, it suffers from serious intrinsic problems like expensive solvent recovery, corrosion and environmental disposal issues associated with the solvents [69]. Adsorption seems to be next promising technology as there is a wide variety of micro- and meso-porous sorbents. These sorbents include activated carbon from various sources, nitrogen enriched carbon, silica gel, advanced membranes, amine incorporated zeolites and amine modified sorbents. These should be cost effective, efficient and environmentally benign [70]. As power generation is poised to be based on fossil fuels (coal) for next two to three decades, an attempt to use wastes generated from the power sector like coal fly ash would be welcome. This coal fly ash contains many inert alumino-silicates that are highly stable even at high temperatures [61]. Also, the CC technology could be commercialized only if it could be successfully integrated with power generation industries. They demand thermally stable sorbents possessing the desired attributes viz., high sorption capacity, selectivity to CO_2, low regeneration energy and easy synthesis protocols [71].

3.1 SORBENTS AND THEIR PROPERTIES

Many sorbents like activated carbons, zeolites, alkali oxides, ceria based sorbents, amine doped sorbents, etc. have been reported to be applied only for low temperature CC applications. They showed rapid decay in sorption rates and capacities after multiple cycles at high temperatures besides poor mechanical strengths and high regeneration temperatures [72,73]. Ceramic based materials, hydro-talcites and titanium silicates were reported to be suitable for high temperature applications. This was due to their thermal stability, rapid sorption-desorption kinetics and high CO_2 uptake capacity [74].

CC studies have been reported employing CaO, CaO-MgO and coal fly ash based sorbents individually. But not many sorbents were available with these combinations. Attempts have been made with limited success to enhance thermal stability of CaO and MgO based sorbents. Enhanced thermal stability could be achieved using pretreatments which include hydration, thermal treatment, surfactant addition and chemical modification [75,76]. The dispersion of these materials with inert precursors with high Tammann temperature (Tr) using wet or dry processes showed promising results [77,78]. Hence, the coal fly ash, an abundantly available industrial waste, due to its composition of alumino-silicates, favorable kinetics and thermodynamics in the temperature range of 400-800^{o}C would enhance thermal stability and CO_2 uptake of the otherwise vulnerable materials (CaO and MgO) [79,80].

3.2 SELECTION OF FLY ASH

The composition of the two CFA samples taken from XRF analysis is given in **Table 3.1**. These two types of samples are used as inert support to dope the active sorbent of mixed metal oxide in this experiment for further studies on CO_2 capture.

Table 3.1 XRF analysis of the two Coal fly ash Samples.

Sample	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	TiO_2	SO_3
CFA-C(wt%)	17.34	30.78	0.99	36.27	11.54	0.41	0.97	1.67
CFA-F(wt%)	24.01	50.3	5.03	8.89	7.63	1.45	1.72	0.96

Note: CFA-C: coal fly ash- class C type; CFA-F: coal fly ash-class F type

The CFA samples have been named as CFA-C and CFA-F types as their composition matches with standard C and F types with marginal deviation in minor constituents. The typical composition of standard C type is Al_2O_3 (15-20wt%), SiO_2 (20-50wt%), Fe_2O_3 (5-10wt%), CaO (10-40wt%), MgO (3-10wt%), Alkalis (≤8wt%) and that of F type is Al_2O_3 (20-30wt%), SiO_2 (45-65wt%), Fe_2O_3 (4-20wt%), CaO (<10wt%), MgO (0-5wt%), Alkalis (≤ 5wt%)[63]. The standard flyash C and F types were derived from lignite/sub-bituminous and anthracite/bituminous coals respectively. Marginal deviations might be observed in compositions due to geographical location of coal source and does not depend on each other type of CFA. Sorbents were synthesized in powder form.

3.3 EXPERIMENTAL

3.3.1 Experimental setup and procedure

The experimental set-up employed for our studies consists of a fixed bed reactor with necessary temperature controls and an integrated pre-heater. The reactor was made of quartz that can withstand temperatures upto 1200°C. **Figure 3.1** and **Figure 3.2** show the line diagram (discussed in 2nd chapter) and photograph of the experimental set-up respectively [63]. The pre-heater was used to achieve high temperature of gas mixture before entering into furnace (nearly 250°C). The length and diameter of the quartz tube were 55cm and 2.54cm respectively. Gas leakage was prevented using an inert graphite gasket ring installed in the reactor. The reactor temperature was raised in steps of 50°C at a rate of 16°C/min to avoid any damage to the internal circuit. Thermocouples were installed at various locations of the reactor to record the temperatures as a function of time and position during the CC studies.

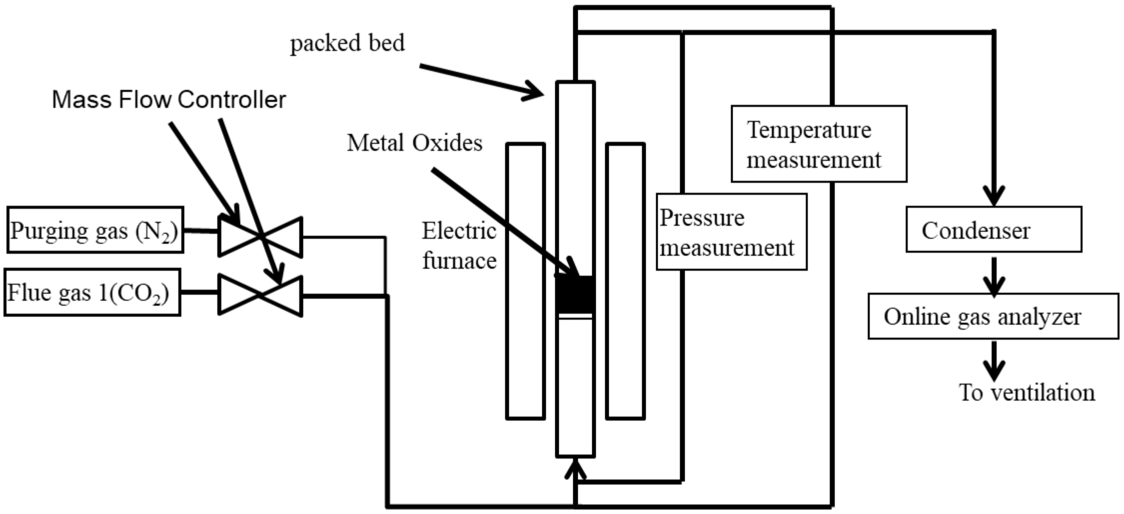


Figure 3.1 The schematic of the packed bed reactor.

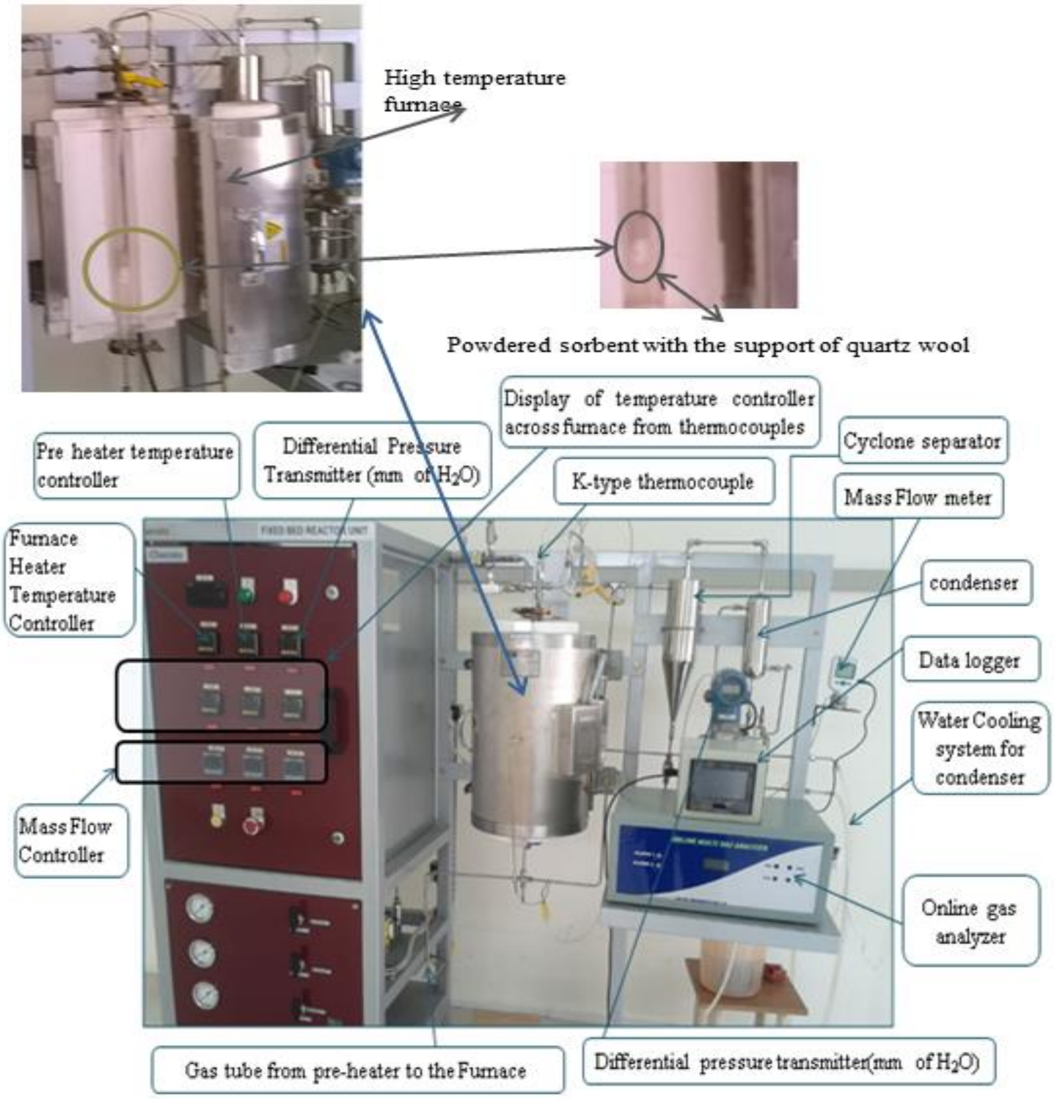


Figure 3.2 Packed Bed Reactor with its accessories.

The desired amount of adsorbent was loaded into the quartz tube and was fixed into the experimental set-up to function as a fixed bed reactor. The power was switched ON and the inert N_2 gas was purged at atmospheric pressure. Heating was continued till the desired temperatures $\leq 250^oC$ of preheater and furnace temperature $\leq 950^oC$ were attained. The temperature controllers of pre-heater and furnace heaters were operated simultaneously. The CO_2 and N_2 gases were made to flow through the reactor at a pre-determined composition. The flow rates of these gases were regulated by the mass flow controller to attain the desired composition. The exit gas composition was measured by an online gas analyzer with data logging facility. The CC data as a function of time was recorded to plot the required breakthrough curves [81]. The CC achieved was estimated using the equation (3.1) below

$$Q_{ads} = \frac{F_o(\rho/M_{wt})(C_o - C_a)t_q}{W} \text{ --(3.1)}$$

Where F_o is feed flow rate (cm^3/minute),

ρ is the density of CO_2 gas at room temperature (mg of CO_2/cm^3),

M_{wt} is the molecular weight of CO_2 gas,

Q_{ads} is CO_2 capture capacity of adsorbent (mmol of CO_2/g_{ads}),

W is sorbent weight (grams),

C_o and C_a are inlet and outlet CO_2 concentrations (cm^3 of CO_2/liter) at time t_q (minutes) respectively.

t_q is breakthrough time taken to capture CO_2 by the adsorbent (minutes) which is given by equation (3.2),

$$t_q = \int_{t=0.05Co}^{t=0.95Co} \left(1 - \frac{C_a}{C_o}\right) dt \text{ --(3.2)}$$

In this case we have taken the t_q as 60 minutes for further analysis of sorbent.

3.3.2 Materials and Analytical Tools Employed

Various materials required for the synthesis of sorbents were CaO, MgO, Al_2O_3, $NaHCO_3$, $MgCO_3$, etc. These were of LR (Laboratory Reagent) grade with purity of >99.7% and were procured from SD Fine-Chem Ltd, Mumbai, India. Coal fly ash (based on lignite coal) was procured from National Thermal Power Corporation (NTPC), Ramagundam, India. The analytical tools employed to understand the physico-chemical changes in these studies were D5000 SIEMENS X-ray diffractometer using Ni-filtered CuK_α radiation ($\lambda = 1.506$ Å) for assessing crystalline nature, SEM Carl Zeiss AG-EVO, 40 Series at an accumulation voltage of 10kV and system resolution of 98eV for morphological studies. BET Surface analyzer from Smart instruments for surface area and pore volume measurements has been used. Energy dispersive X-ray fluorescence (ED-XRF) analysis was done using a Panalytical /Epsilon-1 instrument and a Shimadzu TG-DTA60 have been used for thermo gravimetric differential thermal analysis (TG- DTA) of adsorbents.

3.3.3 Synthesis of Sorbents

All the adsorbents are synthesized in powder form. The initial sorbent selection is governed by factors like abundant availability, desirable oxide combinations, affordable cost, environmental acceptability and desired thermal, mechanical and attrition characteristics. The active metal oxides (limestone, CaO, Fe_2O_3, CuO, NiO, MnO_2, etc) and supporting metal oxides (Al_2O_3, SiO_2, CFA, etc.) were blended with surfactants or dispersant polymers, pelletized and regenerated at temperatures >1050^0C in order to make them sustainable at rigorous operating conditions as shown in **Figure 3.3**[63]. Eight samples (**Table 3.2**) of CaO and its compatible combinations with other metal oxides doped with two types of fly ash (C& F types) were selected for the study. The eight candidate metal oxides are synthesized using dispersion method.

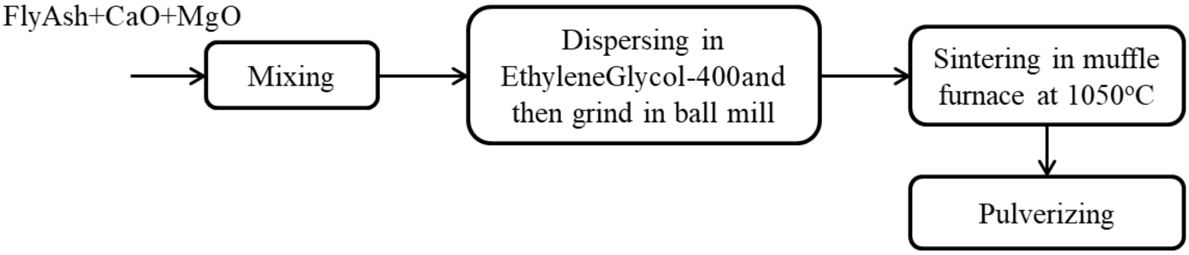


Figure 3.3 Flow sheet of sorbent synthesis.

3.4 TWO LEVEL PROCESS STANDARDIZATION

3.4.1 Parameters Selected

The parameters considered for the first level screening of the nine candidate metal oxides were cost, pore volume, surface area and CC capacity. The fixed bed reactor facility as shown in Error! Reference source not found., was employed for the screening process. The nlet gas consisting of 40% CO_2 and 60% N_2, was fed into the reactor at a flow rate of 250 ml/minute. The exit gas composition was measured by an online gas analyzer. All the first level screening experiments have been conducted at 650^0C with 20g of sorbent for duration of 60 minutes. **Table 3.2** contains the outcome of the first level screening process employing single, two and three component sorbent systems.

Table 3.2 Comparison of doped fly ash sorbents

Sorbent systems	Sample Code	Feed mixture % CO_2	Car-T (^oC)	Cal-T (^oC)	S.A (m^2/g)	P.V (cm^3/g)	Pore size (Å)	CC ($mmolCO_2/g_{ads}$)	Reference
Single component	Limestone(CaO)	40	650	950	3.1	0.00316	40.8	9.2	This work
	CaO(100)*	15	650	900	10.41		500-1000	15.1	[82]
Two component	RHA(Li_2CO_3-SiO_2 4.1:1)	100	710	800	6.2		0-200	7.36	[83]
	FA-Li_4SiO4(SiO2: Li_2CO_3-1:2)	100	500	950				<0.11	[84]
	K-FA 1:1	100	500	500				0.32	[85]
	Diatomite (Li_4SiO_4-SiO2 2:1)	50	700	700				6.9	[86]
	K-FA 2:1	100	500	500				0.23	[85]
	K-FA 2:1	100	600	600				0.36	[85]
	K-FA 2:1	100	700	700				0.82	[85]
	K-FA 1:1	100	700	700				1.45	[85]
	CaO(90):Yb_2O_3(10)	15	650	900	7.15			9.09	[82]
	CaO(30)FA-F(70)	40	650	950	4.2	0.0057	54.29	5.09	This work
	CaO(50)MgO(50)	100	650	950	3.3	0.00671	81.3	11.00	This work
	CaO(50)H-Beta(50)	100	650	950	2.33	0.0047	80.7	11.2	This work
	CaO(50)H-ZSM-5(50)	100	650	950	62.09	0.1892	121.9	11.1	This work
Three component	CaO(30)MgO(30)FA-C(40)	100	650	950	2.9	0.00423	58.4	11.0	This work
	CaO(30)MgO(30)FA-F(40)	100	650	950	2.8	0.00267	38.2	10.8	This work
	CaO(30)MgO(30)Al_2O_3(40)	40	650	950	4.5	0.00654	58.1	7	This work
	Li_2CO_3-FA(40%K_2CO_3)	100	600	950				4.3	[84]
	K-FA 1:1-10%Li_2CO_3	100	700	700				2.4	[85]
	FA-LiSiO4(1:2)-10%K_2CO_3	100	600	600				0.59	[84]
	FA-LiSiO4(1:2)- 20%K_2CO_3	100	600	600				1.27	[84]
	FA-LiSiO4(1:2)- 10%K_2CO_3	100	650	650				0.48	[84]
	Li/Na-FA(0.5:0.5:1)$^{\#}$	14	500	700	1.58			2.54	[87]
	Li/Na-FA(1:1:1)$^{\#}$	14	600	700	0.82			0.86	[87]

Note: CaO(100)*: Synthetic sorbent derived from calcium oxalate; #: carbonation at 12%H_2O in feed gas mixture; Car-T: Carbonation temperature(^oC); Cal-T: Regeneration temperature in N_2 gas; K-FA:K_2CO_3:SiO_2(FA); FA-C: Flyash (C-type); FA-F: Flyash (F-type); Ca is CaO; Mg is MgO; Al is Al_2O_3; H-ZSM-5: H-ZSM-5 zeolite.

3.4.2 Design of Experiments

The Taguchi method, is based on orthogonal array experimentation to provide reduced variance for the optimized control parameters [88,89]. The variation of the chosen parameters include temperatures from 350 to 650^0C, contact time (50 to 60 minutes) of carbonation and sample quantity (20 to 50g) have been chosen as the main process variables. The following mixed oxide compositions have been chosen for optimization process besides above said parameters.

Sample No.	CaO	:	MgO	:	CFA
C1	60	:	0	:	40
C2	50	:	10	:	40
C3	40	:	20	:	40
C4	30	:	30	:	40

Experimental design adopted using the Taguchi optimization process is shown in **Table 3.3**. The relatively better performing sorbent compositions along with a combination of process parameters have been selected for rigorous standardization involving a number of carbonation-regeneration cycles **Figure 3.4** to **Figure 3.7**, shows the analysis of the results of the optimization process.

Table 3.3 Overall CC results post Taguchi method of optimization

Composition (%)	Temperature (^oC)	Time (minutes)	Quantity (gm)	Flow rate (cm^3/mnt)	CC ($mmol/g_{ads}$)
C1	350	15	20	100	4.5
C1	450	30	30	150	7.2
C1	550	45	40	200	6.2
C1	650	60	50	250	5.6
C2	350	30	40	100	3.9
C2	450	15	50	150	3.5
C2	550	60	20	200	11.1
C2	650	45	30	250	8.1
C3	350	45	50	100	6.8
C3	450	60	40	150	3.9
C3	550	15	30	200	7.1
C3	650	30	20	250	8.6
C4	350	45	30	100	4.9
C4	650	60	20	150	11.2
C4	550	30	50	200	8.3
C4	450	15	40	250	6.8

*CC values correspond to 40%CO_2 with N_2.

3.5 RESULTS AND DISCUSSION

3.5.1 Sorbent Selection

Table 3.2 shows that the CC capacity of composite metal oxide samples of this work were found to be in the order CaO(50)H-ZSM-5(50) > CaO(50)H-Beta(50)> CaO(50)MgO(50) > CaO(30)MgO(30)FA-C(40)> CaO. Samples of CaO(50)H-ZSM-5(50) and CaO(50)H-Beta(50) containing zeolite constituents were not only expensive but have been reported to possess inferior surface characteristics beyond 300^0C [58,90,91]. From cost considerations, they were the most expensive for large tonnage CC operations. They were, therefore, not considered for further screening. It has been reported that MgO and MgO – CaO binary mixtures experienced pore blocking during repeated carbonation-regeneration cycles. These were reported to exhibit rapid decay rates and unfavorable thermodynamic conditions at high temperatures [58,92,93]. Hence they too were not considered for further investigations.

The sample CaO(30%)MgO(30%)-FA-C(40%) containing CaO, MgO and flyash (C type) has been chosen as the potential candidate for further optimization owing to its reasonably high CC and high thermal stability due to the presence of fly ash (FA). From these results, it could be understood that efficacy of fly ash in enhancing the CC was highly complex as was reported with contradicting results. This also depends on the composition of flyash, particle size, ash content and ash-metal oxide interactions [6,58]. In our studies, FA-C has given favorable results compared to FA-F owing to the difference in the composition where C type had more CaO content aiding in achieving higher CC. This FA has been reported to form an inert material, gehlenite ($Ca_2Al_2SiO_7$) which has a very high melting point, exhibiting good thermal durability, acting as a physical barrier to prevent sintering and agglomeration of $CaCO_3$ nanoparticles during calcination thereby giving cyclic stability at high temperatures [94,95]. It was also interesting to note from the initial screening results that sample CaO(30%) FA(70%) gave a low CC of 5 mmol CO_2/g_{ads} and this could be clearly attributed to a large amount of FA taken. Though FA acts as a thermal stabilizer leading to a minimal CC, there has to be an optimum amount beyond which it leads to a decrease in the active capturing sorbent material and below which sorbent loses sintering resistance [6,96,97]. Also, greater ash content leads to larger heat consumption in the calciner. The optimum FA/CaO ratio could be predicted by the three dimensional percolation theory to maximize CO_2 uptake [98].

3.5.2 Effect of Critical Process Parameters

Figure 3.4 shows the effect of carbonation time on sorbent performance for the sorbent compositions C1 to C4 at 650^{o}C with 20g of sample quantity. It has been found that the sorbent compositions C2 and C4 have shown the highest CC of >11mmolCO_2/g sorbent at 40% CO_2 gas mixture (0.822cm/s) in 60 minutes. At 650^{0}C, employing pure CO_2, the CC achieved was much higher than that reported (2.4 mmolCO_2/g) for fly ash alone but slightly lower than that reported for CaO-MgO (15.9mmolCO_2/g with 100%CO_2 feed gas in TGA) owing to the difference in composition. It has been reported that the rate of carbonation increases with increase in MgO content in a CaO-MgO mixture and hence maximum CC could be attained faster in C4 sample due to its higher MgO content under identical conditions and hence our results were in perfect agreement with those reported [99,100]. Since MgO is an expensive material, its maximum content in the mixed oxides employed in this work was kept at 30%. The positive influence of FA-C could be attributed to its improved surface attributes, inherent CC ability by the presence of alkaline metal oxides viz., CaO, MgO, Al_2O_3 and SiO_2 besides others.

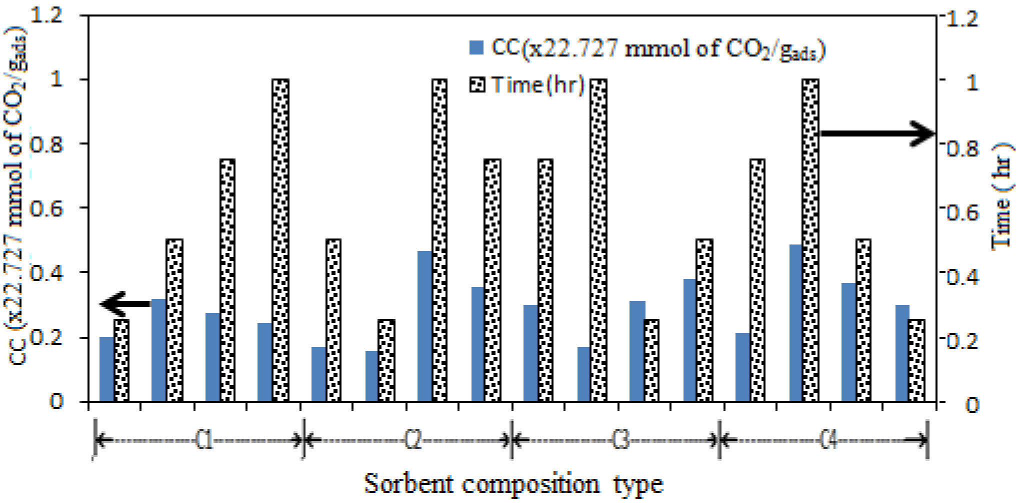


Figure 3.4 Effect of carbonation time on CC

Figure 3.5 Effect of temperature shows the effect of carbonation temperature (350 to 650^{0}C) on the sorbent performance for the sorbent compositions C1 to C4 at 20g sample and 1hr contact time (0.822cm/s). A maximum CC of 11.2 mmol CO_2/g has been achieved by them at 550^{o}C respectively. The increased CC at higher temperatures was due to the enhanced carbonation rate [92]. It has been reported that the carbonation temperature and the partial pressure of CO_2 on CC was very critical and interrelated [101]. It was also reported that the increase in temperature leads to the increase in CC but beyond certain temperature this was offset by the negative impact of sintering of the sorbents. Hence there is always an optimum temperature for achieving maximum CC which was found to be a function of the CO_2 partial pressure/concentration in the feed gas. In our studies too, similar trend has been observed where CC reached a maximum between the temperatures of 550-600^{o}C beyond which it dropped. It has been reported that the optimum carbonation temperatures were around 800^{o}C for pure CO_2 and 660-710^{o}C for 15% CO_2 [102,103]. The TGA and AFM trapping mode studies of these samples have shown that at temperatures beyond 550^{o}C-600^{o}C, the adsorption surface was covered with the carbonated product operating under diffusion controlled regime dominated by grain boundary and lattice diffusional processes [104].

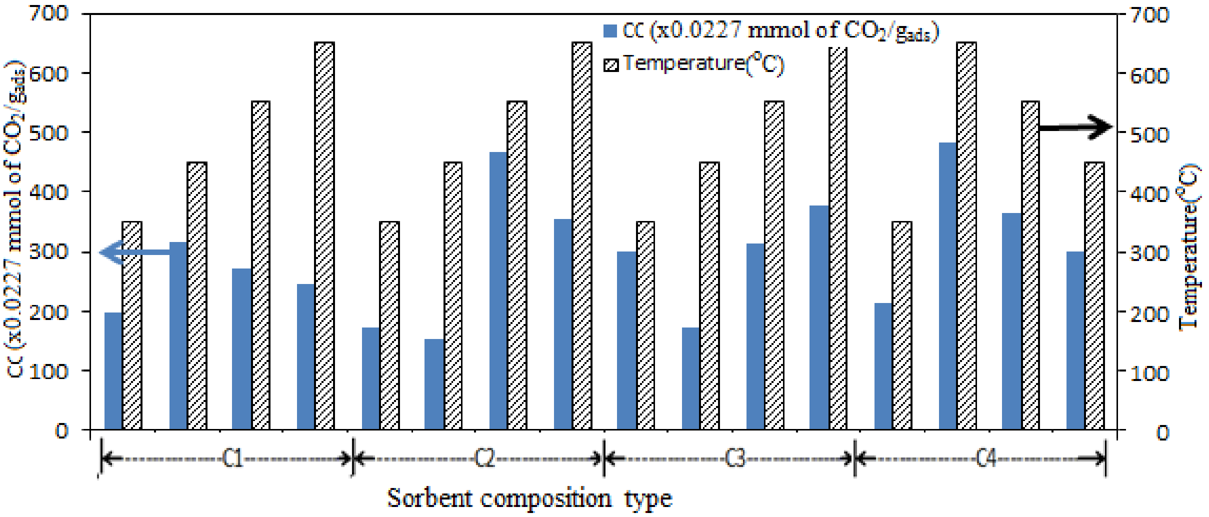


Figure 3.5 Effect of temperature on CC

Figure 3.6 shows the effect of gas flow rates on sorbent carbonation performance for sorbent compositions C1 to C4 at 20g sample and 1hr carbonation contact time (650^{o}C). It has been reported that the carbonation occurs in two stages. Fast carbonation stage upto 1min and slow carbonation stage upto 120min [102]. As the time taken was 60min, increase in CC was observed as the study was within this overall carbonation time frame. It was also reported that maximum CC achievable increases with the CO_2 partial pressure [101]. Hence, as the gas flow rate was increased, the amount of CO_2 to be captured increased. The trends at the corresponding temperatures were taken. It was to be noted that high temperatures and high CO_2 concentrations would lead to undesired sintering effects resulting in a decrease in surface area and pore volume [105]. Accordingly, the gas flow rate and the carbonation times need to be adjusted carefully to avoid this phenomenon. The influence of high gas flow rates at much longer carbonation times need to be studied to gain further insight into this phenomenon and the mechanisms.

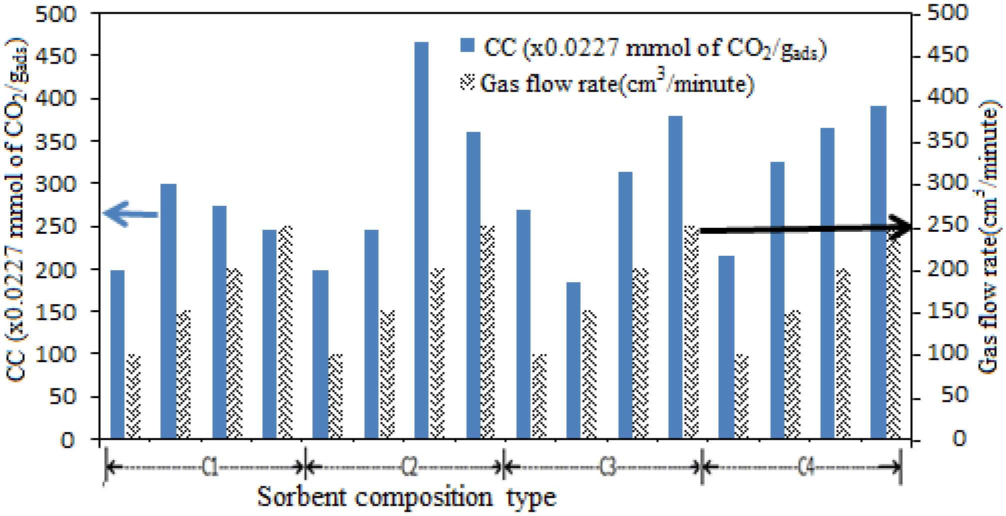


Figure 3.6 Effect of gas flow rate on CC

Figure 3.7 shows the effect of sorbent quantity on sorbent carbonation performance for sorbent compositions C1 to C4 at 650^{o}C with 1hr sorbent carbonation contact time or breakthrough time of adsorption (superficial velocity of 0.822cm/s). It establishes the need for providing optimum sorbent quantity for the carbonation process beyond which it would be counter-productive due to improper contact of the gas with the sorbent. The sorbent C4 provided CC of >11mmolCO_2/g at 20g level for our laboratory set-up. It could be attributed to the availability of enhanced alkalinity and sorption sites and also the presence of larger amount of MgO, the divalent cationic basic oxide. The reported literature has shown the need upto 300g of sorbent loading in the case of laboratory scale packed bed reactors [63,106]. But caution needs to be taken as larger amounts would contribute to greater pressure drops and the undesired channeling effects. The adsorbent amount is strongly dependent on the reactor capacity and design.

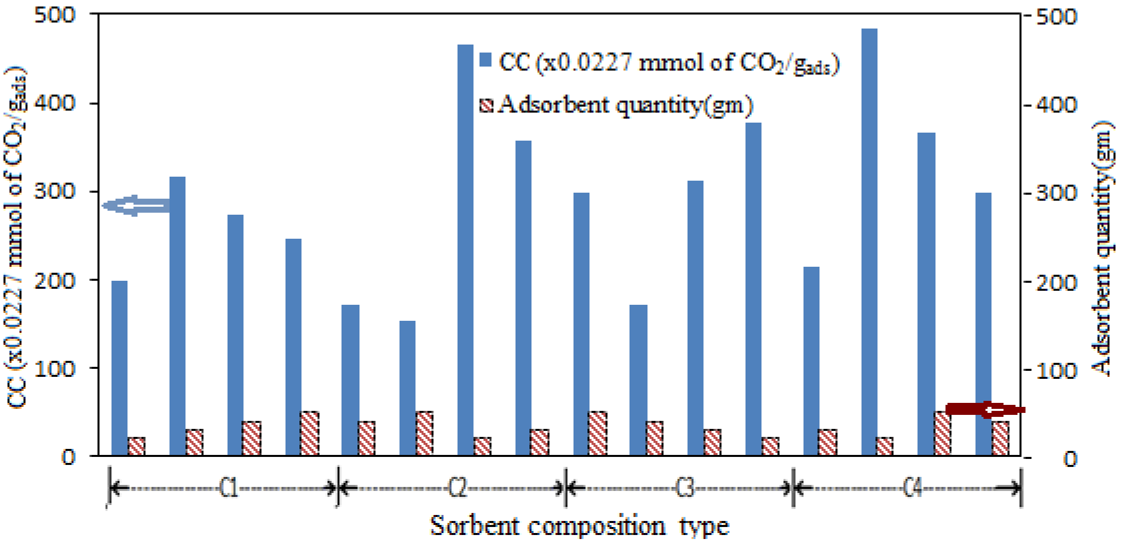


Figure 3.7 Effect of adsorbent quantity on CC

3.6 STUDIES ON SORBENT STABILITY

3.6.1 Procedure Adopted

The CC performance was compared for 15 cycles for the powdered sorbents, C2 and C4 at both 550°C and 650°C respectively (**Figure 3.8**). Regeneration in the presence of N_2 gas was chosen to mitigate the sintering of the sorbents. The heating rate was set at 16°C/minute for a regeneration temperature of 950°C. A pre-regeneration time of 20minutes was maintained. A sample of 20g has been used for each regeneration-carbonation cycle with 60minutes duration. Both C2 and C4 samples registered an increase in CC during the initial few cycles before getting stabilized. The increase in CC initially was due to the self-reactivation effect which would be counteracted by sintering under rigorous regeneration conditions [77]. This was further reinforced by our XRD studies that showed enhanced crystallinity during the initial cycles. This has enhanced the diffusion controlled reaction of CO_2 along the grain boundaries [63,82]. It might also be due to the enhanced surface area availability for carbonation during initial three cycles and calcium silicates decomposition with CO_2 due to the synergistic effect of alkaline metals present in the CFA [63,107].

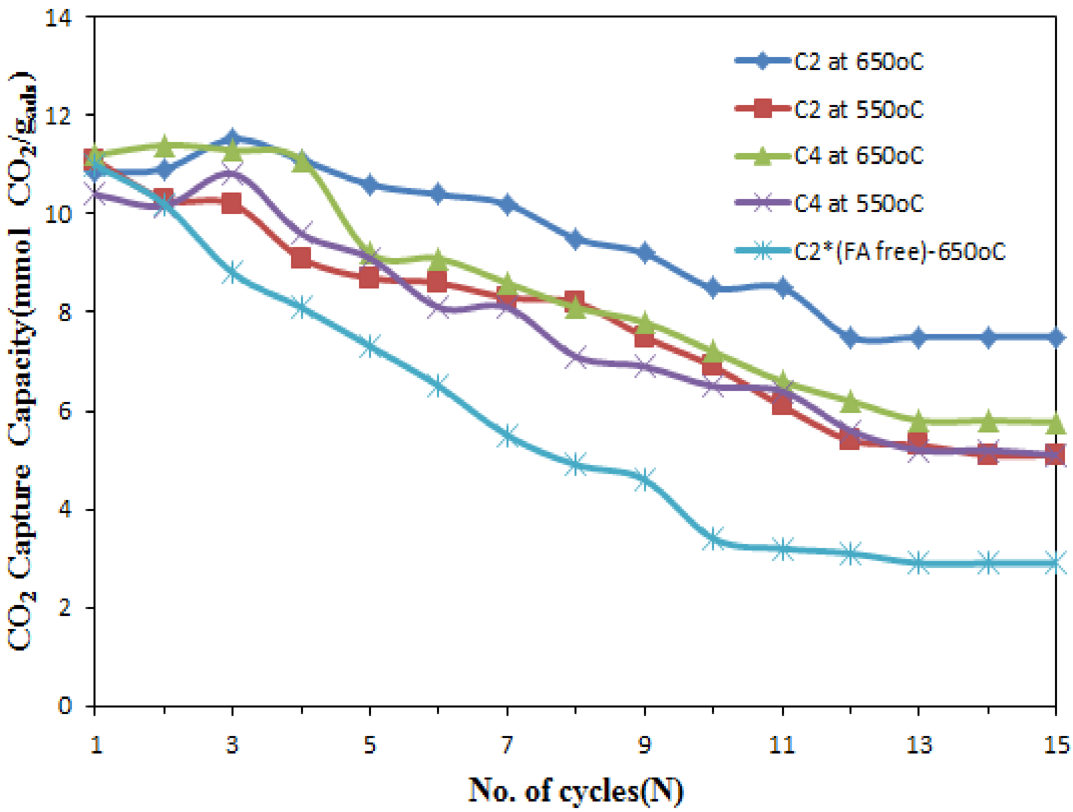


Figure 3.8 Comparison of sorbent cyclic performance carbonation.

C2 and C4 sorbents showed much better cyclic stability than those reported with fly ash and CaO which showed a decay of more than 50% in 15 cycles [6]. Our trends were similar to those reported with fly ash with higher CC achieved under the given conditions [6,77]. Among the sorbents taken, the C2 sample performed better than C4 sample throughout the 15 cycles of operation in terms of CC and the stability. This was in line with reported results where the increase in MgO content led to a decrease in the surface area for CaO to get carbonated [92,108]. Both the samples performed better at 650°C than that at 550°C even at the end of 15th cycle which could be ascribed to the increased surface area, pore diameter, pore volume and absence of sintering effect at higher temperatures. **Figure 3.8**, clearly demonstrates the stability of carbon capture capacity upto 15 cycles with marginal fluctuation. Though studies have been reported on sorbents based on CaO and MgO, very few studies have been reported using fly ash doped sorbents in high temperature carbon capture [63,109]. This adsorbent proved to be a good performing one giving almost an equivalent capture capacity as of CaO-MgO combinations due to beneficial role played by the components of the fly ash.

3.6.2 XRD and SEM studies

A sustainable higher capture capacity of CFA based sorbents was due to the synergistic effect of alkali and alkaline earth metal compounds present in it that would form an inert thermally resistant phase. It has been reported that the presence of alkaline carbonates and SiO_2 enhances regeneration - carbonation looping of CaO based sorbents. Experimental data presented in **Figure 3.8** corroborates the reported finding [63,110]. This was due to the positive contributions made by $CaCO_3$, $MgCO_3$, SiO_2 and other constituents of fly ash in terms of lower activation energy and accelerated rate of carbonation [63,107].

To understand the physico-chemical changes during the CC process, the better performing C2 adsorbent has been subjected to powder XRD, SEM and EDX analysis. The XRD patterns of the used C2 samples from 1st to 15th cycles were shown in **Figure 3.9** and **Figure 3.10**. The decrease in crystalline peak for dolomite and the increase in crystalline peak of $CaCO_3$ were observed from 10th to 15th cycle carbonation due to the synergetic effect of alkaline metals in flyash for the sustainable CC. There were XRD line peaks from 5th cycle to 15th cycle pertaining to the crystalline formation of CaO, $CaCO_3$ and $MgCO_3$. It was due to the decomposition of $CaSiO_3$ with CO_2, emitted by regeneration of other alkaline carbonates at higher temperatures >400°C. It is the synergetic contribution of sorbents alkaline ratio ($CaO:SiO_2$) of >5 need to be present for the carbonation of calcium silicates and magnesium silicates at higher temperatures (>400°C).

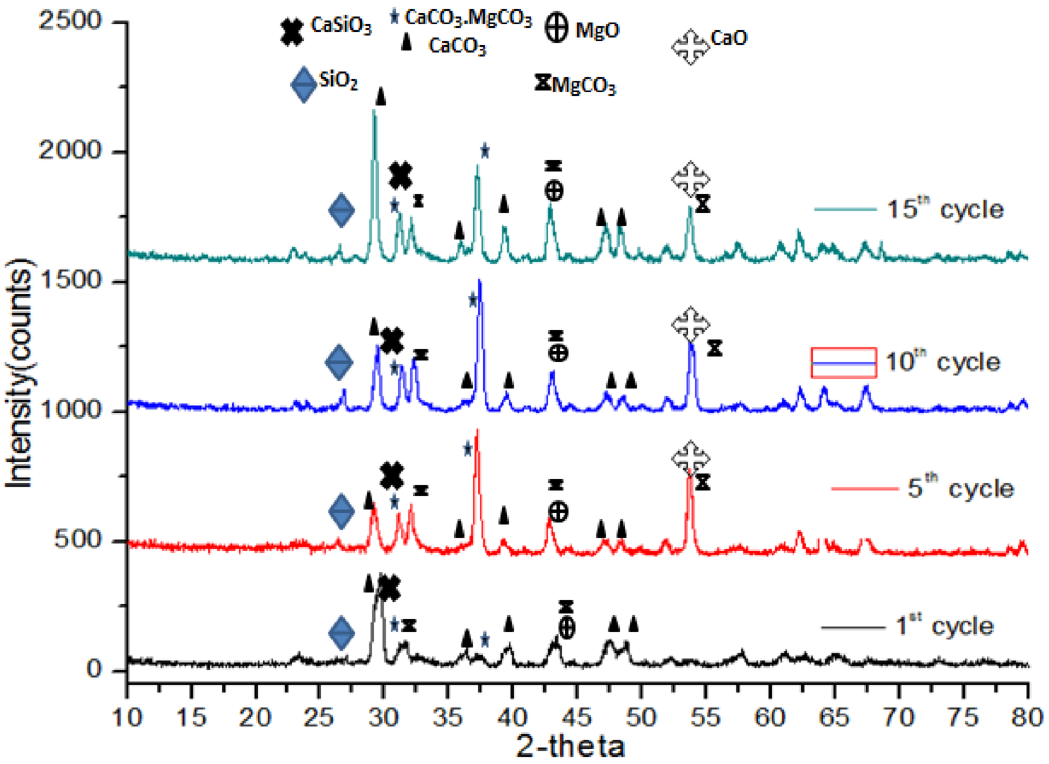


Figure 3.9 XRD of carbonated doped sorbent upto 15 cycles

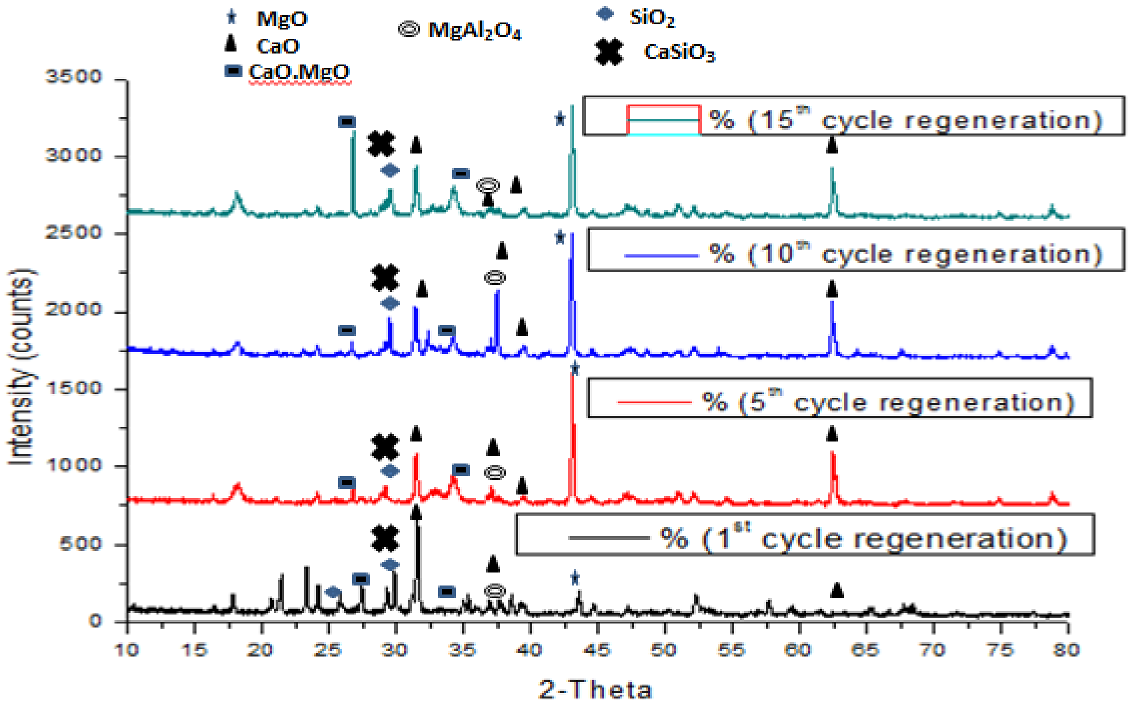


Figure 3.10 XRD of regenerated doped sorbent upto 15 cycles

The surface areas (S.A) of carbonated samples after 1st cycle, 5th cycle, 10th cycle and 15th cycle were 2.01 m^2/g, 3.87 m^2/g, 2.44 m^2/g and 1.81 m^2/g respectively. These areas increased from 1st to 5th cycle carbonation in line with XRD peaks of carbonated samples from 1st to 5th cycle and the capture capacity has increased due to chemical reaction over surface of adsorbent. From the 5th to 15th cycle the S.A has decreased but XRD peaks increased due to diffusion reaction as the dominant contributor for carbonation reaction. Various crystalline phases identified in different peak intensities include, $CaSiO_3$, SiO_2, $MgCO_3$, $CaCO_3$, $MgCO_3.CaCO_3$(dolomite), MgO, CaO and other unidentified phases. Most of these peaks were relatively broad at 1st cycle indicating amorphous or poorly crystalline nature of the materials. Interestingly, there was a gradual increase in the intensity and sharpening of peaks from 1st to 15th cycle indicating better crystallization of the materials with repeated cycles. From 5th-10th cycle, there was a gradual increase of dolomite formation and then decrease of dolomite crystallinity peak at 15th cycle carbonation. Further no new XRD line pertaining to the formation of new crystalline compounds or disappearance of the peaks due to the decomposition and formation of amorphous compounds was observed. However the increase in the intensity of peaks pertaining to $CaCO_3$ and $MgCO_3$ was more due to effective carbonation of the corresponding alkaline metal oxides. The XRD results clearly conform to the stable performance of the C2 adsorbent owing to the stable nature of the constituent materials. **Figure 3.9** and **Figure 3.10**, clearly indicate that regeneration process was highly effective retaining the crystallinity upto 15 cycles and hence CC ability.

The calcined (regenerated) sorbent peaks were represented and analysed in **Figure 3.10**. The regenerated sample shows CaO for 2θ values at an angle of 32.248, 37.4 for (1,1,1), (2,0,0) reflections marginal decrease in crystalline peak from 1st cycle to 15th cycle regeneration (JCPDS37-1497) FCC crystal structure [63,111]. $CaSiO_3$ for 2θ were 29.978^o and 28.858^o values in a plane of (3,2,0) and (2,0,2) reflections respectively with (JCPDS 43-1460) decrease in trend for crystallinity. MgO at an angle of 42.826^o with plane of (2,0,0) FCC (JCPDS 04-0770) shows an increase in crystalline peak from 1st cycle to 15th cycle regeneration. CaO.MgO at an angle of 2θ is 27.2^o values in a plane of (1,1,1) with FCC. $MgAl_2O_4$(spinel) at an angle of 2θ is 37^o value in a plane of (1,1,1) with FCC(JCPDS 21-1152). The SEM micrographs of regenerated and carbonated C2 samples from 1st to 15th cycles were shown in **Figure 3.11** to **Figure 3.18.**

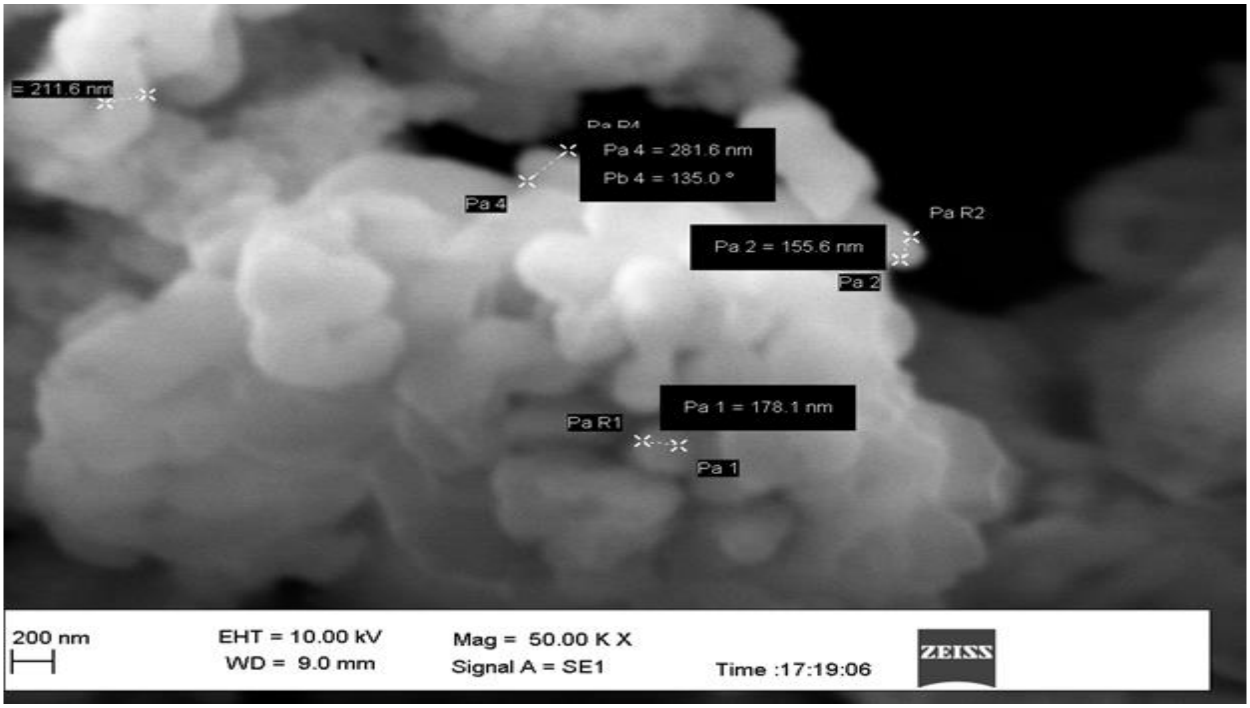


Figure 3.11 SEM analysis -1st cycle carbonation

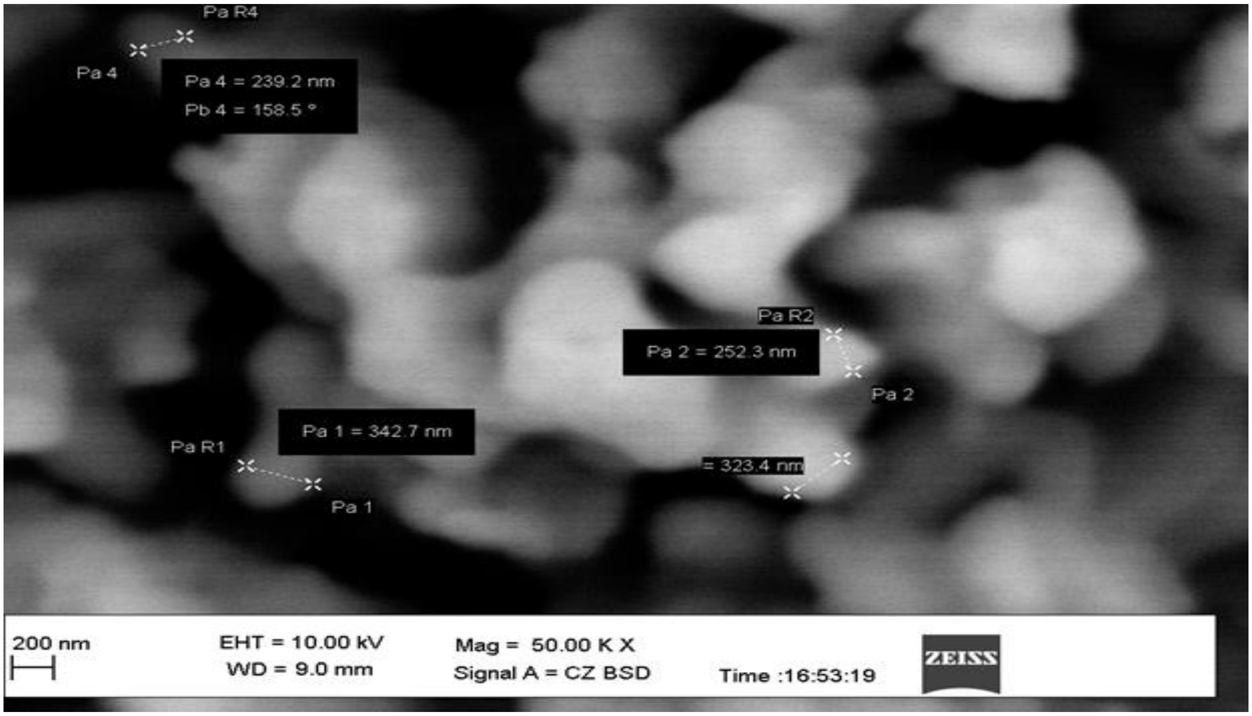


Figure 3.12 SEM analysis - 1st cycle regeneration

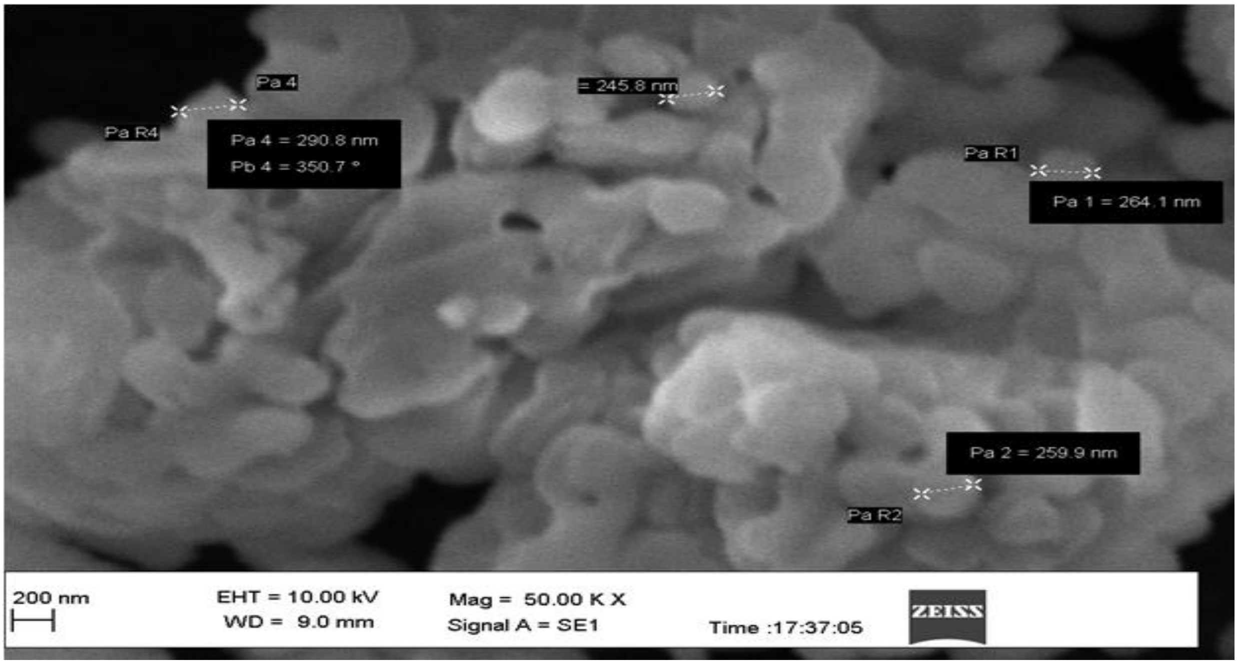


Figure 3.13 SEM analysis - 5th cycle carbonation

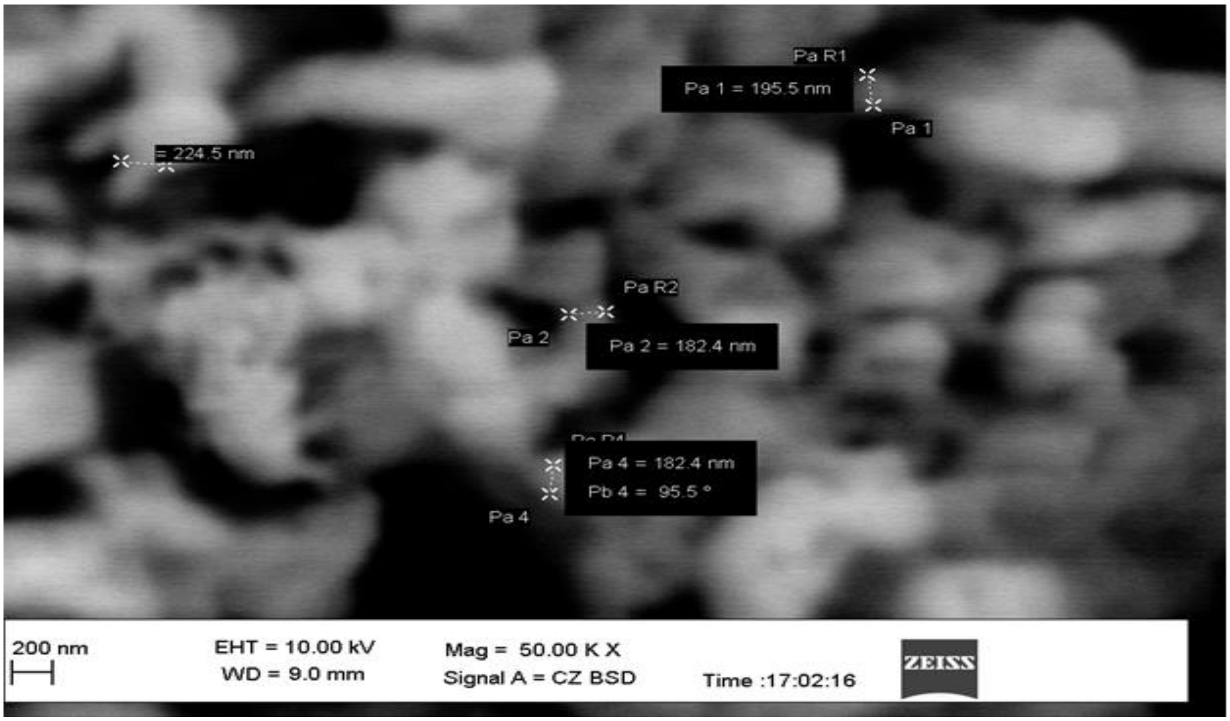


Figure 3.14 SEM analysis - 5th cycle regeneration

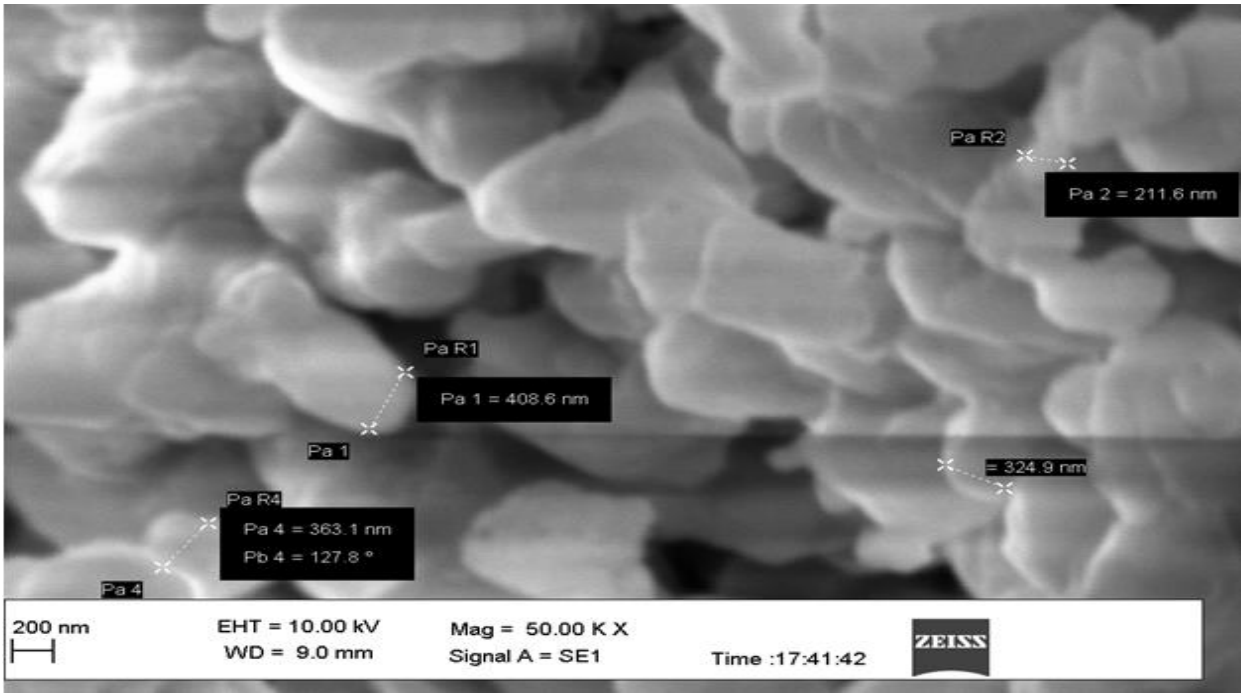


Figure 3.15 SEM analysis - 10th cycle carbonation

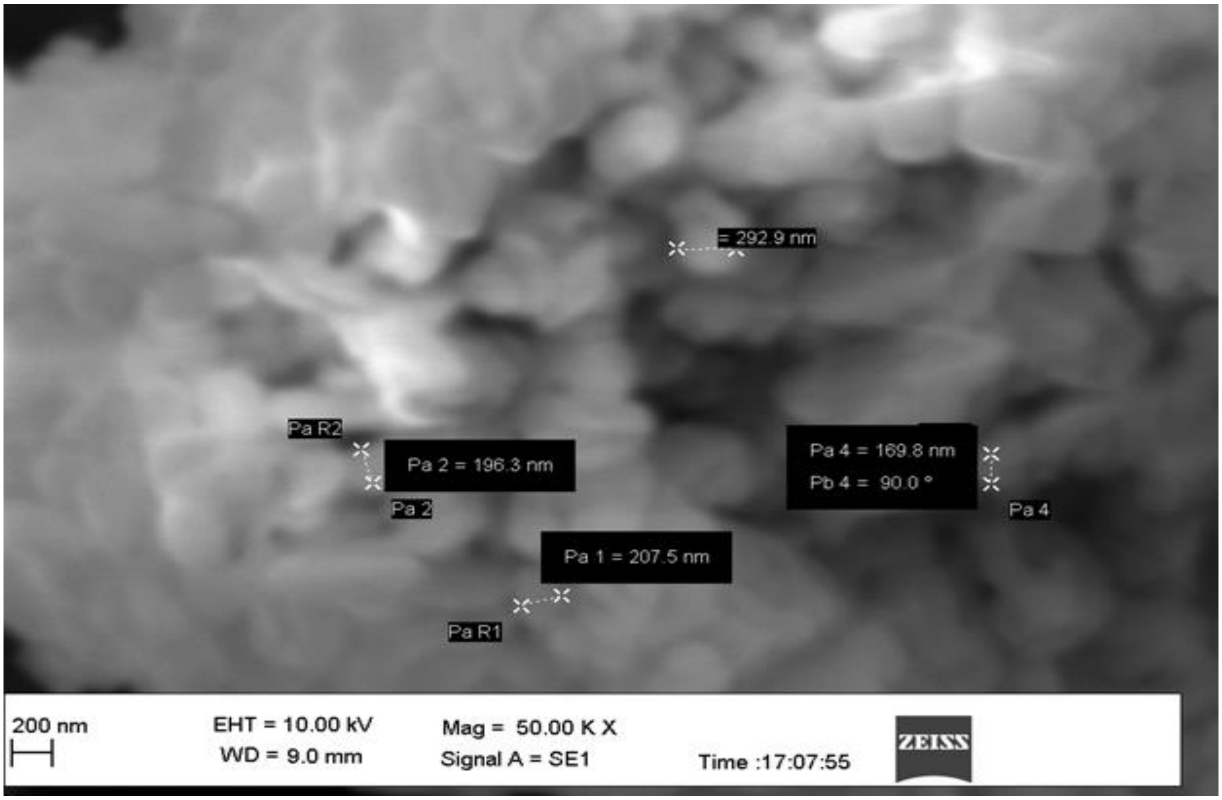


Figure 3.16 SEM analysis -10th cycle regeneration

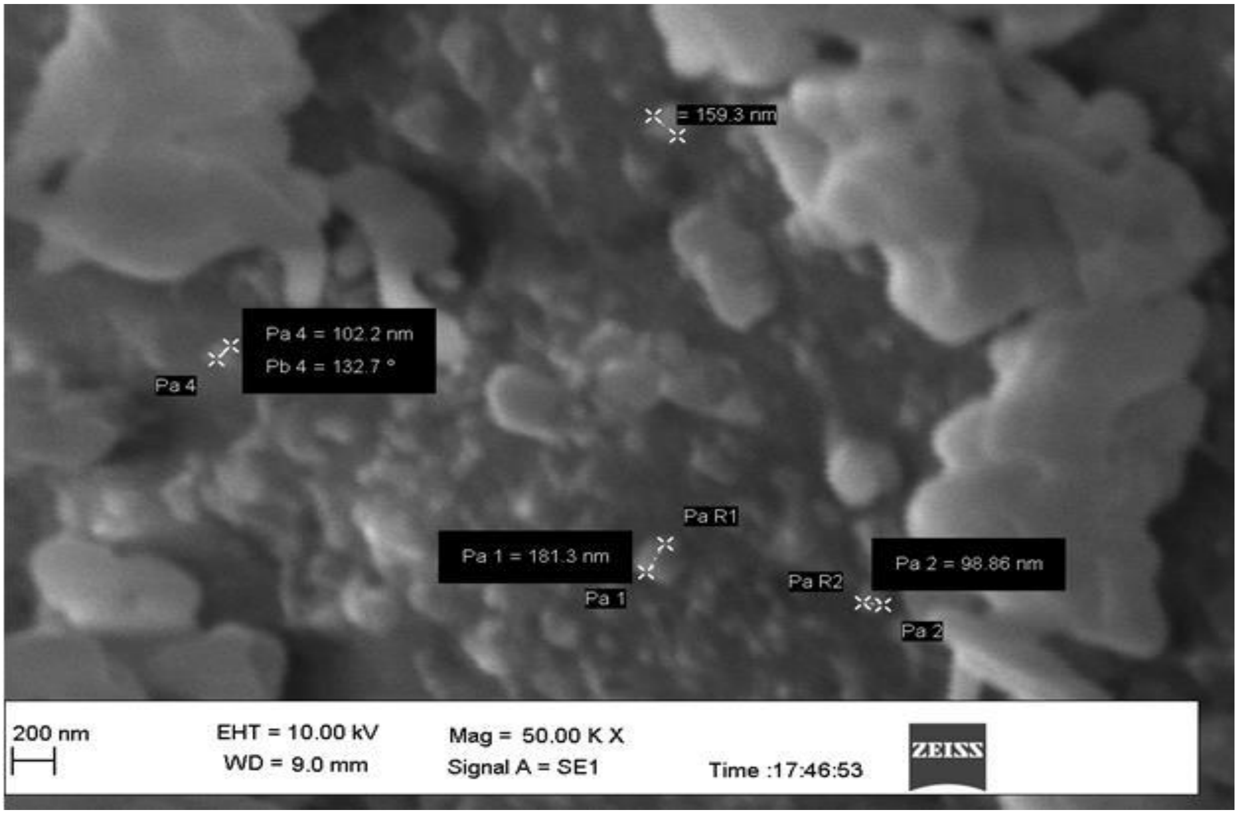


Figure 3.17 SEM analysis -15th cycle carbonation

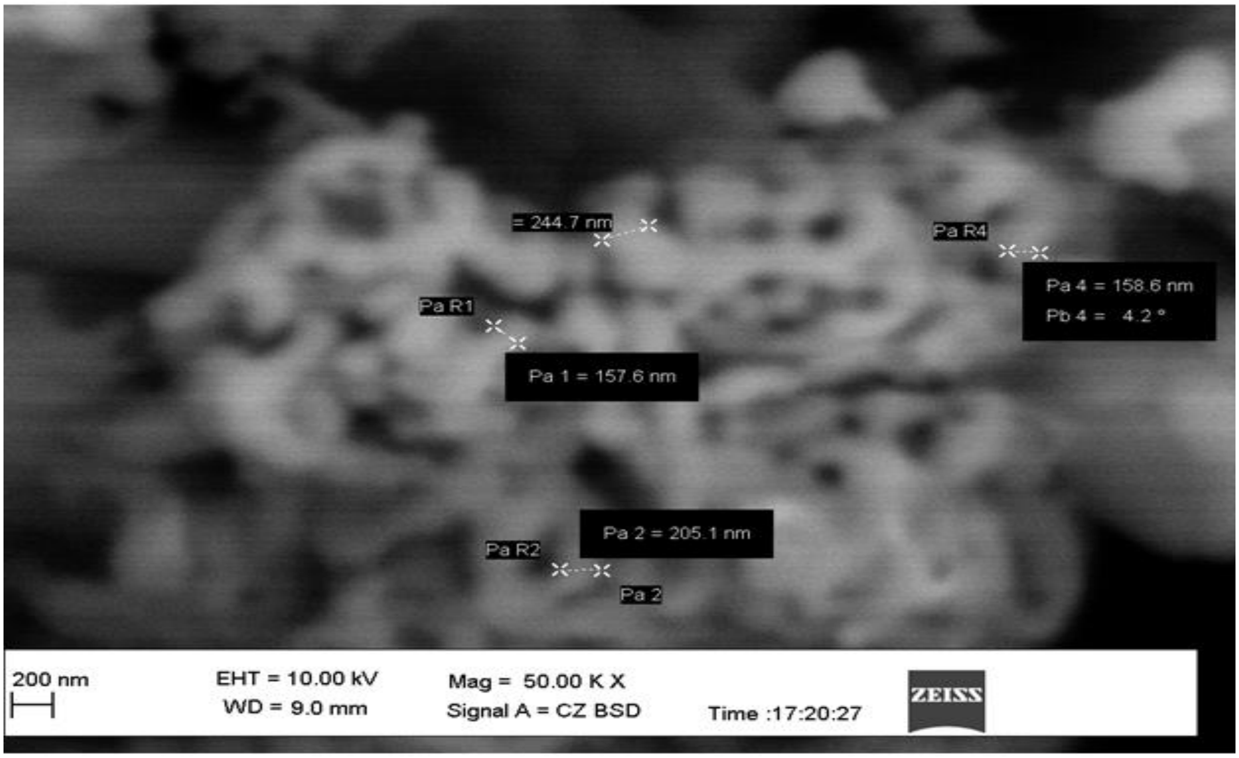
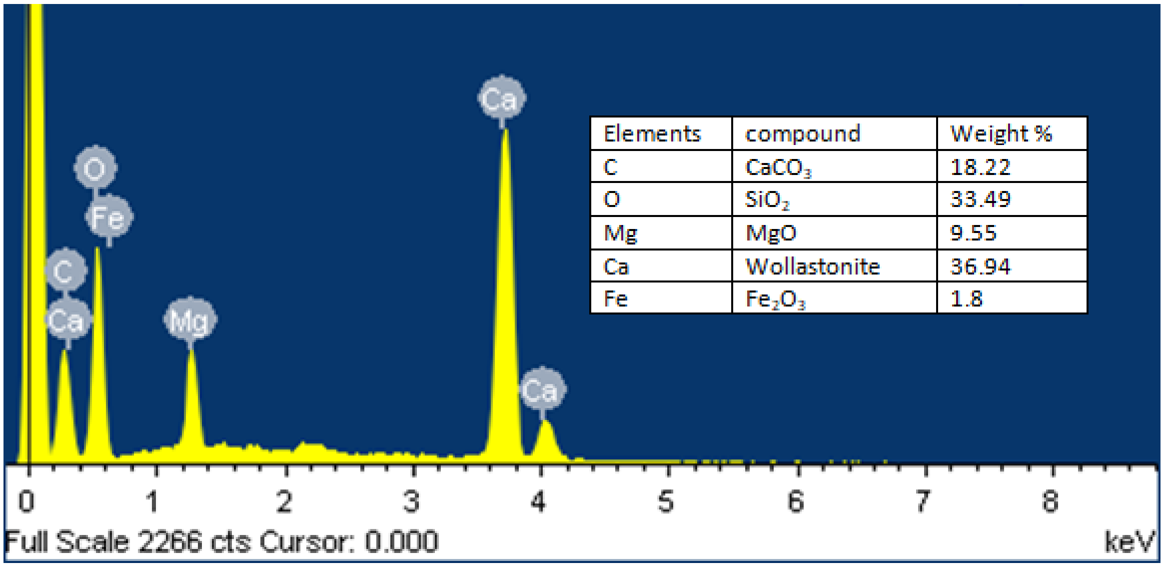


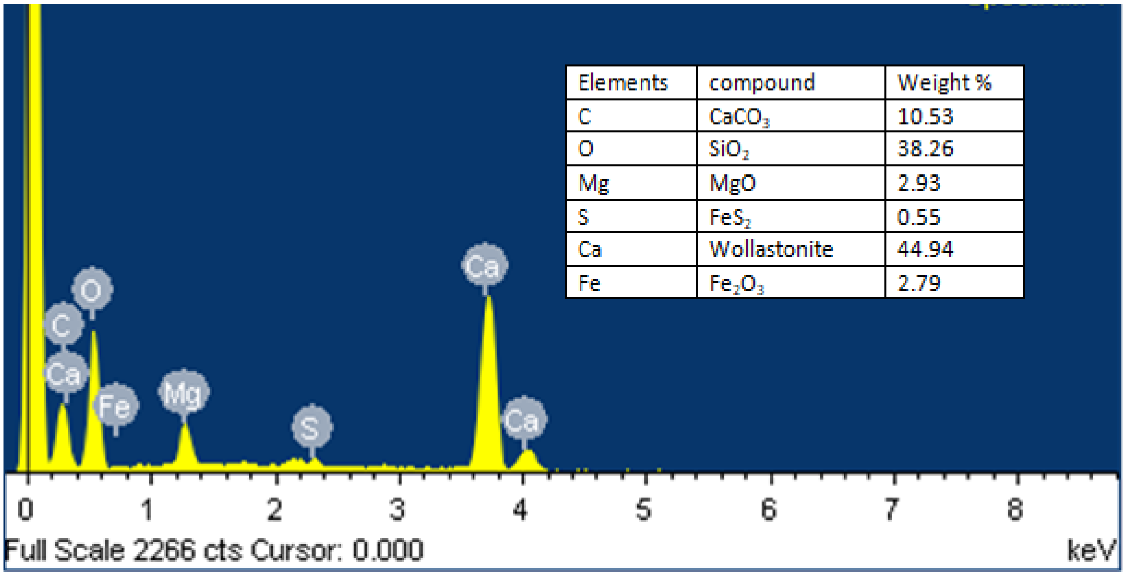
Figure 3.18 SEM analysis -15th cycle regeneration

The corresponding EDX patterns of C2 sample carbonated in 1st and 15th cycles were shown in **Figure 3.19** and **Figure 3.20**.



Elements	compound	Weight %
C	$CaCO_3$	18.22
O	SiO_2	33.49
Mg	MgO	9.55
Ca	Wollastonite	36.94
Fe	Fe_2O_3	1.8

Figure 3.19 EDX analysis -1st cycle carbonation



Elements	compound	Weight %
C	$CaCO_3$	10.53
O	SiO_2	38.26
Mg	MgO	2.93
S	FeS_2	0.55
Ca	Wollastonite	44.94
Fe	Fe_2O_3	2.79

Figure 3.20 EDX analysis -15th cycle carbonation

It showed the sustainable CC with an increasing trend during initial three cycles and stable CC with marginal change for the remaining number of cycles. This is in agreement with the results presented in **Figure 3.4** to **Figure 3.7**. The SEM images of all samples reveal uniform distribution of the particles irrespective of the number of cycles. There was a gradual increase in the crystalline size from 1st to 15th cycle due to better crystallization of the materials in line with XRD results. This was due to mixed effect of the presence of alkaline metals for carbonation and resistance to the agglomeration by the doped FA. The corresponding EDX patterns also support the uniform distribution of component metals, metal oxides and metal carbonates as expected in these samples. On the whole, the XRD, SEM and EDX results support the stable nature of the C2 adsorbent for repeated cycles of CC.

3.6.3 Sorbent Stability Achieved

High temperature carbon capture studies have been conducted using various sorbents doped with two different types of coal fly ash (CFA). After initial screening of more than twenty sorbents, the relatively best performing combinations have been subjected to rigorous standardization employing Taguchi method. The CC has been optimized with reference to critical process parameters viz., adsorbent composition, quantity, synthesis protocol, adsorption temperature, gas flow rate, carbonation time and morphology. It has been found that CaO-MgO-FA-C combination of 50-10-40 weight percent has given highest CC of more than 9mmolCO_2/g_{ads} after 15th cycle. This is higher than the reported values for CFA. The weight of 20g, gas flow rate of 250ml/min (superficial velocity of 0.822cm/s), temperature of 650^oC and the powder form were found to be optimized set of parameters to maximize CC. This work establishes the superior performance and advantages of employing CFA as a major constituent in conjunction with CaO and MgO as sorbent mixture for CC.

4 THERMODYNAMICS OF CALCIUM LOOPING PROCESS

4.1 THERMODYNAMIC FEASIBILITY

The carbonation (500-750^{o}C) and regeneration (880-950^{o}C) temperatures of limestone based sorbents limit their deployment due to high energy penalty involved. In this section, thermodynamic parameters viz., ΔG, ΔS, ΔH were estimated using HSC Chemistry software for our sorbent used in the CC process. These indicate the thermodynamic nature, feasibility and spontaneity of the process and the factors influencing the same. The primary objective of these studies was to minimize sorbents' regeneration temperature so as to reduce the energy penalty by using the appropriate sorbent composition. This was achieved by doping CaO with MgO and an inert supporting sorbent of CFA. CFA is an industrial waste made of alkaline metal oxide heteroatoms (Al_2O_3, SiO_2, Fe_2O_3, K_2O, Na_2O, MgO etc). This increased alkalinity due to metal silicates was responsible to lower the regeneration temperatures minimizing energy penalty and enhanced stability of sorbent. **Table 4.1**, gives the mole & weight ratios of various metal oxides present in the synthesized sorbent from the XRF analysis.

Table 4.1 XRF analysis – comparison of alkaline molar ratio with doped sorbent

Sorbent (CaO50MgO10FA-C40)	$CaO:SiO_2$	$(CaO+MgO):SiO_2$	$MgO:SiO_2$	CaO:MgO
Weight ratio	9.13	14.1	4.92	1.85
Molar ratio	9.78	17.3	7.343	1.33

$$3.6CaO+MgO+4.6\ CO_2(g) \leftrightarrow CaMg(CO_3)_2+2.6CaCO_3 \qquad (4.1)$$

The above equation 4.1 has been assumed as the major reaction to take place to represent carbonation of active sorbent (CaO: MgO with molar ratio of 3.6) without fly ash composition.

Table 4.2, gives the estimated values of various thermodynamic parameters of ΔH, ΔS and ΔG along with equilibrium constant for the adsorbent used in our study. All these values demonstrate the thermodynamic nature, feasibility and spontaneity of the process in the temperature range given. Thermodynamic parameters estimation have been reported using HSC chemistry software for high temperature CO_2 capture using potassium doped fly ash sorbent [85]. As stated in the preceding sections, doping of CFA in CaO-MgO was found to promote the spontaneity and feasibility of the capture process at high temperatures. The negative values of ΔH and ΔS indicate the exothermic nature of the carbonation process. The shift of ΔG, from negative to positive value also indicates the regeneration temperature which would further be reinforced by the plots employing HSC Chemistry software in the following section. Also, the negative value of ΔS indicate the reduced randomness and disorder at the solid/gas interface [112].

Table 4.2 Thermodynamic parameters of sorbent without CFA

T(^oC)	ΔH(kJ/mol)	ΔS(J/K.mol)	ΔG(kJ/mol)	K	Log(K)
0	-766.33	-754.83	-560.14	1.338E+107	107.12
100	-764.55	-749.41	-484.91	7.682E+067	67.88
200	-761.78	-742.86	-410.29	1.994E+045	45.30
300	-758.25	-736.11	-336.34	4.529E+030	30.65
400	-753.98	-729.27	-263.07	2.605E+020	20.41
500	-748.95	-722.31	-190.49	7.435E+012	12.87
600	-743.08	-715.18	-118.62	1.250E+007	7.09
700	-736.31	-707.85	-47.46	3.533E+002	2.54
800	-728.61	-700.32	22.94	7.642E-002	-1.11
900	-719.89	-692.56	92.58	7.536E-005	-4.12
1000	-710.14	-684.59	161.44	2.374E-007	-6.62

Note: The active sorbent contains molar ratio of CaO: MgO is 3.6:1; HSC chemistry software was used to estimate thermodynamic parameters of equation 4.1

Figure 4.1, a plot of ΔG vs temperature for two sorbents of different mole ratios of CaO: MgO clearly demonstrate that the sorbent selected was more suitable for high temperature CC than the other. The increased temperatures range of (ΔG<0 to ΔG>0) carbonation from over 600^{o}C to nearly 800^{o}C is shown in the **Figure 4.1** leading to higher CC.

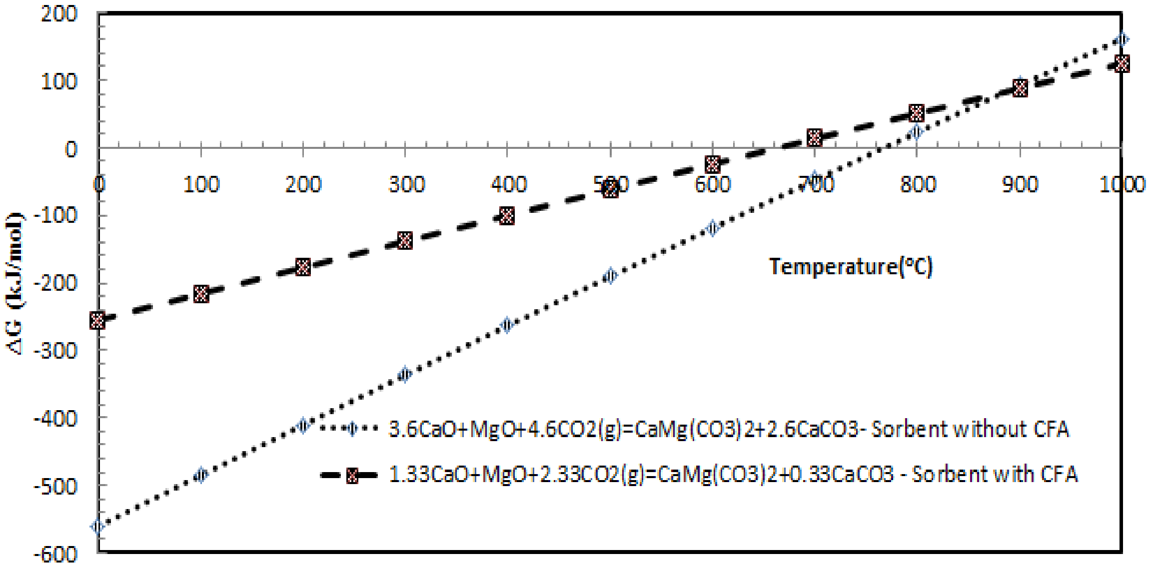


Figure 4.1 Molar ratio of CaO and MgO with & without fly ash

Critical role of CaO: MgO ratio, that is the role of CFA on the temperature ranges of carbonation-regeneration was also evident from the **Figure 4.1**. The efficacy of the doped sorbents was clearly demonstrated using CO_2 partial pressure vs temperature plots to achieve enhanced CC and favorable kinetics in the desired temperature range for both pre-combustion and post combustion modes (T_1 and T_2 respectively) [113]. In our sorbent system of CaO-MgO-CFA, CaO may be viewed as active sorbent with strong interaction towards CO_2 and hence higher values of T_1& T_2 i.e., higher pre combustion and post combustion temperatures while MgO may be viewed as a stabilizer that increases reaction free energy (less negative) and reduce T_1 & T_2 to the practical operating range. The CFA as discussed before further reinforces the stability of the sorbent along with favorable kinetics and thermodynamics.

Figure 4.2 and **Figure 4.3**, demonstrates the inertness of CFA and its constituents of calcium, sodium, aluminium and magnesium based silicates. It is clearly evident from the figures that unlike pure CaO and MgO, the carbonation temperature of CFA is very low i.e., mostly around 300^{o}C that indicate its inertness. So, when mixed with CaO and MgO, this would play a critical role in reducing the carbonation-regeneration switch/inversion temperature (at $\Delta G=0$) thereby reducing the energy penalty and induce favorable kinetics and thermodynamics.

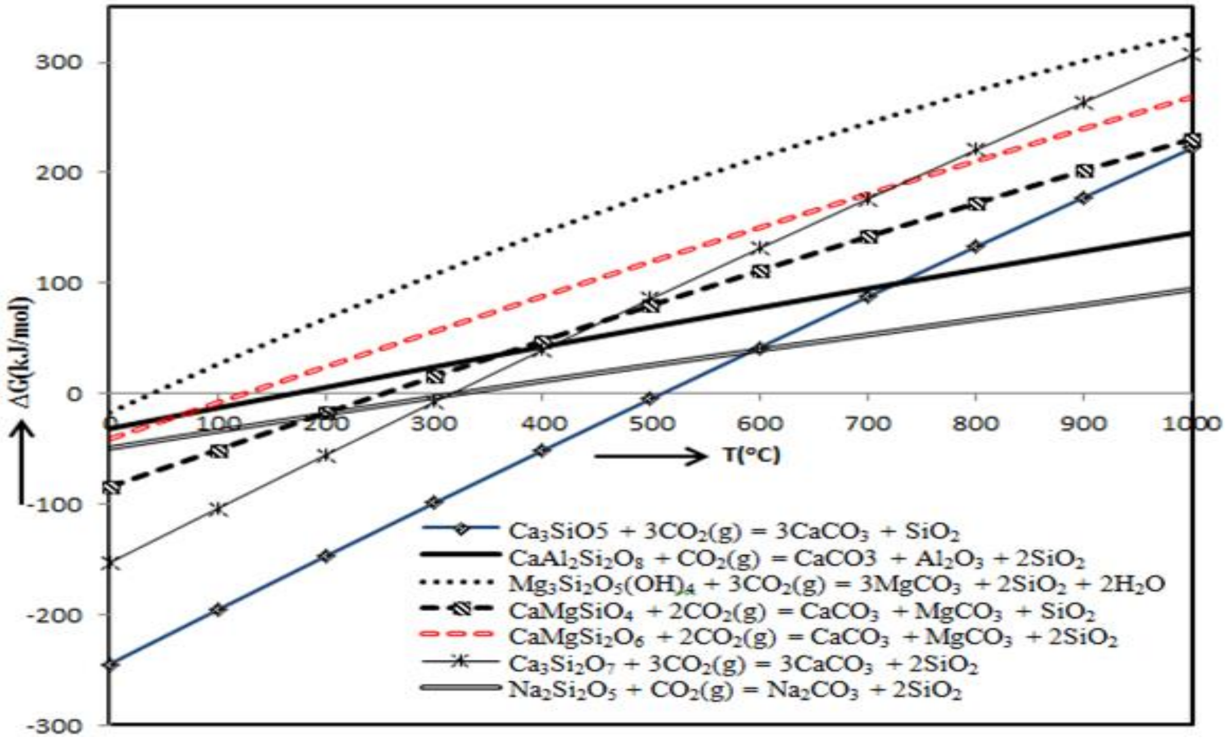


Figure 4.2 Effect of ΔG on temperature (silicates combination-1)

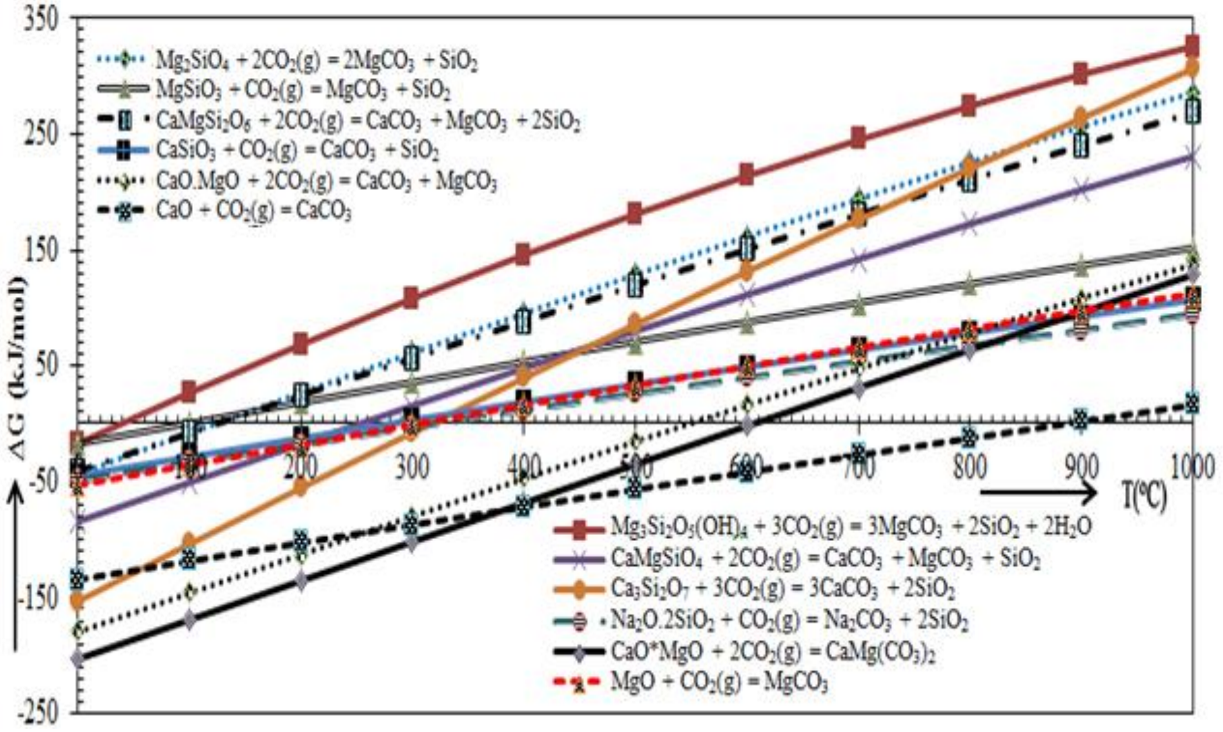


Figure 4.3 Effect of ΔG on temperature (silicates combination-2)

Figure 4.4 and **Figure 4.5** show the influence of doping such inert CFA with an active sorbent as CaO that led to increase in carbonation temperature to a range of 300 to 750°C leading to enhanced capture capacity and stability depending upon mole ratio of the sorbent to calcium silicates in CFA. It can also be understood that there would be an optimum ratio of CaO to calcium silicates to achieve a stable and desired regeneration temperature of 650°C that would lead to successful integration of CC with power generation, H_2 gas production and SESR. This dynamics of the capture process using CFA could be attributed to silicates present in it that would affect the acidity of the sorbent. From these studies, it could be understood that CFA with its constituents would play a significant role in combination with CaO-MgO in achieving enhanced capture stability and the desirable carbonation and regeneration temperatures. HSC chemistry software was used to describe graphical trends of metal compounds from **Figure 4.2** to **Figure 4.5.**

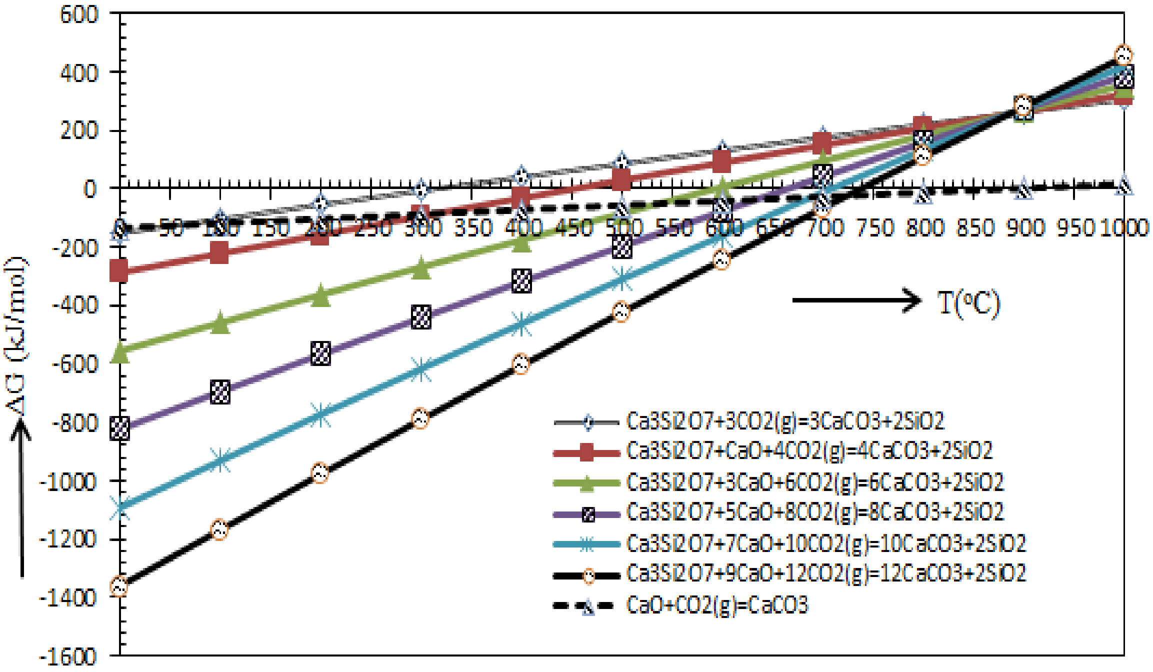


Figure 4.4 Effect of ΔG on temperature for CaO : $Ca_3Si_2O_7$ molar ratio

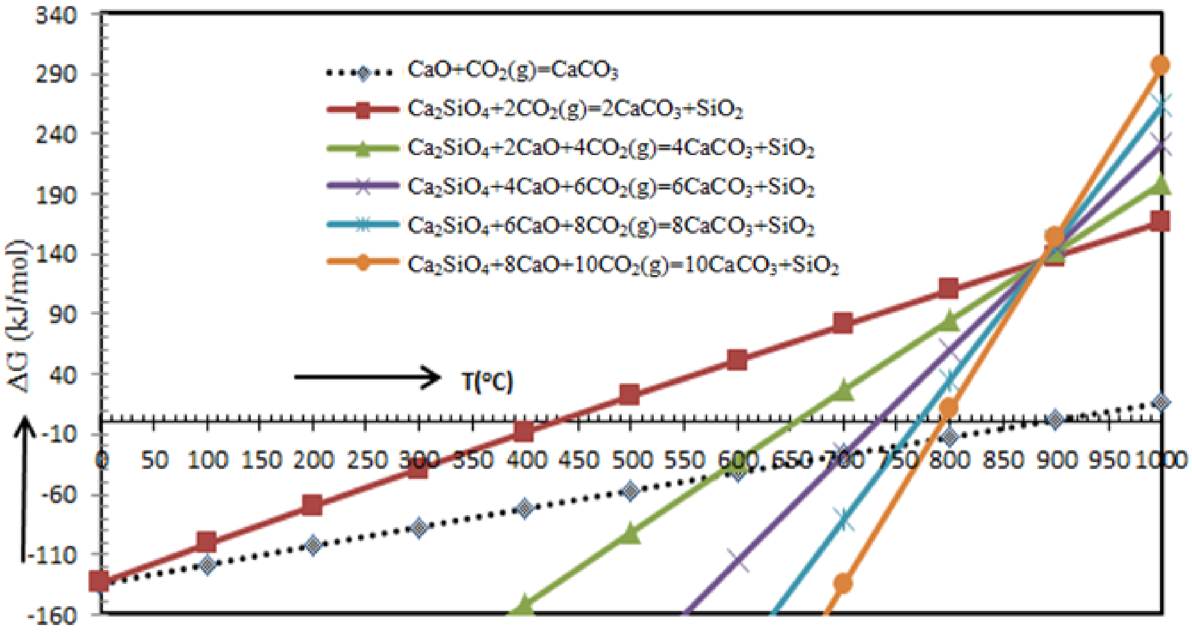


Figure 4.5 Effect of ΔG on temperature for CaO : Ca_2SiO_4 molar ratio

To understand the regeneration phenomena for a number of cycles, **Figure 4.6** and **Figure 4.7** were plotted (using TGA information) where change in mass of the sorbent Δm for various cycles was plotted vs time as a function of temperature and Δm vs temperature as a function of time. From **Figure 4.6** and **Figure 4.7**, it is evident that the regeneration temperatures were around 620-730^{o}C in line with other previous thermodynamic trends where there is a decline in mass due to CO_2 desorption [114]. This also reinforces the fact that there is a dolomite decomposition around 440-550^{o}C in accordance with our XRD results reported earlier [63]. These two plots indicate the duration of regeneration of 10-12 minutes occurring in two zones of AB to CD (dolomite decomposition) and from EF to GH ($CaCO_3$ desorption) .

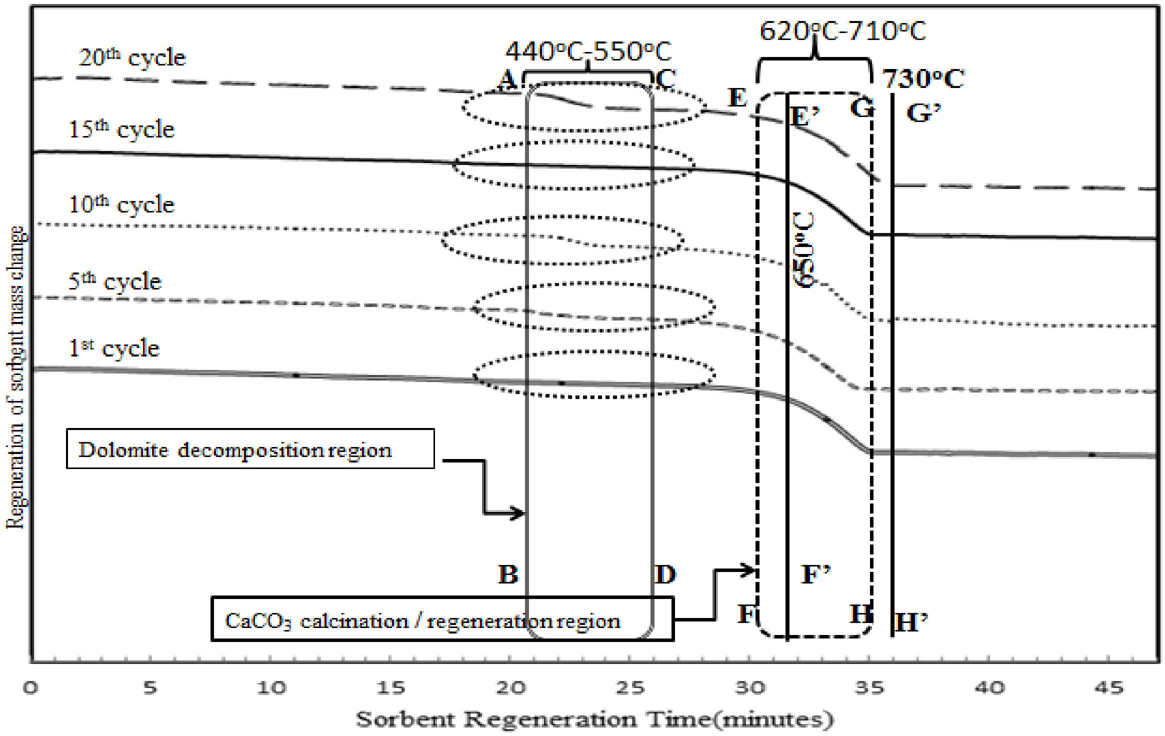


Figure 4.6 TGA - regeneration time relation upto 20 cycles

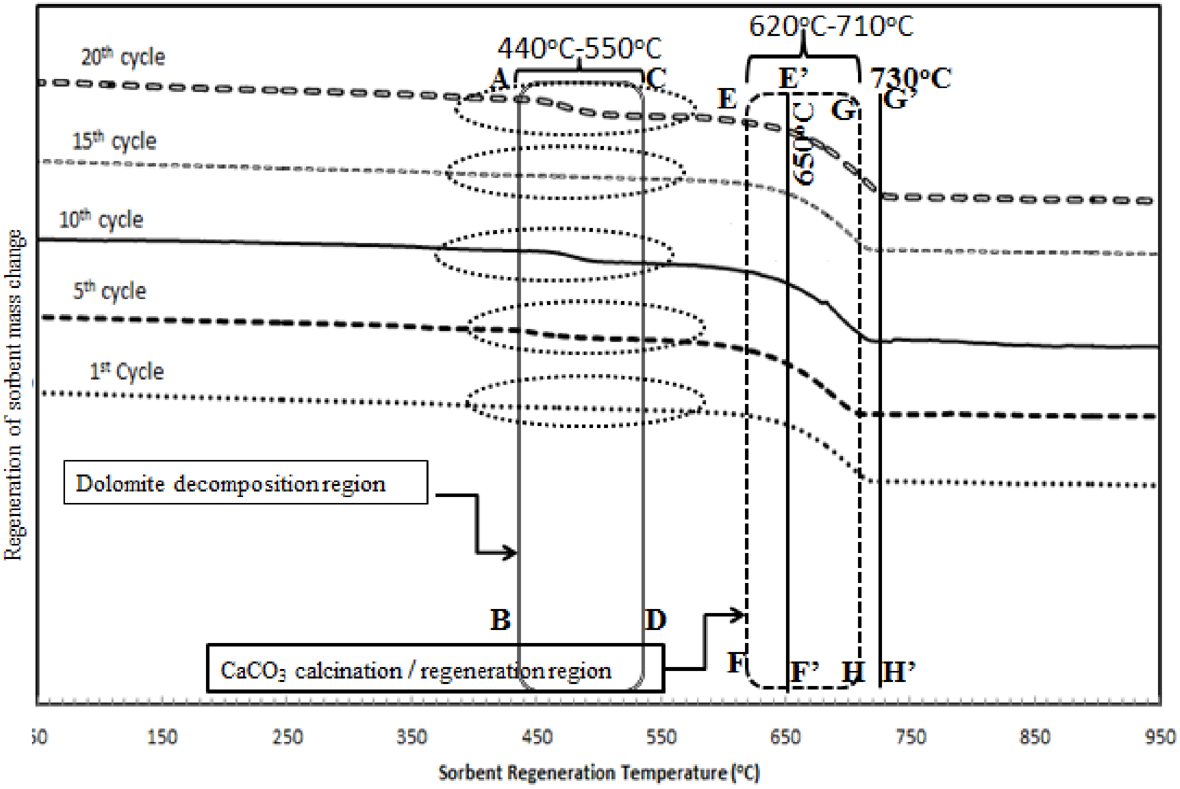


Figure 4.7 TGA - regeneration temperature relation upto 20 cycles

4.2 HEAT OF REACTION

CO_2 adsorption kinetics needed knowledge of heat of reaction, equilibrium constant, enthalpies and Gibbs free energies of $CaCO_3$, $MgCO_3$ and $CaMg(CO_3)_2$ with their thermal decomposition reactions. The objective is to analyze the applicability of calcium and magnesium based sorbent for high temperature CO_2 capture. The CaO and MgO adsorb CO_2 to form calcium carbonate, magnesium carbonate and dolomite (composed by carbonates together). The calcination of these carbonates tends to produce the corresponding metal oxides and pure CO_2. The thermal decomposition of the above said carbonates are as follows.

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{4.2}$$

$$MgCO_3 \leftrightarrow MgO + CO_2 \tag{4.3}$$

$$CaMg(CO_3)_2 \leftrightarrow CaO + MgO + 2CO_2 \tag{4.4}$$

$$CaMg(CO_3)_2 \leftrightarrow CaCO_3 + MgO + CO_2 \tag{4.5}$$

The enthalpy of formation is zero for the elements in their standard states. The heat of reaction or enthalpy of reaction is the change in enthalpy of a chemical reaction at constant pressure. The molar enthalpy, $H_i^o(T)$, of a pure substance i at 1 atm pressure and temperature T is defined as

$$H_i^o(T) = \Delta H_i^f + \int_{298}^{T} dH_i^o \text{ --- } (4.6)$$

where ΔH_i^f is the enthalpy of formation of substance at 1 atm and 298 K. **Figure 4.8** and **Figure 4.9**, show the change of enthalpy during sorbents carbonation with temperature.

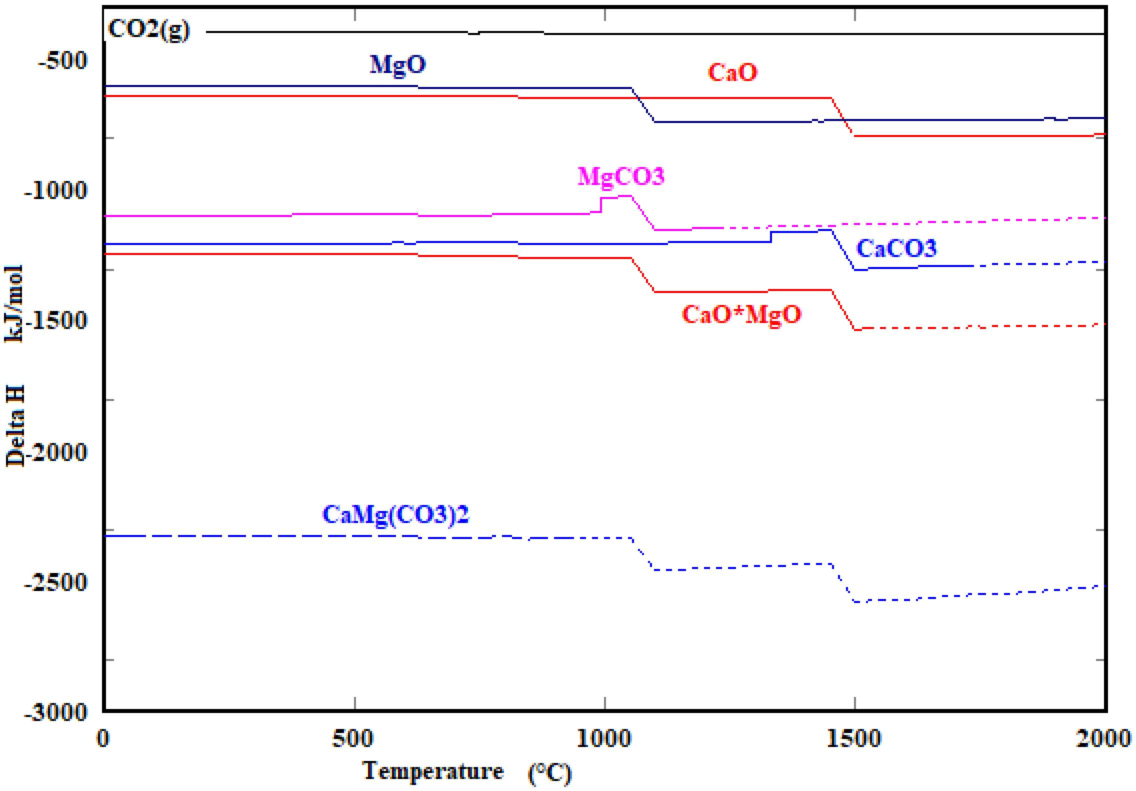


Figure 4.8 Enthalpy of formation for dolomite, calcite and magnesite

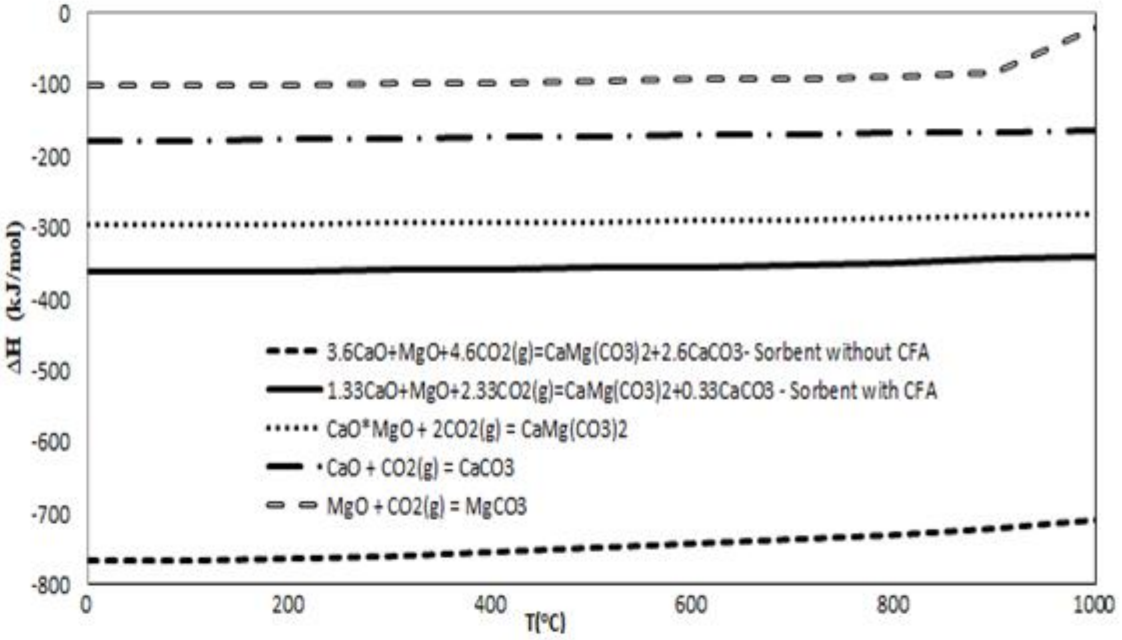


Figure 4.9 Enthalpy of sorbent carbonation at various temperatures.

The dependence of enthalpy on temperature could be expressed in terms of molar heat capacity, $C_i(T)$ at constant pressure,

$C_p(T) = \ dH_i^o/dT$--(4.7)

The molar heat capacity replaces the enthalpy of transformation at temperature T. The enthalpy of a substance, $\Delta H_r(T)$, in terms of heat capacity, $C_p(T)$, and ΔH_{tr} is the change in enthalpy of phase transformation of the substance, becomes

$\Delta H_r(T) = \Delta H_{298}^f + \ \int_{298}^T C_p(T)dT + \ \sum \Delta H_{tr}$---(4.8)

Figure 4.10, shows the variation of heat capacities for sorbents with temperature. The temperature dependency of ΔC_p, in the calculation could be estimated by the experimental heat capacities using equation 4.9 [115]. The thermodynamic data obtained was from HSC chemistry software.

$\Delta C_p = A + B * T * 10^{-3} + C * T^{-2} * 10^5 + D * T^2 * 10^{-6}$--------------------------------(4.9)

Where A, B, C and D are coefficients to be estimated from experimental data

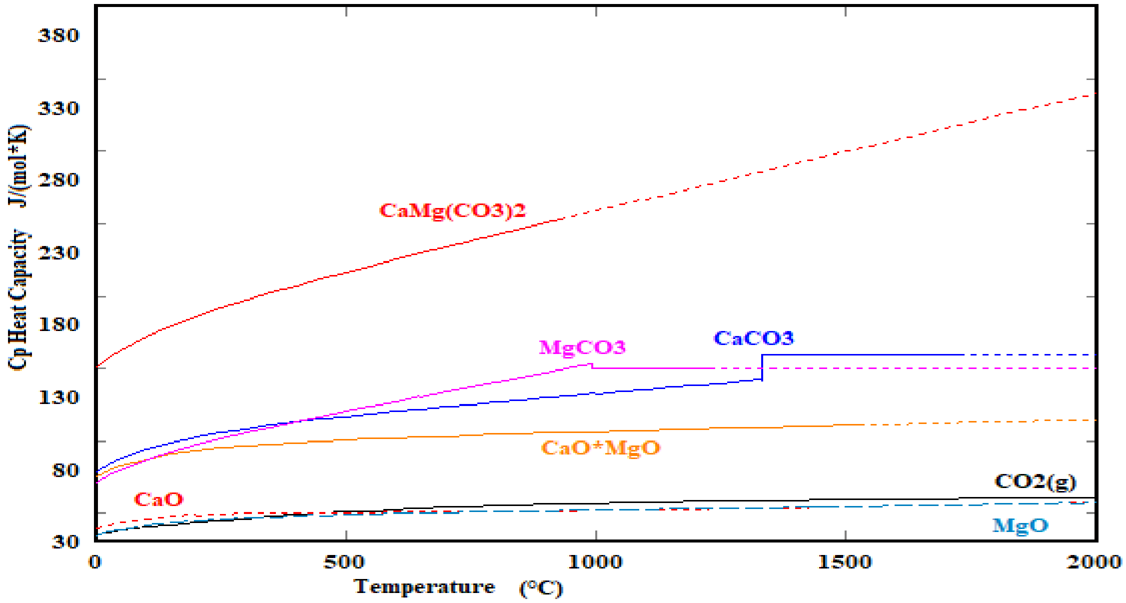


Figure 4.10 Heat capacities of sorbents carbonation at various temperatures.

4.3 EQUILIBRIUM CONSTANTS

The equilibrium constant (K) could be calculated using the standard free energy change ΔG^o for a reaction at equilibrium temperature T using the equation

$$\Delta G^o = -RT \ln K \text{ --- } (4.10)$$

The equilibrium constant (K) is unaffected by the pressure of the system, the presence or absence of inerts, or by the kinetics of the reaction. But, it is affected by the temperature of the system. The thermodynamic equilibrium constant (K) is unaffected by pressure or inert materials, the equilibrium concentration of materials and equilibrium conversion of reactants could be influenced by these variables [116]. In irreversible reaction, experimentally complete conversion is possible with $K \gg 1$. But, the reaction will not proceed to any appreciable extent with $K \ll 1$. **Figure 4.11** and **Figure 4.12**, describes about carbonation of alkaline metal silicates and doped sorbents with fly ash respectively.

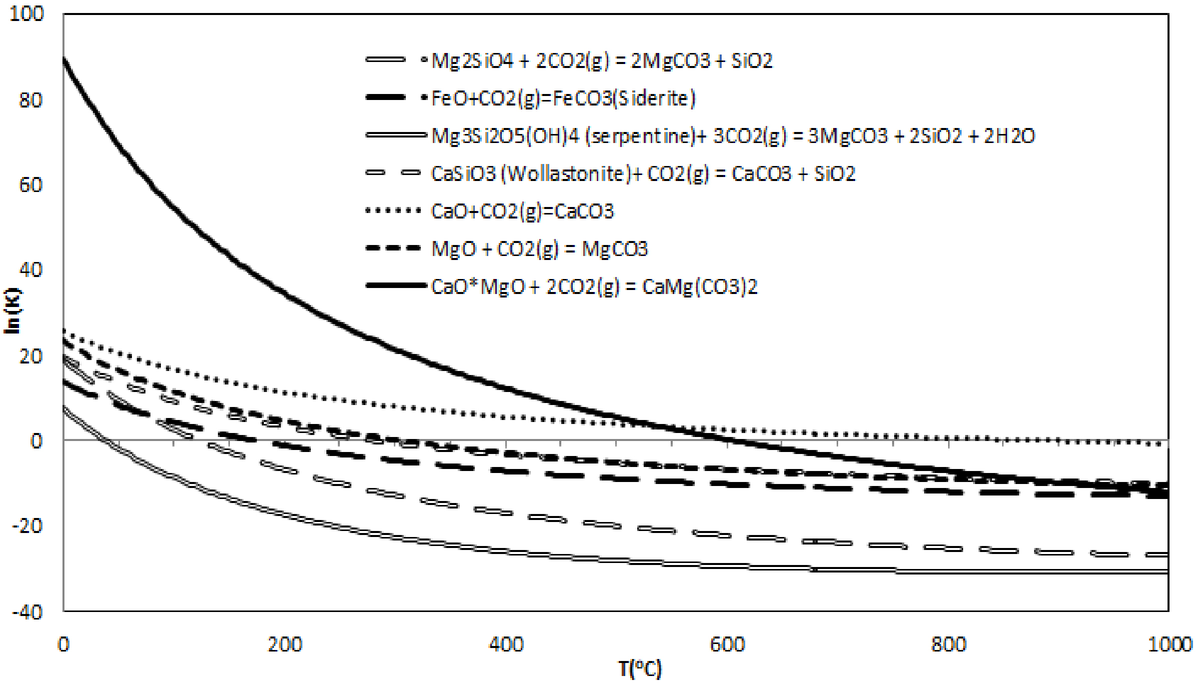


Figure 4.11 Equilibrium constant for carbonation of metal silicates in coal fly ash

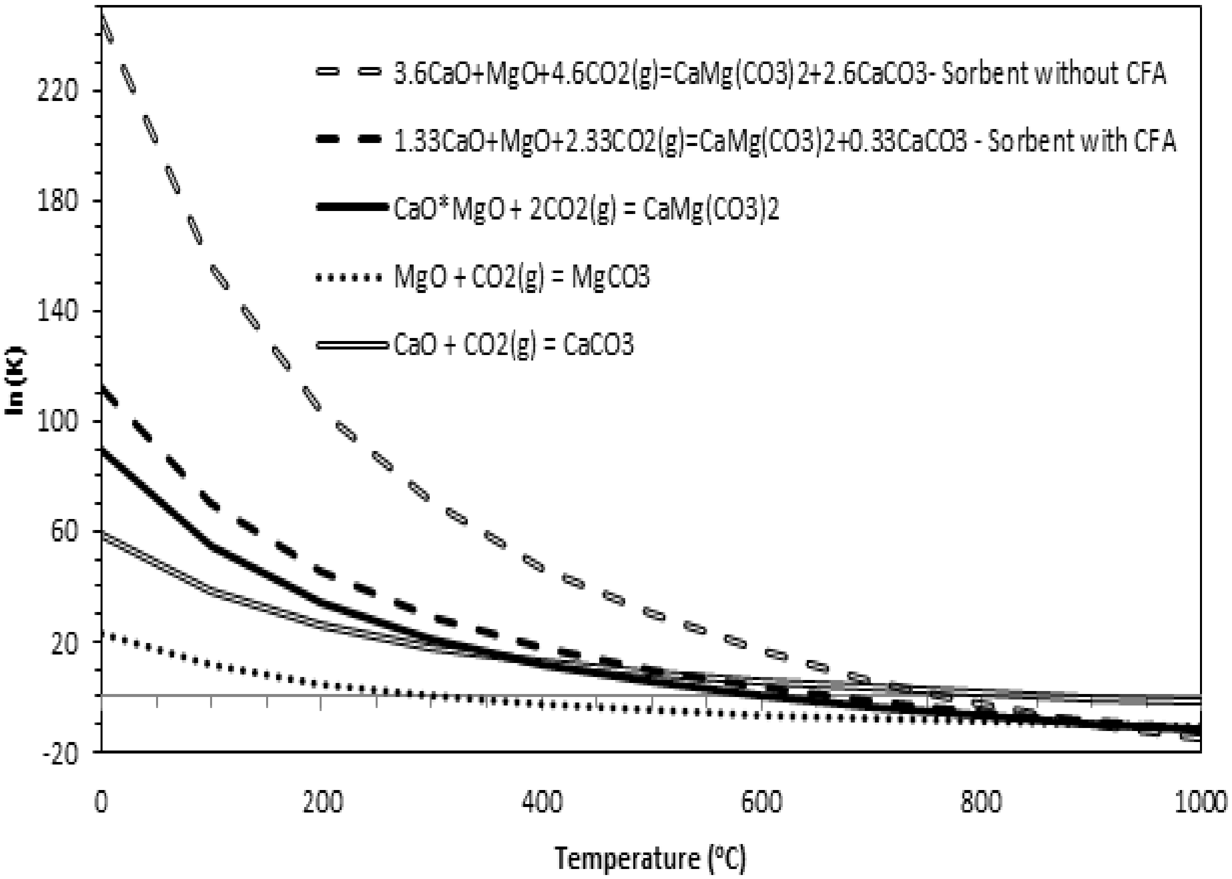


Figure 4.12 Equilibrium constant for metal oxide carbonation in coal fly ash

4.4 EQUILIBRIUM CONVERSION

The equilibrium composition depends on equilibrium constant and its changes with temperature. The change of thermodynamic equilibrium constant with temperature is given by

$$\frac{d(lnK)}{dT} = \frac{\Delta H_r}{RT^2} \text{---}(4.11)$$

when ΔH_r is considered to be constant in the temperature interval and the integration yields

$$ln\frac{K_2}{K_1} = -\frac{\Delta H_r}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{--}(4.12)$$

when ΔH_r is varying with temperature, then substitute its value from equation 4.8 in the above equation 4.12, we get

$$Rln\frac{K_2}{K_1} = [f(\Delta C_p, T_1, T_2)]\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{---} (4.13)$$

The above equation allows us to calculate variation of the equilibrium constant with temperature. **Figure 4.13** and **Figure 4.14**, describe the equilibrium conversion in mol% and wt% of sorbent carbonation respectively. It shows that carbonation with maximum conversion at 600^{o}C with pure CaO sorbent used to estimate conversion with HSC chemistry simulation software and then starts decomposing thereafter in the absence of coal fly ash (CFA) sorbent. But, this equilibrium reaches maximum carbonation conversion at nearly 650^{o}C in the presence of CFA as inert sorbent support and starts decomposing thereafter. The estimation of conversion and decomposition rate parameters for the synthesized sorbent with coal fly ash as inert supporting sorbent were discussed in the next section of carbon capture studies. **Figure 4.13** and **Figure 4.14,** shows that only N_2 gas exists upto 300^{o}C and then the mole ratio of N_2 gas decreases in the available gas mixture due to the increasing amount of CO_2 from metal carbonate decomposition.

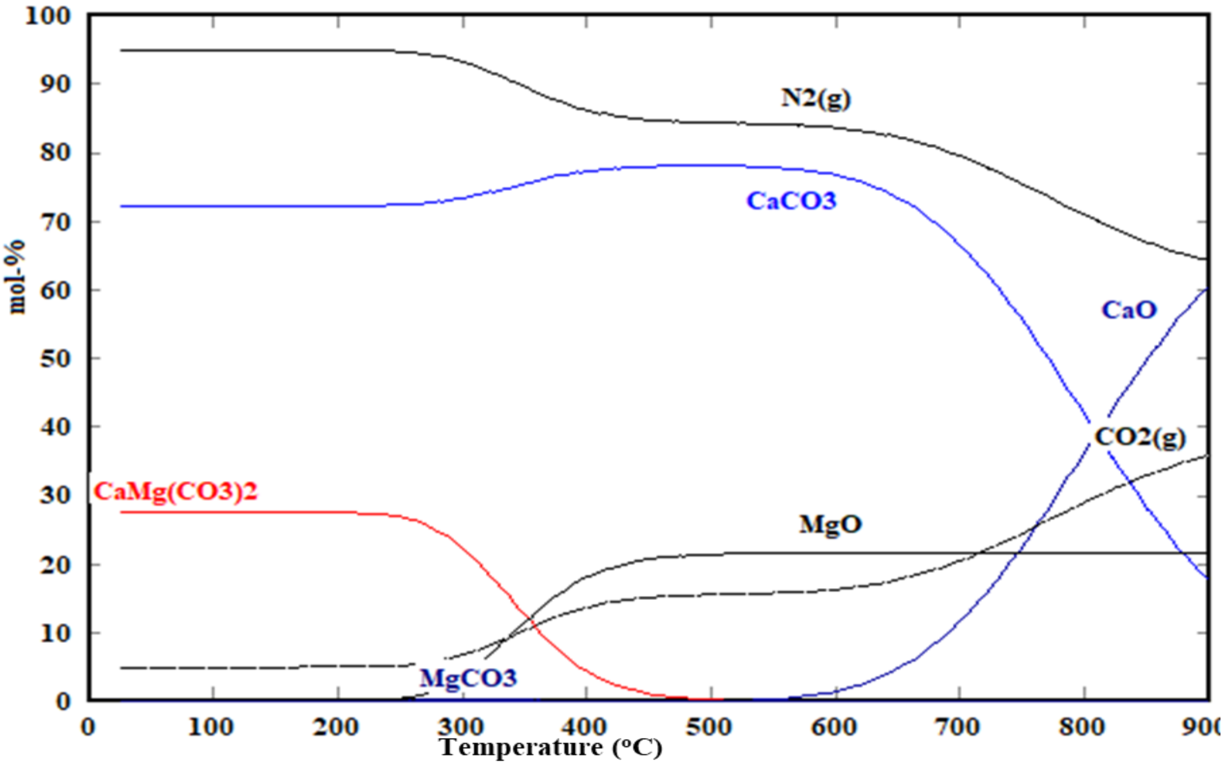


Figure 4.13 Equilibrium conversion in mol% for carbonation of CaO and MgO

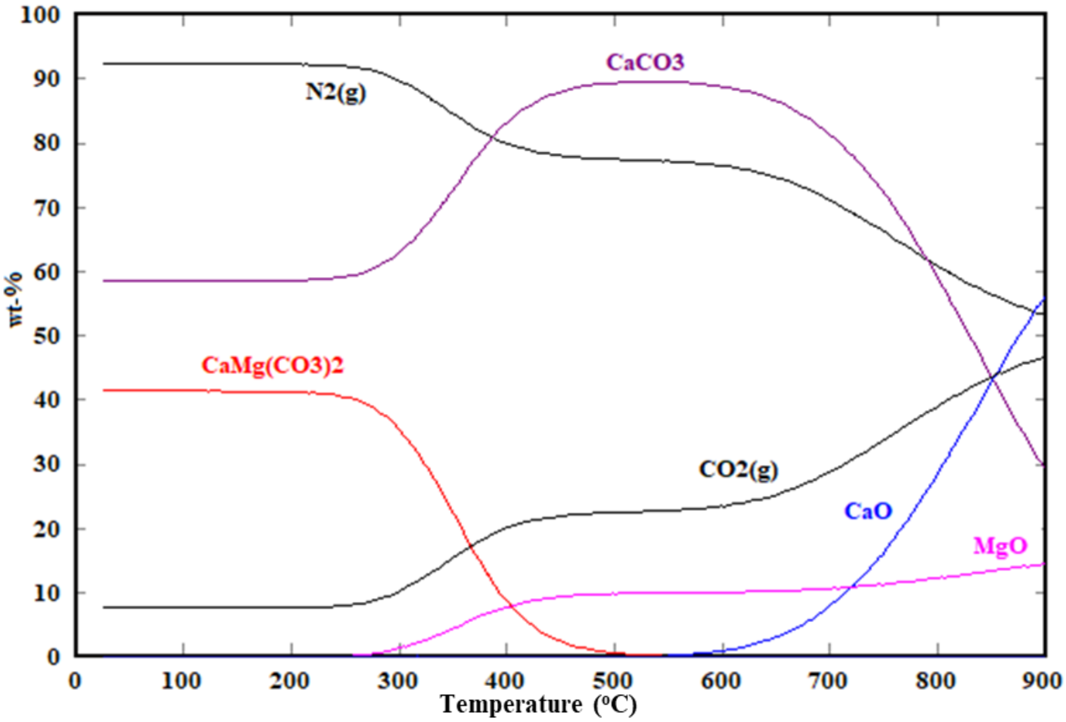


Figure 4.14 Equilibrium conversion in wt% for carbonation of CaO and MgO

It is important to have a good thermodynamic understanding of the adsorption processes for characterizing the adsorbents. Adsorption of CO_2 from flue gases could be evaluated from breakthrough curves of adsorption [58,63]. The time taken for adsorption (t_q) is calculated based on the equation (4.14) and the extent of sorbent adsorption of CO_2 gas (Q_{ads}) is evaluated from equation (4.15) in terms of mmole of CO_2/gram of sorbent.

$$t_q = \int_0^{\infty} \left(1 - \frac{C_A}{C_o}\right) dt \qquad (4.14)$$

$$Q_{ads} = \frac{FC_o t_q}{W} \qquad (4.15)$$

Adsorption isotherms, which are isothermal pressure-composition curves, could be determined experimentally or theoretically through model based simulations. The isosteric heat of adsorption (Q_{iso}) is a partial derivative of the enthalpy change of a system with respect to adsorbed amount at a certain temperature, pressure, adsorbed amount and surface area. It can be calculated from the Clausius–Clapeyron equation

$$lnP = \frac{Q_{iso}}{R}\frac{1}{T} + C \text{ --}(4.16)$$

The adsorption isotherms can also be calculated from Q_{iso} and adsorption enthalpy (ΔH) [117]. CO_2 adsorption (q) based on Langmuir isotherm is given by

$$q = q_m\left(\frac{K_L P}{1+K_L P}\right) \text{---}(4.17)$$

where K_L is the equilibrium constant of Langmuir isotherm. The key assumptions made are ideal gas behavior, adsorption as mono layer, equality of all adsorption sites and no interaction between molecules to be adsorbed. Adsorption kinetics used for adsorption capacities (q_t) of CO_2 gas can be calculated from adsorption kinetic models of equations 4.18, 4.19 and 4.20 [118].

$q_t = q_e(1 - \exp(-k_1 t))$ pseudo 1st order kinetic model (4.18)

$q_t = \frac{k_2 q_e^2}{1+k_2 q_e t} t$ pseudo 2nd order kinetic model (4.19)

$q_t = q_e[1 - exp(-(k_a t)^{n_a})]$ Avrami kinetic model (4.20)

Non-local (NLDFT) and quench solid (QSDFT) density functional theories have been used for micro- and meso-porous material evaluation with reference to capillary condensation, cavitation and pore blocking of different geometries of MCM-41, SBA families and MOFs [58].

5 KINETIC STUDIES OF CARBON CAPTURE

Direct high temperature CC was employed to improve energy efficiency avoiding the need to cool the flue gases to ambient conditions [119]. Its importance also includes H_2 gas production in SESR of fuels [63]. A significant research has been done on the deployment of solid sorbents for high temperature CO_2 capture (CC) [6,44]. The advantage of using industrial waste (fly ash) as an inert supporting material with active CaO-MgO was to increase the cyclic stability and capture capacity due to the presence of alkaline metal oxides [58,63]. Fly ash has significant amount of alkaline metal oxides to promote carbonation of the active sorbent and to reduce the regeneration temperatures thereby reducing the energy penalty [63]. These mineral oxides / silicates result in minimizing the regeneration temperature on par with the carbonation temperature of CaO. The fly ash was found to exhibit better thermal stability, favorable kinetics and chemical stability between 400-800^{o}C [80]. Limestone with MgO doped fly ash sorbent was found to perform better with a CC of 11mmol/g of sorbent at 650^{o}C with 40%CO_2+60%N_2 gas mixture [63] and the regeneration atmosphere maintained was nitrogen gas. Studies were reported recently on calcium looping carbon capture employing Ca-Mg acetate and fly ash doped CaO sorbents elucidating the role of fly ash in enhancing the capture performance [120,121]. Contactor configurations employed depend on sorbent material and its cycling between adsorption and regeneration operations. The thermo-kinetics and associated parameter estimation are important for further scale-up to industrial applications [68].

The estimation of kinetic parameters was reported employing random pore model (RPM) at different temperatures using the experimental data on CaO sorbent conversion [122,123]. Micro grain-grain model was reported with three reaction stages that include short kinetically controlled regime (0-17%conversion) followed by mixed carbonation regime (both reaction and diffusion) from 17-50% conversion and diffusion regime till 100% conversion [124]. Structural properties of the sorbent estimated using various models were used to describe reaction controlled regime and diffusion controlled regimes [125]. These regimes were explained using grain and pore models in the kinetic analysis of limestone sorbent carbonation using TGA [125]. Sorbent carbonation during reaction control regime was reported to show 1st order at 0-10kPa of CO_2 partial pressures [126]. The interpretation of reported models depend on intermediate metastable product formation at the interface of chemical reaction [127]. The other models reported were based on production and growth of nuclei following nucleation mechanism [128]. The $CaCO_3$ sorbent decomposition and carbonation of CaO were represented by the rate equations of adsorption-desorption phenomena using chemical reaction kinetic models [123]. There have been CC studies based on CaO, MgO and fly ash individually but not kinetics with a combination of these three sorbents together. It was observed that the mixed sorbent had higher surface area when CaO was synthesized either from its precursors or doped with MgO+Fly ash [63,109]. **Table 5.1**, shows the reported activation energies of sorbents used in high temperature CC [129].

Table 5.1 Comparison of activation energies for sorbent carbonation

	Sorbent carbonation	
Sorbent	T(^{o}C)& gas mixture	E_a (kcal/mol)
CaO-carbide slag	400-700&….**	2.87-8.84
Limestone	550-650&….**	17.21-40.63
PCC	550-700&….**	17.21-24.38
Limestone	400-725&….**	45.17
Commercial CaO	450-650&….**	28.9±6
Dolomite	570-850&….**	44.7
Limestone	500-850&….**	51.4
Mesoporous CaO	550-725&….**	24.38-45.17
Commercial CaO	550-725&….**	45.17
Na-FA(0.5:1)	700&……….*	2.1-7.11
Na-FA(1:1)	700&……….*	2.6-5.1
$Ca(OH)_2$	500-750&….**	9.56
P-Li_4SiO_4	500-650&….**	17.02-19.93
RHA1-Li_4SiO_4	500.-650&….**	10.95-14.36
CaO	650-800&100%CO_2	47.8-54.97
CaO	>600&100%CO_2	57
CaO	200-600&….**	9.49

Note: PCC: precipitate calcium carbonate; **: CO_2&N_2 gas mixture:*: 100%CO_2

In our previous studies, initial screening of sorbents was done from over 20 sorbent candidates based on zeolites, CaO, MgO, fly ash, fly ash doped CaO, MgO, etc. After rigorous standardization and cyclic stability studies, this sorbent of CaO50MgO10FA-C40 was selected as the best. This gave best CC besides exhibiting good stability. **Table 5.2**, below gives XRF analysis of this sorbent done with two different types of CFA used for doping. The detailed analysis on stability studies of sorbent and analytical instrumental studies used in this experimental work were reported in our previous chapters [63]. A detailed discussion is presented in the following sections on kinetic and thermodynamic studies that were carried out with this sorbent to facilitate further scale-up to industrial level. Coal fly ash contains inorganic compounds of metal silicates and has negligible CO_2 capture capacity at high temperature (at 650°C).

Table 5.2 XRF analysis of CFA samples before doping and after doping (wt%) with CC

Sorbent	CC[#]	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	TiO_2	SO_3
CFA-C	--	17.34	30.78	0.99	36.27	11.54	0.41	0.97	1.67
CFA-F	--	24.01	50.29	5.03	8.89	7.63	1.45	1.72	0.97
Ca50M10FA-C40	11.2	3.73	5.39	0.59	59.27	26.57	0.12	0.24	0.62
Ca50M10FA-C40[##]	---	4.473	6.564	1.745	60.759	25.049	0.142	0.3	0.682

Note: [#]: mmol of CO_2/g_{ads}; [##]: doped sorbent after CC

In this work, kinetic studies were conducted using the sorbent carbonation of CaO (50 wt%), MgO (10 wt%) and CFA (40 wt%). The best process conditions of carbonation temperature, time, amount of sorbent and its composition were taken from our previous studies on process standardization and cyclic stability. CC-time profiles have been obtained under the optimal conditions using which kinetic model has been proposed for both carbonation and regeneration processes. This kinetic model was then validated with our experimental data. The assumptions taken for model formulation have also been stated. Thermodynamic estimations also were presented to prove the improved feasibility of the CC process. The kinetic parameters estimated were presented and compared with those reported.

5.1 CARBONATION

5.1.1 Model selection

Extensive reports were available on the kinetics of sorption based CC, $CaO\text{-}CO_2$ reactions of solid and gas phases [63]. It is a very important reaction in carbon capture, energy storage, H_2

production with IGCC and chemical heat pump. The kinetics of high pressure carbonation reaction using calcium looping process were reported to follow the first order w.r.t CO_2 partial pressure upto certain value of total pressure beyond which it followed zero order of reaction [114]. A non-catalytic gas- solid reaction of chemisorption for CO_2 was found to follow the basic steps of external mass transfer, intra-particle diffusion, inter particle diffusion, diffusion through the product layer and surface reaction that could occur sequentially or simultaneously. When the gas phase mass transfer resistances were neglected, the carbonation reaction, a non-catalytic gas solid reaction followed two rate controlling regimes viz., initial fast reaction at the surface followed by slow diffusion of the species through the $CaCO_3$ layer surrounding the CaO particles. The role played by each step would depend on the temperature, structural properties of the sorbent and the particle size. At very low particle size, the rates were reported to be high and also it was assumed that the influence of temperature on adsorption kinetics was minimal [130].

Simple models developed to explain this phenomenon were uniform reaction model and the shrinking core model [131]. The later assumes that, reaction occurs at outer layer of the particle, forming a product layer around the unreacted core. This core shrinks with the progress of the reaction before getting totally diminished [130]. Of late, adsorption kinetics are being preliminarily assessed using adsorption half-time [132]. Four models of pseudo first order, pseudo second order, Elovich and inter-particle diffusion models were tested for CC employing activated carbon derived from bio-mass using regression analysis [129]. CO_2 capture with activated carbon was found to follow pseudo second order model with physisorption as the process of adsorption with low activation energy [133]. Both pseudo first and second order models have been tested recently for CO_2 adsorption on nitrogen enriched carbon sorbents and it was found that the former fitted well with experimental data than the later over the entire range of adsorption with physisorption as the mechanism [134]. Very recently, modified LDF (linear driving force) with variable mass transfer coefficient was successfully developed to explain adsorption and equilibrium kinetics of activated carbon based CC using gravimetric analysis [135]. For the first time XRD was employed, to understand the intrinsic kinetics of CaO-CO_2 reaction at 1bar and temperatures between 450 to 750^oC by monitoring different crystalline phases during CO_2 uptake. These studies indicated the strong dependence of kinetics on the particle size of the sorbent besides other parameters like temperature and pressure [136]. The kinetics of CC by solid sorbent in continuous model that assumes rapid diffusion of gaseous reactant into a particle was more suitable than the chemical reaction and unreacted core model/SCM. The former was found to be unsuitable to explain gas-solid reaction and the later represented by equation 5.1 (reaction control regime) and equation 5.2 (diffusion control regime) given below was found to be much better.

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3} \text{ --(5.1)}$$

$$\frac{t}{\tau} = 1 - 3(1 - X)^{2/3} + 2(1 - X) \text{ ---(5.2)}$$

$X = [\Delta M/\Delta M_\infty] = [(M_o - M_t)/(M_o - M_\infty)]$---(5.3)

where t is the time,

X is CaO conversion,

τ is the time taken for complete conversion,

ΔM is the change in sorbent mass during carbonation duration of Δt,

ΔM_∞ is the total change of sorbent mass from beginning to the end of carbonation reaction cycle time,

M(t) is the sorbent mass at time “t”,

M_o is the initial mass of sorbent sample.

The sorbent samples of 20g with 60 minutes carbonation time were used in this experiment.

In this work, a simple kinetic model was proposed to explain the carbonation by our sorbent system consisting of CaO (50%)-MgO(10%)-FA-C type(40%) and tested with the experimental data obtained from our previous work [137]. The kinetic parameters estimated were presented and compared with the reported values. It was found that carbonation rates were high at low conversions with initial rates being dependent on temperature and the rates approached nearly 0 at ultimate conversion of X_u, for different temperatures. This could be expressed as the equation 5.4 below, where k is intrinsic rate constant (time^{-1}) which itself is the rate at low conversions. But as the conversions increase, rate slows down by the attenuation term,$\left(1 - \frac{X}{X_u}\right)^n$, becoming zero at $X=X_u$.

$$r_{CO_2} = \frac{1}{M_{CaO}}\left[\frac{dX}{dt}\right] = k\left(1 - \frac{X}{X_u}\right)^n \text{ --(5.4)}$$

where r_{CO_2} is the molar rate of CO_2 removal per unit mass of sorbent, n is a parameter. To get explicit function of conversion versus time, n was assumed to be 1 or 2 and the equations 5.5 and 5.6 could be obtained respectively. Equation 5.5 is similar to the low temperature kinetic model proposed for $Ca(OH)_2$ with CO_2 in humid conditions [138]. This was derived assuming sorbent carbonation influenced by reaction control due to surface coverage by the product.

$$X = X_u\left[1 - exp\left(-\frac{k}{X_u}t\right)\right] \text{ --(5.5)}$$

$$X = \frac{X_u t}{(X_u/k)+t} \text{ ---(5.6)}$$

Regression analysis on equations 5.5 and 5.6 with conversion-time data (**Figure 5.1a**) has been done to find the best suited equations from the above two i.e equations 5.5 and 5.6. It has been found that correlation coefficients close to unity were achieved using equation 5.6 i.e 0.99, 0.98, 0.96 and 0.96 respectively at temperatures 350°C, 450°C, 550°C and 650°C while the corresponding values using equation 5.5 were 0.9, 0.87, 0.98 and 0.95. Hence equation 5.6 was considered for all our further studies. Similar trends were reported for CaO based kinetic studies [137]. It was also found that identification of the suitable model depends on the nature of sorbent and more importantly temperatures.

If b is the time taken to attain half the ultimate conversion, $X = X_u/2$ at t=b, then equation 5.6 becomes

$$X_u = kb \text{ ---(5.7)}$$

By substituting eq. (5.7) in eq.(5.6), we get

$$X = \frac{kbt}{b+t} \text{ ---(5.8)}$$

The rate of reaction could be derived from above equation 5.8 and expressed by equation 5.9 below assuming that there is no external mass transfer limitation of CO_2 on CaO50MgO10FA-C40 sorbent.

$$\frac{1}{X} = \frac{1}{k}\left(\frac{1}{t}\right) + \frac{1}{kb} \text{ --- (5.9)}$$

where t is the time taken for the CaO or sorbent conversion of X

5.1.2 Model fit with Experimental data

The kinetic parameters could be estimated according to the following kinetic rate expression [114,116].

$$-r_a = kC_A^n = \frac{\Delta M}{\Delta t} \text{ ---(5.10)}$$

where C_A is the concentration or partial pressure of CO_2 in the gas mixture at time ‘t’,

n is the order of the reaction with respect to CO_2,

k is the reaction rate constant,

ΔM is the change of sorbent sample mass at time Δt.

The experimental conversion data of sorbent at various temperatures of 350°C, 450°C, 550°C and 650°C were shown in **Figure 5.1** which show that temperature had a positive influence on initial conversions which were high initially and get saturated after certain time. A double exponential model for 1st order kinetics was adopted to explain the total sorption capacity of the sorbent in the form of product layer (reaction controlled regime) and alkaline diffusion layer (diffusion controlled regime) [84]. The straight line graph in **Figure 5.2**, of ln (carbonation reaction rate) vs ln(CO_2 concentration) clearly demonstrates that the carbonation reaction was of first order w.r.t CO_2. **Figure 5.3,** shows the experimental and model derived conversion vs time plots for both reaction and diffusion controlled regimes at two different temperatures of 550°C and 650°C respectively. From these studies, we find that diffusion control regime showed a better fit throughout the process while the chemical reaction control regime performed better in the initial stages. Our trends are in agreement with the reported studies employing CaO sorbent [137]. To estimate the activation energies and pre-exponential factors, Arrhenius plot was drawn between ln(k) vs 1000/T for both regimes of reaction and diffusion control as shown in **Figure 5.4**. The diffusion control regime value (30kJ/mol) obtained was found to be closer to experimental value (33kJ/mol) when compared to the reaction of control regime (23kJ/mol).

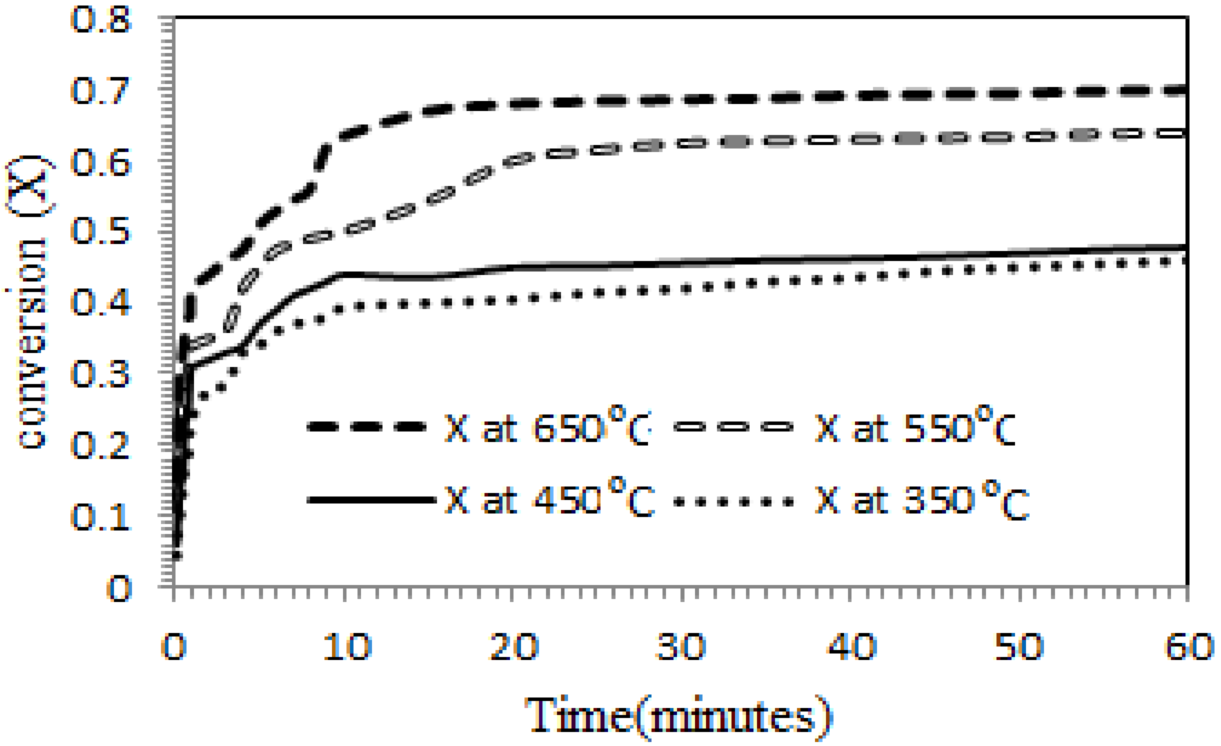


Figure 5.1 Effect of sorbent conversion with carbonation time

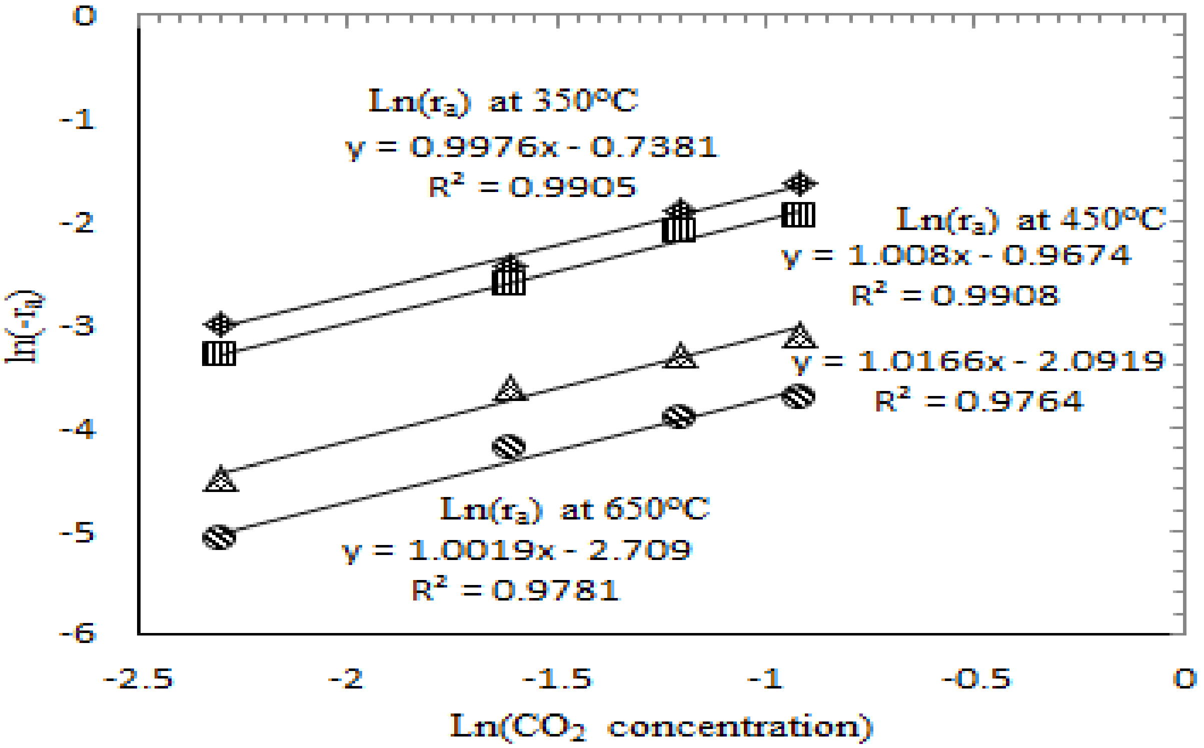


Figure 5.2 Estimation of reaction order (experimental).

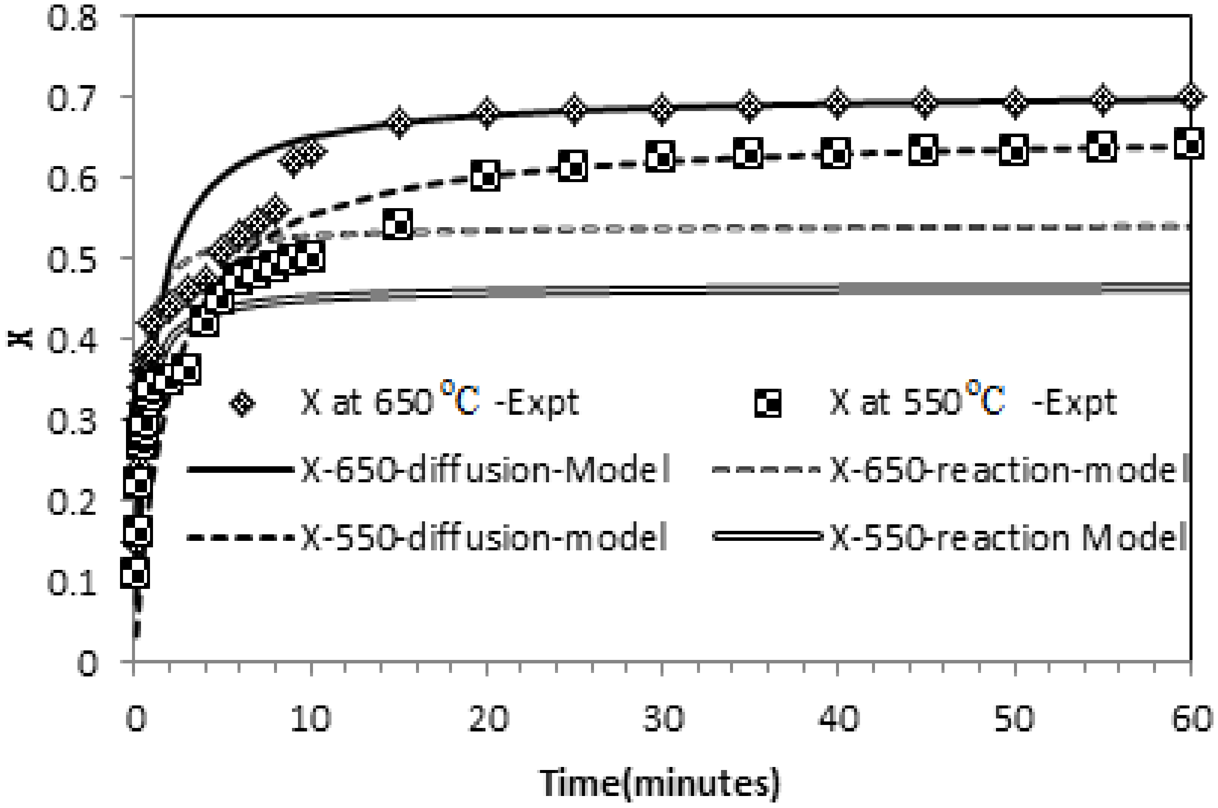


Figure 5.3 Experimental data vs reported model

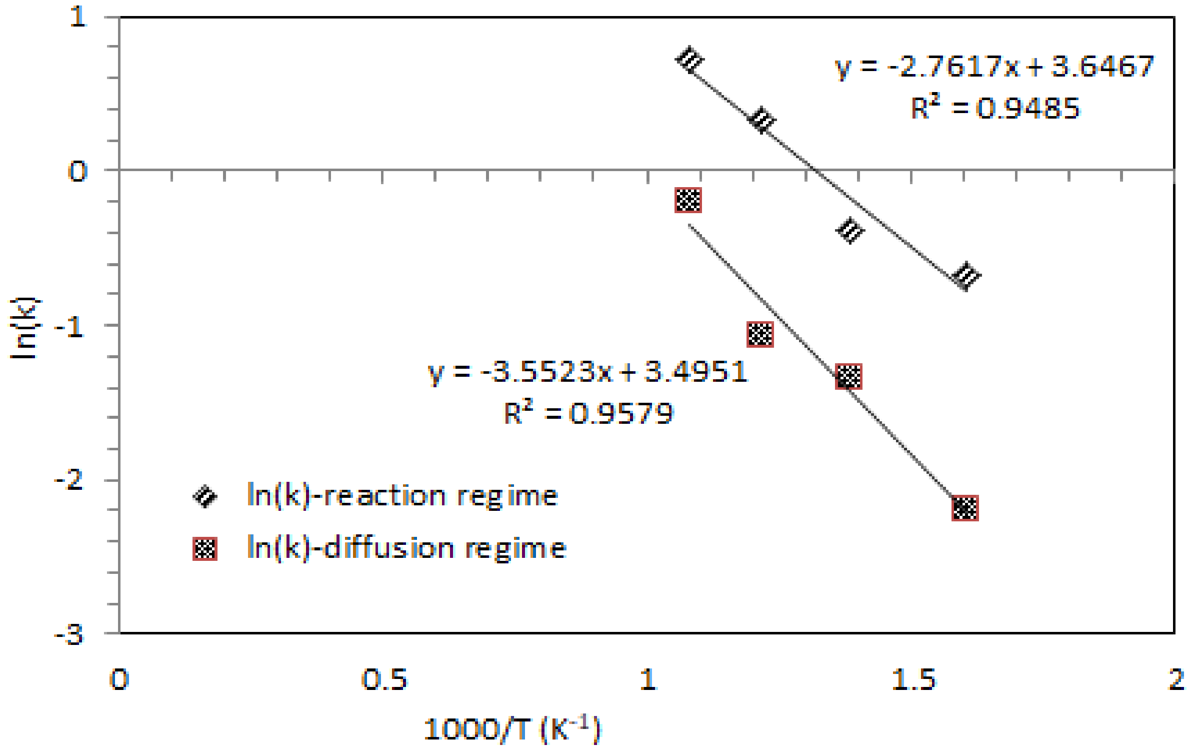


Figure 5.4 E$_a$ from rate constants

5.1.3 Results and Discussion

As shown in **Table 5.3**, increasing trend was observed with the rate constants of reaction control regime from 350°C to 650°C due to the presence of higher alkalinity in the sorbent which was similar to that observed with non-isothermal sorbent regeneration trend at >650°C in **Figure 4.6** and **Figure 4.7** [129]. The ultimate conversion using the reported model in reaction regime at 650°C is lower than at 550°C and 450°C due to marginal decomposition of sorbent. The diffusion control regime shows an increase in rate constant from 350°C to 650°C and the ultimate conversion increased to 0.71 at 650°C. It is due to inter grain and intra-grain diffusion of the sorbent carbonation. It is in agreement with carbonation in diffusion controlled regime which is promoted by the restoration of nano crystalline CaO structure due to inert MgO grains from dolomite decomposition [139].

Table 5.3 Kinetic parameters - Estimated

Temperature (°C)	**Chemical reaction control regime**			**Diffusion control regime**			Ref
	k(min^{-1})	b(min)	X_u	k(min^{-1})	b(min)	X_u	
650	2.54	0.2643	0.543	0.814	0.87	0.708	this work
550	1.3835	0.3375	0.467	0.3465	1.906	0.66	this work
450	0.681	0.6375	0.434	0.261	1.87	0.487	this work
350	0.51	0.7686	0.392	0.1117	4.37	0.49	this work
585	0.406	0.587	0.24	0.049	14.875	0.73	[140]
615	0.600	0.489	0.29	0.110	6.821	0.75	[140]
655	0.925	0.506	0.47	0.344	2.241	0.77	[140]
690	1.070	0.637	0.68	0.759	1.001	0.76	[140]
725	1.855	0.404	0.75	2.111	0.352	0.74	[140]
550	0.273	1.435	0.39	0.074	0.167	0.68	[141]
600	0.563	0.967	0.54	0.165	4.581	0.76	[141]
650	0.858	0.863	0.74	0.375	2.325	0.87	[141]

Table 5.3, gives the Arrhenius parameter values (activation energies and pre-exponential factors) for both reaction and diffusion control regimes. The calculated experimental values were

compared with those reported. This comparison clearly indicates that nature of sorbent along with the process conditions mainly temperature and CO_2 partial pressure play a vital role in the distinction. Doped sorbent by CFA addition possesses higher values of frequency factor and lower values of activation energies. This sorbent (CaO50MgO10-FA-C40), for both the regimes (reaction and diffusion), reinforce the enhanced rate and improved thermal stability. The performance of doped sorbents is superior when compared to un-doped sorbents. The experimental activation energy is marginally higher than estimated values in reaction regime and diffusion regimes of this sorbent. These were in agreement with the reported activation energies of fly ash derived sodium silicates (Na-FA 1:1) in reaction regime (10.7kJ/mol) and in diffusion regime (21.2kJ/mol) [109]. Another set of sorbent of sodium silicates of fly ash (Na-FA 0.5:1) was reported to have activation energies in reaction regime (8.6 kJ/mol) and diffusion regime (29.7kJ/mol) [109]. The other reported CaO based sorbents in **Table 5.4**, were without the fly ash having E_a values from 72 to 190 distributed between reaction regime and diffusion regime respectively [141]. A recently published report was available on Spanish limestone sorbent using random pore model (RPM) showing activation energy in reaction regime (21.3kJ/mol) which was in agreement with our sorbent but has significantly higher value in diffusion regime (140kJ/mol) than our sorbents activation energy (29.53kJ/mol). With lower activation energy in diffusion regime, this is not sensitive to temperature probably due to higher alkalinity in our sorbent.

Table 5.4 Carbonation kinetic parameters-Experimental

Kinetic parameter	Experimental	Reaction regime-model	Diffusion regime-model	Ref
E_a(kJ/mol)	32.76	22.961	29.53	this work
	---	72.2	189.3	[140]
		72.7	102.5	[141]
		21.3	140	[142]
Pre exponential factor(min^{-1})	$1.08x10^3$	$38.35x10^3$	$32.95x10^3$	this work
	-----	$1.03x10^4$	$1.57\ x10^{10}$	[140]
		$1.16\ x10^4$	$2.33\ x10^5$	[141]
		$28x10^6$	$48x10^6$	[142]

For a comparison purpose, while the activation energy for carbonation was around 30 kJ/mol, it was around 37.7 kJ/mol for regeneration at a temperature of 650-710^{o}C. From this, we understand that reducing the energy requirements in regeneration was always a challenge to make this technology economically viable. This could be achieved by effective energy integration, integration of CC with power generation and H_2 gas production using sorption enhanced steam reforming.

5.2 CALCINATION

Kinetics of carbonation for the sorbents based on CaO for high temperature CC were widely studied. But, less attention was given to de-carbonation or regeneration kinetics of energy intensive doped CaO sorbent [143]. Kinetic investigations depend on sorbent material, contacting configuration and optimal parameters. The key objective was to have a suitable equilibrium model under which the sorbent properties need to be calculated. The adsorption-regeneration cycle conditions were needed for further kinetic estimations. Industrial implementation of this technology needs to address cyclic operation of CLP in a continuous chemical reactor operation. Decomposition is inhibited with a bulky sample in packed bed due to local high partial pressures of CO_2 in the pores or in the interstices of particle bed. The rate of regeneration can be measured under differential conditions while ensuring the known CO_2 concentrations. Decreases in calcination reaction rate results with an increase in CO_2 partial pressure or total pressure of the system[144]. The reported activation energies of limestone were found to be proportional to CaO content for that derived from cockle shell sorbent in particle size range of 0.125mm-4mm during decomposition or regeneration [145]. For magnesite ($MgCO_3$), regeneration (560-680^{o}C) activation energies (61-72.2kcal/mol) were found to be in proportion to their particle size [146]. The packed-bed reactor design was aimed to achieve effective calcination temperature of $CaCO_3$ and should be kept at minimum heat requirement during calcination as sorbent deactivation needs high temperature requirement [147]. **Table 5.5,** shows the comparison of reported regeneration activation energies of CaO and its doped sorbents[148].

Table 5.5 Comparison of activation energies of sorbent regeneration

Sorbent	T(^{o}C)& Gas mixture	E_a (kcal/mol)
Limestone[149]	671-923&20%O_2/80%CO_2	297.6
Limestone[149]	671-23&20%O_2/80%N_2	41.82
Calcium propionate[150]	354-699& N_2 gas	45.2
Limestone[151]	761-900&0-15%CO_2+air	42.16
CaO[152]	550-800& N_2 gas	41.51
Limestone[153]	850-950&CO_2+air	33.222
PCC[154]	700-900& N_2 gas	29.85

5.2.1 Model selection

Calciner need higher calcination efficiencies and these may not be achieved at low temperatures (near carbonation temperatures). There is no agreement on general reaction mechanism and the semi empirical models are still used for each practical application [127]. The decomposition of small particles (1-90µm) of limestone sorbent is chemically controlled and the increase in particle size is controlled by internal mass transfer [122]. The model in which over all reaction kinetics does not depend on reactant particle size is called uniform conversion model (UCM) [155]. In UCM, the overall rate limiting step is chemical reaction controlling regime. The more suitable models for gas-solid reactions for analyzing the results is the grainy pellet model (GPM) [156]. The shrinking core model (SCM) and UCM are the two suitable models to describe the sorbent calcination reaction of fine particles [157]. SCM is used to describe the sorbent calcination with very low initial porosity and the UCM could be applied with higher initial porosity of sorbent calcination. The regeneration reaction is due to CO_2 release from inter grain and intra grain diffusion much rapidly. This is considered as chemical reaction controlling regime for the overall limiting step. RPM was developed for sulphation of lime in which the distributed pore sizes were considered as randomly oriented cylinders of uniform diameter [140]. The reaction proceeds with consumption of solid and lost as gaseous product. In this process, a rise in pore size and surface area was observed before decreasing to zero. Shrinking core model or homogeneous model was considered for radial conversion due to heat and mass transfer processes within all the smallest particles [144].

The degree of sorbent conversion (f_{calc}) is determined by the following equation [157,158].

$$f_{calc} = \frac{\Delta M}{\Delta M_{\infty}} = \frac{(X_{carb} - X_{calc})}{X_{carb}} = \frac{moles\ of\ CaCO_3}{(moles\ of\ CaO)(X_{N-1})} \quad \text{----------------------------------}(5.11)$$

where f_{calc} is the fraction of $CaCO_3$ calcined to CaO present in synthesized sorbent (CaO50.MgO10.FA-C40) with reference to moles of $CaCO_3$ sorbent from former carbonation and ranges from 0 to 1 in every cycle.

ΔM is the mass loss of sorbent during regeneration at time (t),

ΔM_{∞} is the mass loss of all the sorbent assumed to have completely regenerated.

X_{calc} and X_{carb} are the final and initial $CaCO_3$ contents of calciner (both expressed in moles of $CaCO_3$ per mole of CaO), respectively.

$X_{carb} - X_{calc}$ is the $CaCO_3$ sorbent in the sorbent calcined per mole of CaO in the sorbent.

$$X_N = \frac{1}{\frac{1}{(1-X_r)} + kN} + X_r \quad \text{--}(5.12)$$

where k is the deactivation constant with a value of 0.52 and X_r is the sorbent residual molar concentration value of 0.075 at $T_{calc} < 950^{o}C$. These values were constant for carbonation – calcination cycles higher than 50 [147].

The order of reaction could be calculated with following equation (5.13) and is shown in **Figure 5.2**.

$$-r_a = kC_A^n = \frac{\Delta M}{\Delta t} \text{---}(5.13)$$

Evaluation of pore structure for sorbent calcination conversion reaction was done with modified random pore model [159].

$$\frac{df_{calc}}{dt} = k_c(1 - f_{calc})^{2/3}(C_{eq} - C_{CO_2}) \text{ --- }(5.14)$$

where k_c is the kinetic constant of $CaCO_3$ calcination ($m^3.kmol^{-1}.s^{-1}$)

C_{CO_2} is the concentration of CO_2 in the gas phase ($kmol/m^3$).

C_{eq} is the equilibrium concentration of CO_2 in the gas phase ($kmol/m^3$).

$$f_e = \frac{10^{[7.079-(8308/T)]}}{P} \quad \text{--}(5.15)$$

$$P_{CO_2,eq} = 10^{[7.079-(8308/T)]} \text{ ---}(5.16)$$

where P_{CO_2}, is the partial pressure of CO_2 and $P_{CO_2,eq}$ is the equilibrium partial pressure of CO_2. Then $C_{CO_2} = \frac{P_{CO_2}}{RT}$ and $C_{eq} = \frac{P_{CO_2,eq}}{RT}$ where R is gas constant (8.314 J/mol.K), T is the temperature (K).

$$P_{CO_2,eq} = \ 0.1333 \times 10^{[10.4022-(8792.3/T)]} \quad \text{--- (5.17)}$$

The above equation 5.16 was not selected in this work due to its validity between 1-300atm of CO_2 and 900°C-1200°C [101]. But, the equation 5.17 was selected for kinetic parameter estimation due to its validity between 0-1atm of CO_2 pressures at 449°C-904°C [160].

The limestone particle conversion in each calcination cycle N is calculated from experimental data measured as per the reaction equation 5.11 normalized with maximum achievable carbonated content from the previous cycle. The calcination rate per mole of CaO can be calculated from equation 5.11 and equation 5.14 which is given by

$$\frac{d(X_{carb}-X_{calc})}{dt} = k_c \left\{1 - \left[\frac{X_{carb}-X_{calc}}{X_{carb}}\right]\right\}^{2/3} \left(C_{eq} - C_{CO_2}\right) \quad \text{-----------------------------------(5.18)}$$

$$k_c = k_{c0} exp(-E_{ac}/RT) \quad \text{---(5.19)}$$

E_{ac} is the activation energy of the kinetic constant of $CaCO_3$ calcination.

k_{c0} is the pre-exponential factor of the kinetic constant of $CaCO_3$ calcination.

Upon integrating eq(5.18) and solving for time taken to achieve 100% calcination of carbonated sorbent. We get

$$t_c^* = \frac{3X_{carb}}{k_c(C_{eq}-C_{CO_2})} \quad \text{---(5.20)}$$

t_c^* , is the time needed to achieve full calcination for a particle of any $CaCO_3$ content (s).

5.2.2 Model fit with Experimental data

Sorbent calcination conversion data was obtained from CO2 concentration in the exit gas mixture used to calculate weight changes with time. The global rate of regeneration sorbent is found to follow as 2nd order (**Figure 5.5**) w.r.t. CO_2 concentration in gas mixture[148]. It indicates uniform thermal decomposition process of $CaCO_3$ and was in agreement with the reported regeneration order that varies from 1.647-2.084 [150]. The apparent activation energy depends on overall intrinsic reaction resistance energy limited by the formation and rupture of chemical bonds [157,161,162]. Calcination reaction rate depends on calcination temperature and CO_2 partial pressure but it does not depend on $CaCO_3$ content and particle lifetime [157].

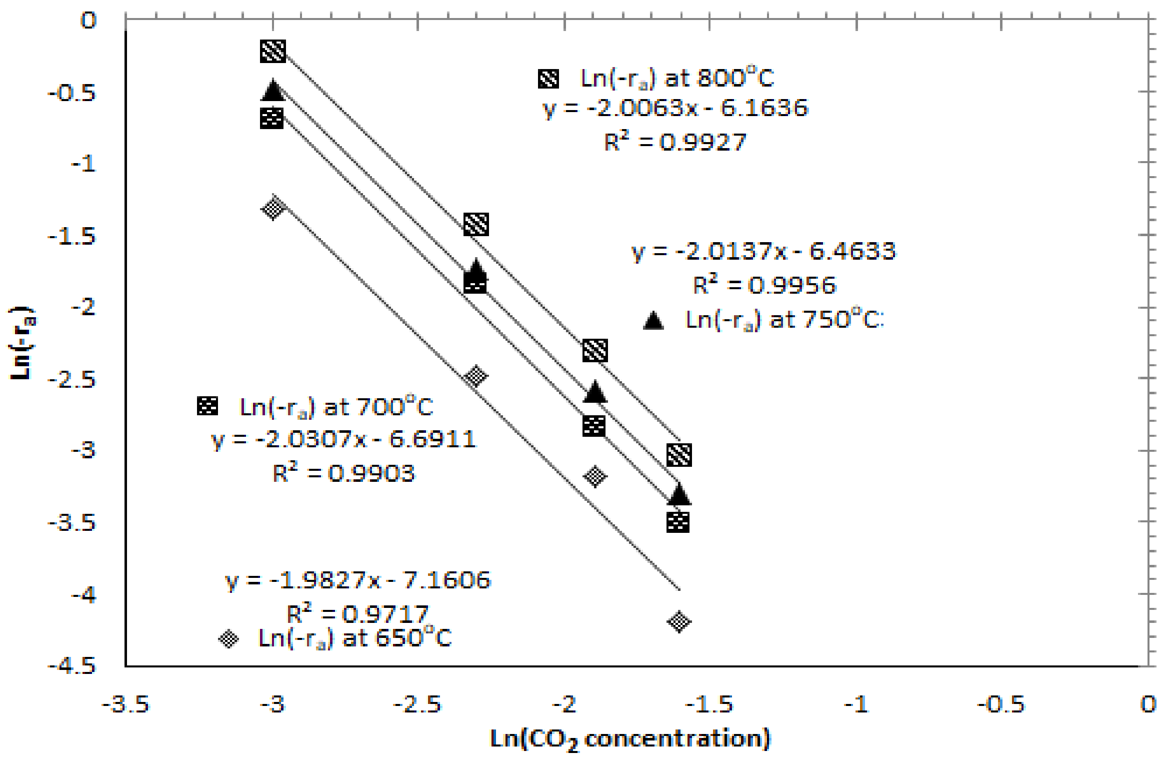


Figure 5.5 Calculation of reaction order for sorbent regeneration

Figure 5.6 and **Figure 5.7**, shows $CaCO_3$ calcined per mole of CaO, (X_{carb} - X_{calc}) vs time and the calcination rates were constant for a given calcination temperature and CO_2 partial pressure in gas phase at different cycle numbers[148]. **Figure 5.8** and **Figure 5.9**, represent the experimental data on conversion with those predicted by model from equation 5.14 upon integration yields a polynomial equation[148]. In this model, each particle is assumed to be a spherical grain of uniformly sized non porous $CaCO_3$ which upon calcination follows a chemical reaction regime under shrinking core model [157].

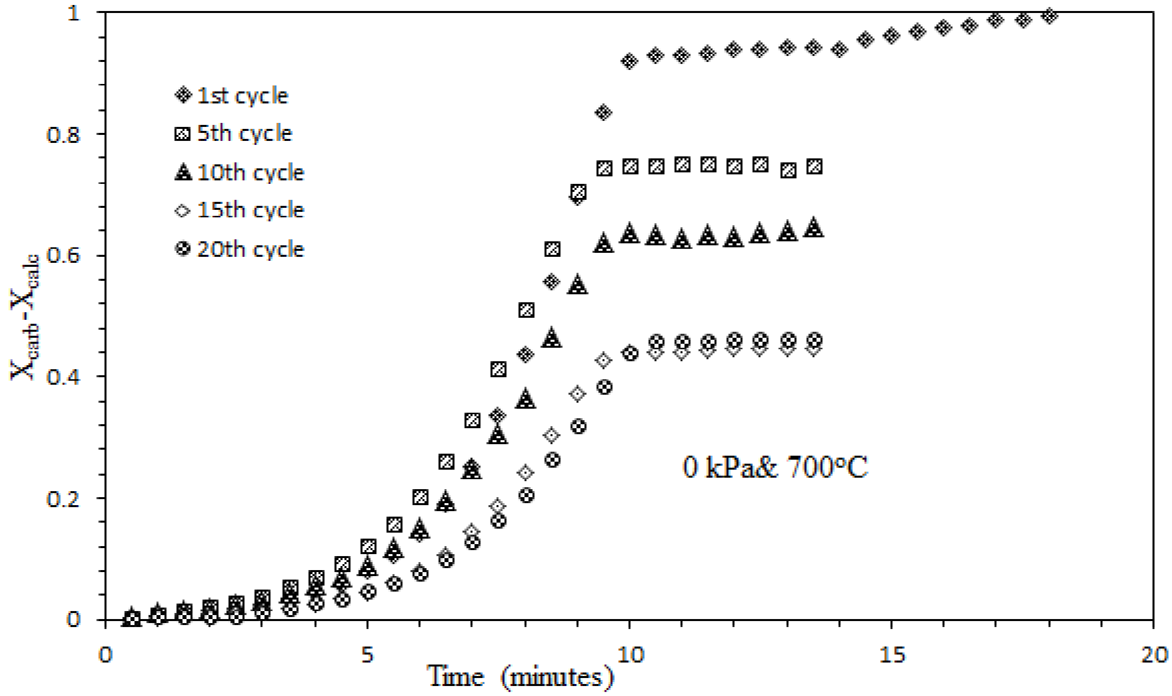


Figure 5.6 Conversion curves for different cycles at P_{CO2} of 0 kPa, 700°C

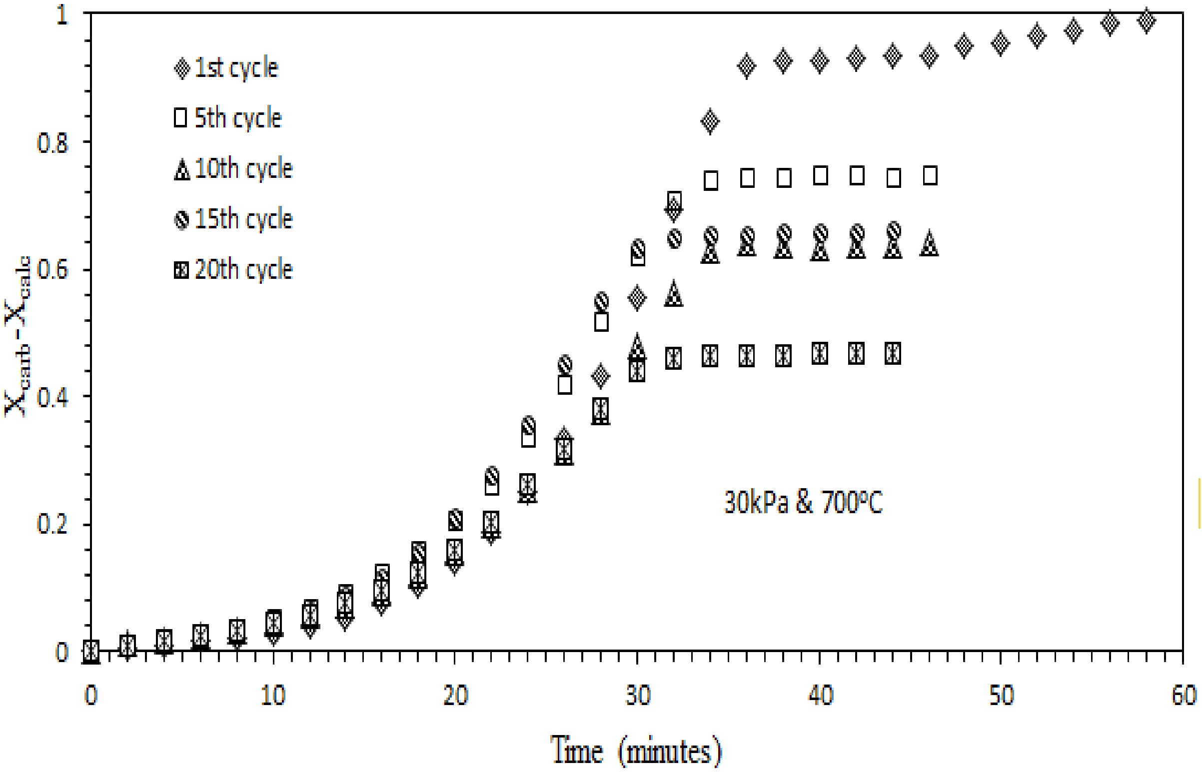


Figure 5.7 Conversion curves for different cycles at P_{CO2} of 30 kPa, 700°C

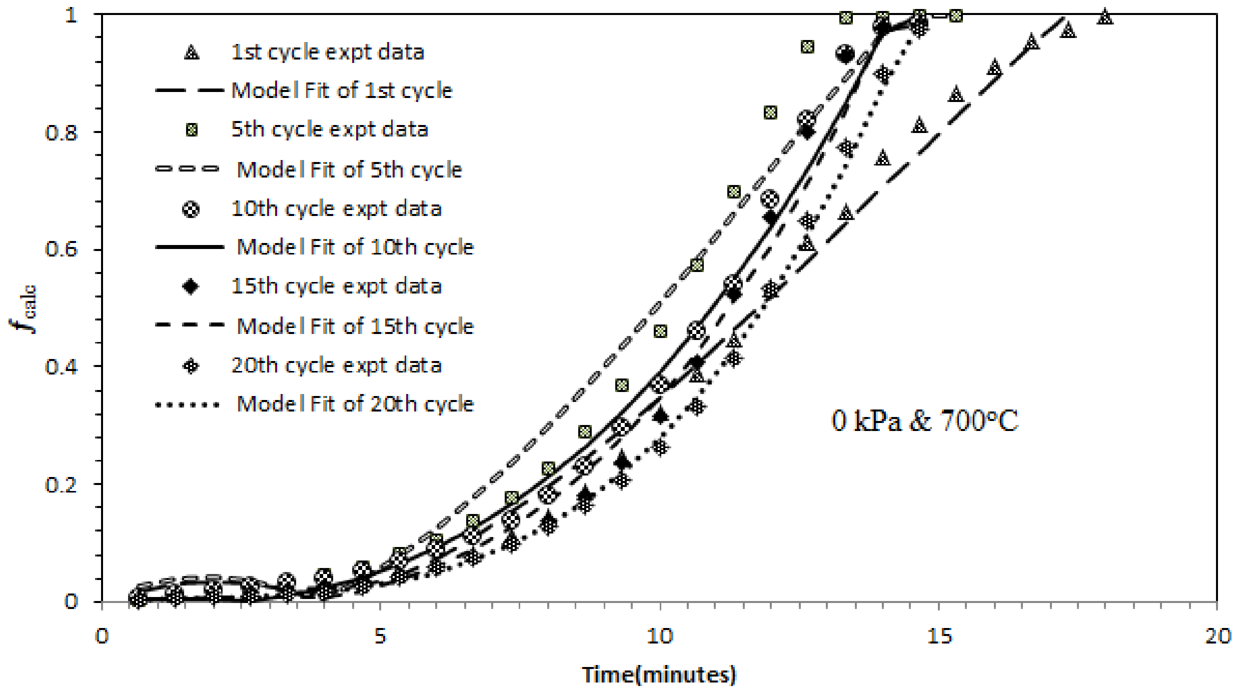


Figure 5.8 Curve fitting of model and normalized conversion curves at 0 kPa, 700°C

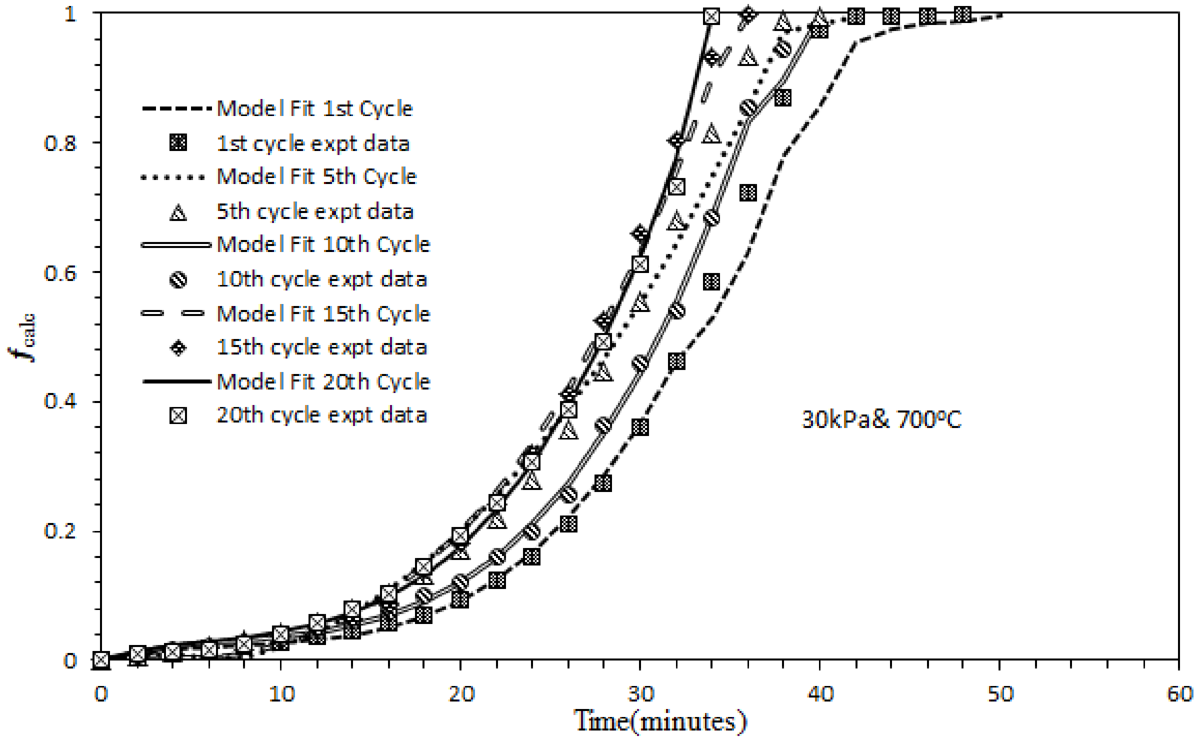


Figure 5.9 Curve fitting of model and normalized conversion curves at 30 kPa, 700°C

Figure 5.10 and **Figure 5.11**, shows the effect of calcination temperature of sorbent (20g sample size) at 20th cycle in the absence of CO_2 and in the presence of CO_2 at 90kPa[148].

Higher calcination rate was observed with increased calcination temperature and was in accordance with reported data [157]. Presence of CO_2 minimizes the reaction rate for a given temperature.

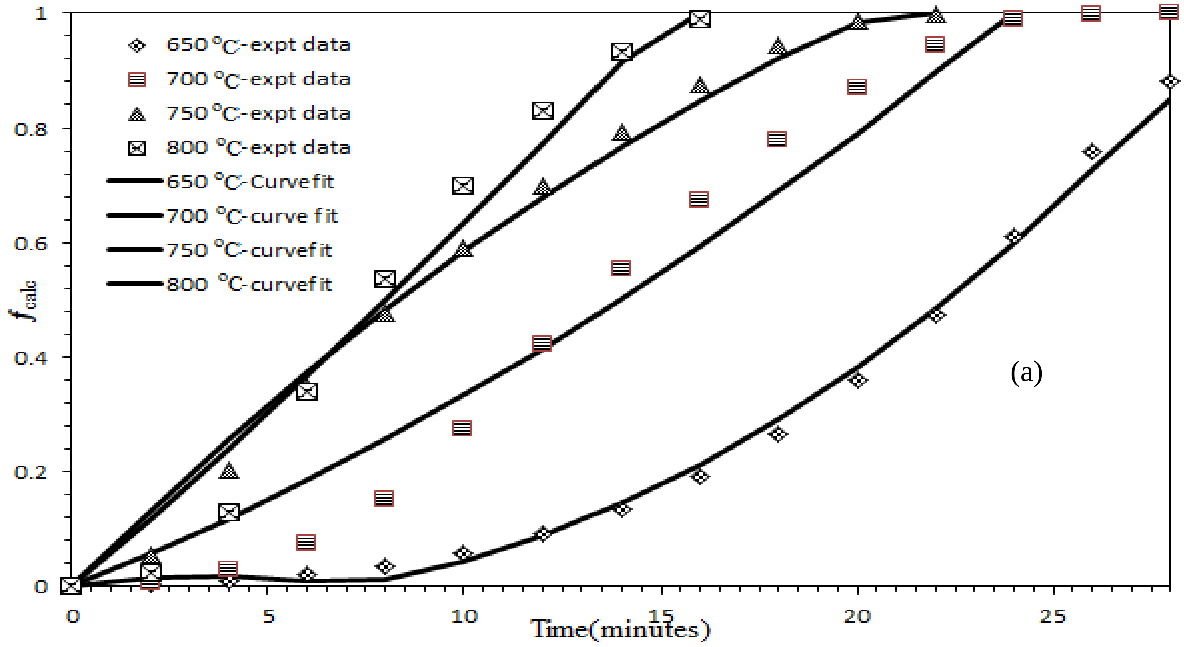


Figure 5.10 Effect of temperature on f_{calc} for 20th cycle calcination at P_{CO2} of 0 kPa

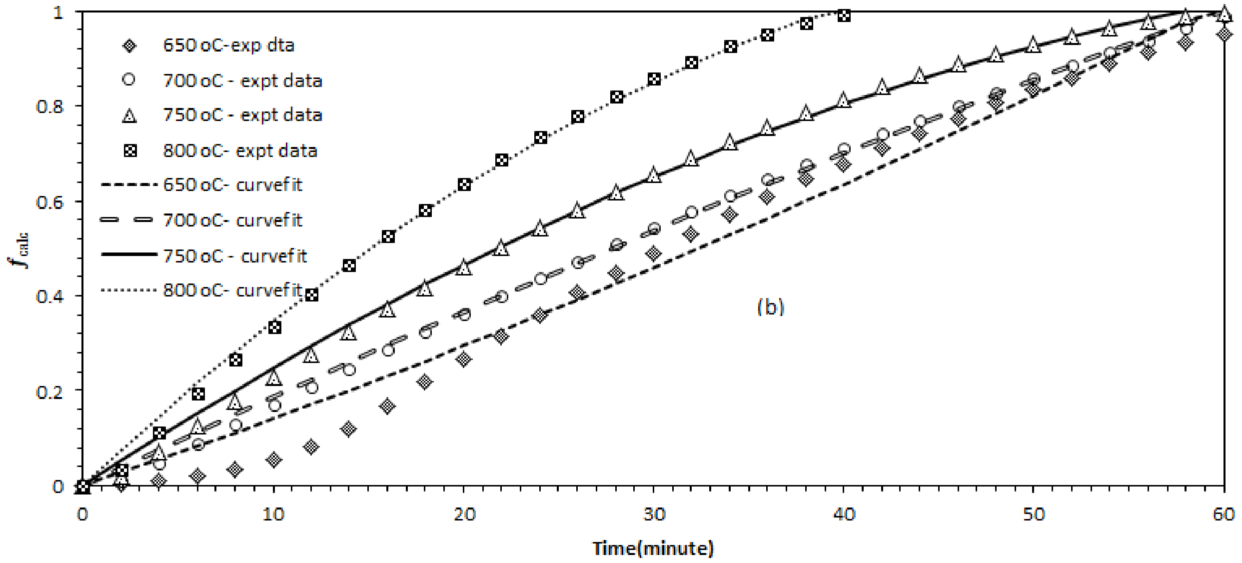


Figure 5.11 Effect of temperature on f_{calc} for 20th cycle calcination at P_{CO2} of 90kPa

Figure 5.12 and **Figure 5.13**, shows the effect of partial pressures of CO_2 upto 101 kPa and also the effect of equilibrium partial pressures of CO_2 calcination at different cycles[148].

When CO_2 concentrations were increased to nearly >90 kPa then calcination rate increased with reaction time. Upon increasing the number of calcination cycles, the reaction time decreased due to decrease in crystallinity of calcined sorbent. Amorphous sorbent is more reactive than crystalline form and is in accordance with the reported [151,163]. 100%CO_2 has been used as carrier gas instead of N_2 gas to study regeneration kinetics of sorbent in PBR while producing 100%CO_2 at atmospheric pressure for further scale-up of process

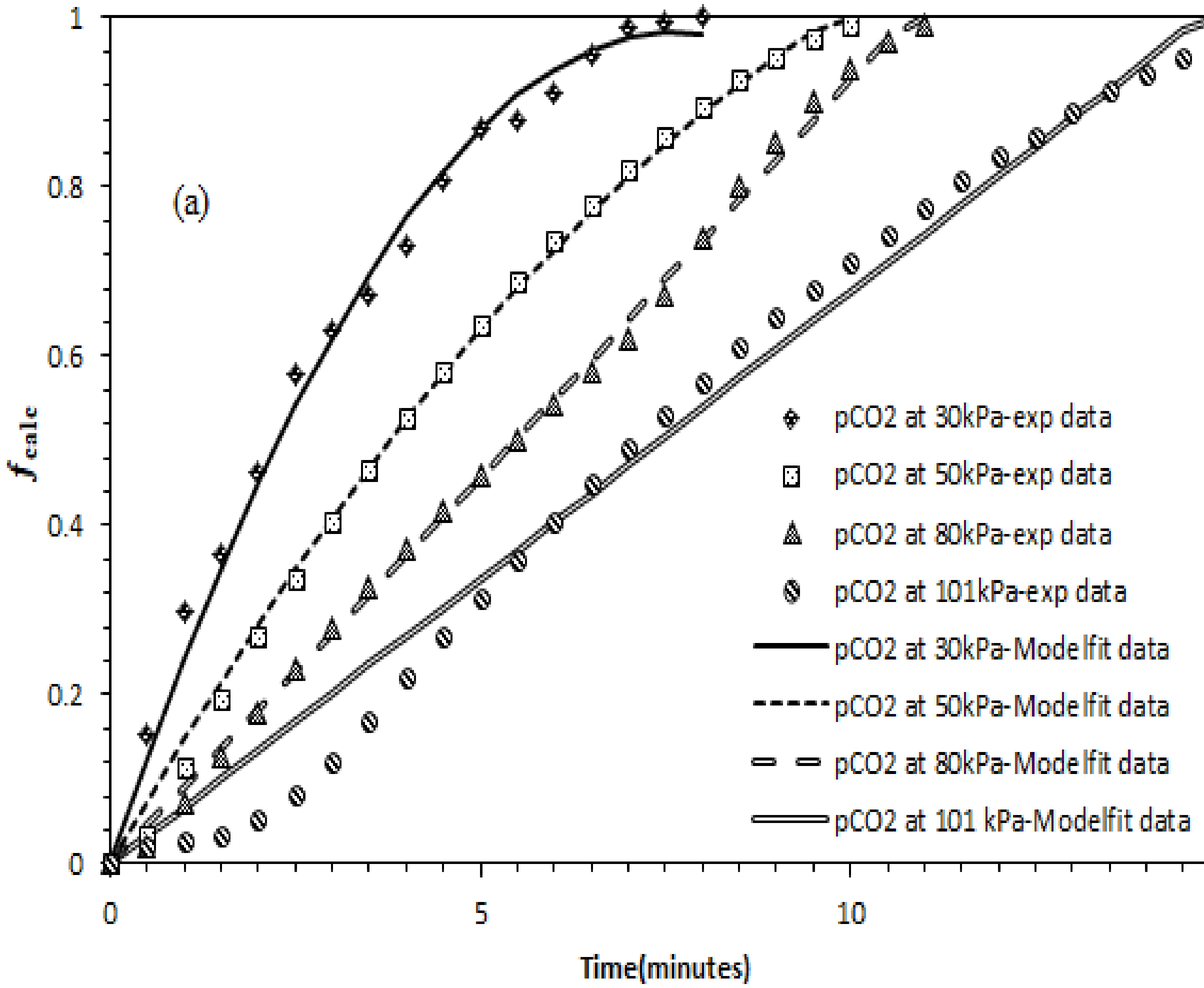


Figure 5.12 Effect of P_{CO2} on f_{calc} for 20th cycle calcination at 750°C

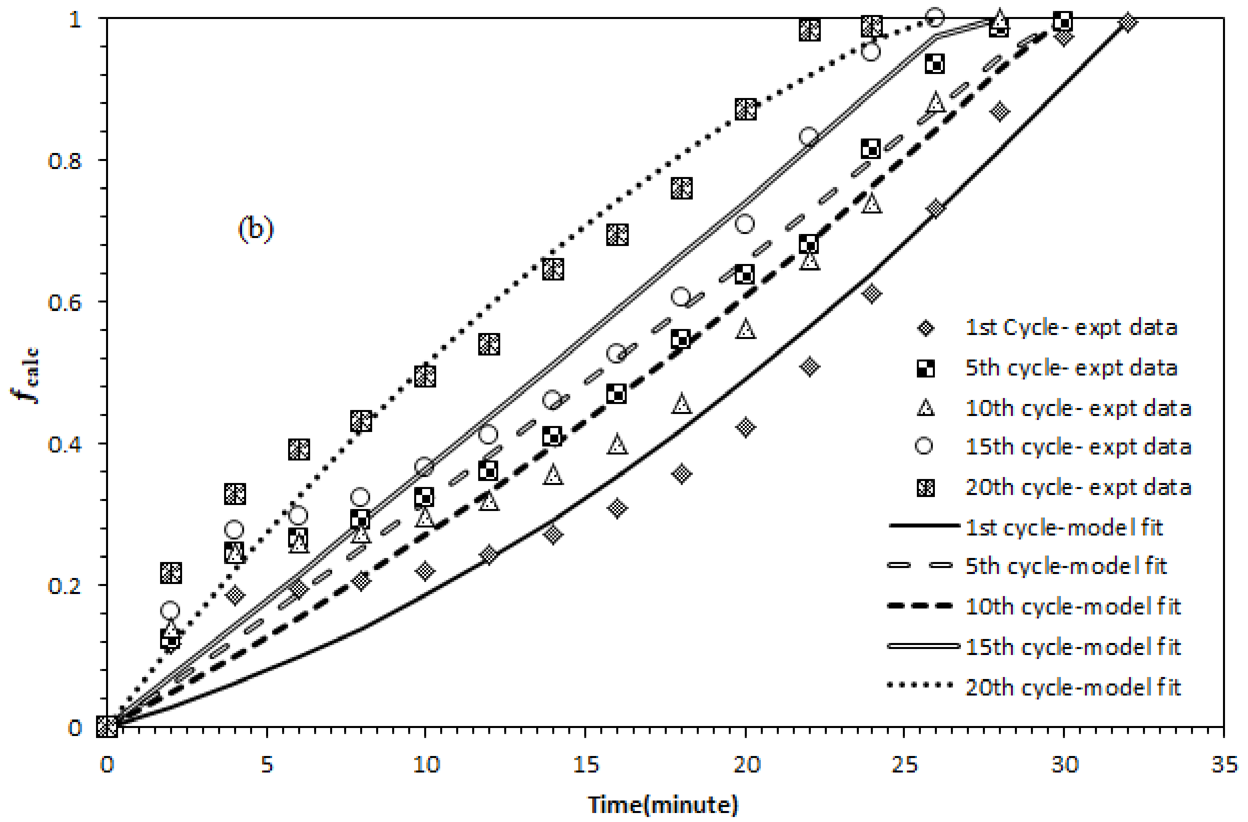


Figure 5.13 Experimental and predicted f_{calc} values at equilibrium P_{CO2}.

It was reported that presence of clay minerals could reduce the activation energy and the presence of aragonite mineral type of impurities were responsible for increase in decomposition energy barrier [164]. Lower activation energy (E_a) values were observed in the absence of CO_2 partial pressures than that of E_a values during regeneration in the presence of CO_2 and these results were in agreement with those reported [165]. Higher activation energies were due to the decomposition of doped sorbent of limestone hindered due to the presence of CO_2 partial pressure and was responsible for higher decomposition temperature with lower regeneration time.

5.2.3 Results and Discussion

A curve fitting exercise was done (from **Figure 5.11**) to estimate the kinetic constant of calcination reaction (k_c), using the experimental data in the packed-bed reactor during calcination. The experimental activation energy (E_a) 37.74kJ/mol is lower than the reported values as shown in **Table 5.6**[148]. But, the reported sorbents were differed with the order of the regeneration reaction.

Table 5.6 Calcination kinetic parameters of doped sorbents

Kinetic Parameter	Reaction regime& temperature	Ref
E_a(kJ/mol)	36	This work
	91.7 (820-910^oC)	[157]
	91.287 (780^oC)	[166]
	205	[167]
	33.4 (800-975)	[163]
Pre exponential factor	1.6 $m^3.kmol^{-1}.minute^{-1}$	This work
	1.22mol.$m^{-2}.s^{-1}.atm^{-1}$	[163]
	2.027x10^{-4} mol.$m^{-2}.s^{-1}$	[159]
	10.303 $m^{0.6}.s^{-1}$	[166]
	6.078x10^7mol.$m^{-2}.s^{-1}$	[167]

Reaction controlling regime was reported as rate controlling in sorbent calcination [167]. The diffusion controlling resistance is negligible for particles with <300μm size due to the sharp decrease in internal resistance during calcination [157].

6 SUMMARY AND CONCLUSIONS

Carbon capture studies using chemical looping process have been conducted after designing a suitable reactor system. Sorbents and their compatible combinations have been synthesized using different protocols in powder and pellet form to be employed in CC studies. Process standardization at first and second levels has been done using well designed experiments by Taguchi method with reference to various critical parameters. Thermodynamic investigations have been done using HSC software to reinforce the feasibility of the process and to estimate energy requirements during carbonation and regeneration. Greater focus on high temperature carbon capture was given as its success would enhance the commercial viability of the CC process. Kinetic studies were done for carbonation and calcination to identify the controlling regimes and suitable model that would fit the experimental data with greater conformity. The kinetic results so achieved were compared with those reported. The conclusions can be summarized as

- Among the synthesis protocols of dispersion method, mechanical mixing and freeze granulation, dispersion method was found to give sorbents with better attributes in powder form.
- Among various sorbents like CaO, MgO, Al_2O_3, zeolites of H-beta and HZSM-5, coal fly ash doped sorbents, the combination of CaO-MgO-Coal fly ash was found to be higher CC besides being cost effective.
- Critical process parameters that would influence the CC are found to be sorbent composition, powder morphology and loading, feed gas flow rate and composition, carbonation time and temperature besides having a properly designed reactor system.
- The optimal set of parameters that gave a maximum CC of around 11mmol/g.ads are adsorbent of CaO40MgO10FA-C40 in powder form, sorbent loading of 20g, temperature of 650^{o}C, carbonation time of 1hour, feed composition of 100% CO_2 and feed flow rate of 250cc/min.
- The sorbent was found to retain its stability upto 15 cycles without losing its capture capacity significantly.
- The capture process followed a first order kinetic model with reaction controlled regime during its initial stages (rate constant of 2.5min^{-1}; activation energy of 23kJ/mol)

and diffusion controlled regime during the most part of the process (rate constant of 0.8min^{-1}; activation energy of 30kJ/mol). These parameters are found to be dependent on the sorbent chosen.

- The positive role of coal fly ash in enhancing the kinetics and creating favorable thermodynamic conditions is reinforced owing to its thermal inertness and capture capacities if used at the appropriate level.
- Kinetics of calcination was also found to follow 2nd order model and the rate constant and activation energy values estimated in the reaction controlled regimes are 1.6 m^3.kmol^{-1}.min^{-1} and 36 kJ/mol respectively.
- The exhausted adsorbent used in manufacture of Pozzolanic Portland Cement and bricks manufacturing. It can also be used in soil pH stabilization and soil mineral content sustainability for cultivation with enhanced growth of suitable crops.

7 RECOMMENDATIONS FOR FUTURE STUDIES

Development of simple and cost effective synthesis protocols of the doped sorbents with better control of the desired properties.

- The role of coal fly ash on the carbon capture studies could be done at micro level to understand the possible reasons in terms of transition in crystalline phases available in coal fly ash.
- The integration of CC process with CO_2 beneficiation could be done wherein it can be converted to useful chemicals in-situ.
- Solid fuels like coal of different compositions could be employed in a well-designed fluidized bed reactor system for carbon capture studies.
- More effective process integration could be employed to reduce the energy penalty during regeneration that has been a major hurdle for the commercialization of this option.
- More rigorous kinetic models including the hydrodynamic aspects need to be developed to understand the process and the influencing factors at a micro level.
- Economic analysis for various options could be done for a better comparison at a glance using suitable economic models.
- Scale up studies need to be conducted under rigorous conditions for commercialization feasibility.

The limitations of present experimental research study for CC include

- CC studies were done on gaseous feed but could not be done using solid fuels like coal due to the reactor limitations.
- Cyclic stability studies could be done only upto 20 cycles which could be further increased.
- Adsorbents were used only in powder form instead of pellet forms due to the possibility of increased pressure drop.
- Catalyst loading upto 20g only could be employed due to reactor size limitation which otherwise would have facilitated for long cycle studies.
- Kinetic studies done did not account for hydrodynamics in the reactor system and also non isothermal conditions.

- More divergent combinations of sorbent systems including amine modifications could be considered for the studies.
- The feed gas considered was either pure CO_2 or in combination with N_2 at a minimum flow rate. The other feed gas compositions like syngas could be done with wide range of flow rates using a suitable and dynamic gas analyser.

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APPENDIX

LIST OF PUBLICATIONS

1.Sreenivasulu B, Sreedhar I, Singh AS, Venugopal A. Calcination Thermokinetics of Carbon Capture Using Coal Fly Ash Stabilized Sorbent. Energy & Fuels 2018. doi:10.1021/acs.energyfuels.7b04147

2.Bolisetty Sreenivasulu, I.Sreedhar, A.Venugopal, B.M. Reddy, and K.V. Raghavan, Thermo-kinetic investigations of high temperature carbon capture using Coal-Flyash doped sorbent, Energy & Fuels, 2017(IF 3.1). http://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.7b00629

3. B.Sreenivasulu, I.Sreedhar, B. Mahipal Reddy, K.V.Raghavan. Stability and Carbon Capture Enhancement by Coal-Fly-Ash-Doped Sorbents at a High Temperature. Energy & Fuels, December 2016 (IF 3.1) http://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.6b02721

4. B.Sreenivasulu, D.V.Gayatri, I.Sreedhar, K.V.Raghavan, A journey into the process and engineering aspects of carbon capture technologies, Renewable and Sustainable Energy Reviews, Volume 41, January 2015, Pages 1324-135.0 (IF 8.1)

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5. B.Sreenivasulu, I.Sreedhar, P.suresh, K.V.Raghavan. Development Trends in Porous Adsorbents for Carbon Capture. Environmental Science &Technology, 2015, 49 (21): 12641–12661 (IF 6.2) http://pubs.acs.org/doi/abs/10.1021/acs.est.5b03149

6. B. Sreenivasulu, I.Sreedhar, K.V.Raghavan. Effect of Composition, Synthesis Protocol and Pellet size of Cost Effective adsorbents doped with Flyash on Carbon Capture, " *International Journal of Environmental Science and Development* vol.7, no.11, pp.801-804, 2016

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INTERNATIONAL AND NATIONAL CONFERENCE PROCEEDINGS

1. Bolisetty Sreenivasulu, Inkollu Sreedhar, Advances in Process Engineering for High Temperature CO2 Capture using Doped Sorbents with Industrial Waste, National Symposium on Emerging Environmental Challenges: An Engineering Approach (EEC-2018 conference), BITS Pilani, Hyderabad Campus, February 16,2018

2.Bolisetty Sreenivasulu, Inkollu Sreedhar and Kondapuram Vijaya Raghavan, "Favorable Thermodynamics in High Temperature Carbon Capture using Coal Fly-ash Doped Sorbents", Proceedings of the 24th National and 2nd International ISHMT-ASTFE, Heat and Mass Transfer Conference (IHMTC-2017),December 27-30, 2017, BITS Pilani, Hyderabad, India.

3. Sreedhar Inkollu, Mohammed Shoebuddin Habeeb and Sreenivasulu Bolisetty, "Friedel Crafts Acylation of Anisole with Modified Zeolites", 9th Agricultural, Chemical, Biological and Environmental Sciences (ACBES'2017), Dubai (UAE) Oct. 17-19, 2017.

4. Bolisetty Sreenivasulu, Rohan Singhvi, I.Sreedhar, K.V. Raghavan. Effect of Composition, Synthesis Protocol and Pellet Size of Cost Effective Adsorbents Doped with Flyash on Carbon Capture.1st International Congress on Recent Advances in Chemistry And Chemical Engineering (ICRACACE - 2016), July 11-13, Dept of Chemistry, College of Engineering, Jawaharlal Nehru Technology University Hyderabad, Hyderabad (T.S), India.

5. B.Sreenivasulu, I.Sreedhar, P.suresh, K.V.Raghavan, BM Reddy. High Temperature Carbon Capture using of Limestone doped with Flyash, SusChemE-2015 international conference, October 8-9,2015, Mumbai.

6. B. Sreenivasulu, Gayatri Dhara, I.Sreedhar, K.V.Raghavan, Carbon Capture by Chemical looping combustion- A critical review on Research status and challenges, International conference on Chemical and Bioprocess Engineering-India(ICCBPE-IN,2013), November 16-17,2013 at National Institute of Technology, Warangal, India.

7. B. Sreenivasulu, Gayatri Dhara, P. Suresh, K.V.Raghavan, “Reaction Engineering Aspects Of Carbon Capture By Chemical Looping Combustion” Proceedings of International Symposium & 67th Annual Session of IIChE in association with International Partners (CHEMCON 2014), Chandigarh, India, Dec 27-30, 2014.

8. B. Sreenivasulu, J. Deepika, I. Sreedhar, K. V. Raghavan, A Critical Review on the Advances in the Materials for Carbon Capture, CHEMIX ’15, A National Conference on Inter- & Intra-Disciplinary Blend of Chemical Engineering,IIChE Nagpur Regional Centre & IIChE Students’ Chapter, VNIT, March 28th & 29th, 2015.

9. D.V.Gayatri, B.Sreenivasulu, I.Sreedhar, Multiphase kinetics of Zeolite Catalyzed Toluene Nitration, Proceedings of International Symposium & 67th Annual Session of IIChE in association with International Partners (CHEMCON 2014), Chandigarh, India, Dec 27-30, 2014.

10. T.Dhanunjay, B.Sreenivasulu, I.Sreedhar, A Review on Solid Oxide Fuel Cells - A key to noise-free Power Generation, National Conference on Innovations in Chemical Engineering (ICE 2013),Nov 15-16,2013, at BITS-Pilani, Hyderabad Campus, India.

11. I Sreedhar, B. Sreenivasulu, Gayatri Dhara, K V Raghavan, "Greener Approaches and their Challenges in Acylation of Anisole", International Conference CHEMCON-2013, Dec 27-30, Mumbai, India.

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He has done his B.Tech in chemical engg from REC Warangal (1993), AP India; the M.Tech in chemical engg from IIT Delhi India with process engg and design as specialization (1994) and the PhD from BITS Pilani, Rajasthan India in chemical engg (2007). He has more than 20 years of industrial experience, research and teaching. He has been working with BITS Pilani since 2001 as a lecturer in chemical eng till 2007, asst prof from 2008 till 2015 and associate professor. since Feb. 2015 till date. His research areas include reaction engg, heterogeneous catalysis, drag reduction, process development, process intensification, carbon capture. Published recently research and review articles in environmental science and technology, renewable and sustainable energy reviews, Korean journal chemical engg and published a book chapter in CRC press. Dr I. Sreedhar is a life member of IIChE, India.

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