

Effect of Composition, Synthesis Protocol and Pellet Size of Cost Effective Adsorbents Doped with Flyash on Carbon Capture

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Abstract—CO₂ influe gas from anthropogenic emission is one of the major contributors for global warming among greenhouse gases (GHG). Alkaline metal oxide (CaO, MgO, etc) adsorbents got industrial importance due to its use at high temperature CO₂ capture in coal gasification to separate hydrogen gas. In this paper, we discussed on the synthesis methods of mechanical mixing, freeze granulation and dispersion methods of adsorbents for CO₂ capture. Operational issues of packed bed reactor used for CC using the alkaline earth metals doped flyash. Pore size and surface areas dependence of monolithic pellets on carbonation - calcination temperatures. CC variation with monolithic pellet size and carbonation temperatures. Breakthrough curves of adsorption for the adsorbents were discussed. Adsorbents of limestone doped with flyash were analyzed using various analytical tools and the findings were reported.

Index Terms—Alkaline metal oxides doped with flyash, carbon capture, operational experiences in packed bed reactor, synthesis protocol of monolithic adsorbents.

I. INTRODUCTION

Industrial implementation of carbon capture has become an urgent issue to mitigate global warming. Carbon capture is done with various technical options of absorption, adsorption, cryogenic separation and membrane separation [1], [2]. CO₂ capture (CC) and separation from industrial process during coal gasification has got industrial importance due to its high temperature (>400°C) capture from H₂+CO₂ gas mixture as shown in Fig. 1 [2].

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 [3]. CC by absorption suffers with regeneration energy penalty, environmental disposability of spent adsorbent and less resistant to impurities in flue gas emissions for CO₂ capture. Membrane separation also suffers with impurities in flue gas mixture, cost and disposability of spent material. Cryogenic separation needs energy penalty due to cryogenic temperatures used for CO₂ separation from flue gas mixture. Limestone and dolomite are two minerals available at a very low cost and the spent material can be used in cement industry. But, this mineral has pore blocking nature is the

obstacle for complete carbonation. To avoid this issue we need to make this adsorbent as porous enough by using industrial waste inert support in the form of flyash. It also contains calcium and magnesium silicate to enhance further CC capacity of adsorbent. Since the CO₂ adsorption depends on active sites availability on surface of adsorbent with basic sites (MgO, CaO) > amphoteric sites (Al₂O₃)>acidic sites (SiO₂) [4], [5].

In this paper, limestone doped with FA is used for CO₂ capture. Alkaline earth metal of Mg(NO₃)₂+NaHCO₃ used for enhancement of alkalinity for faster carbonation reaction. Design of experiments based Taguchi method has been adopted for parameters based on composition of adsorbent, Synthesis method, binders and monolithic pellet size. Operational experience of experimental setup and measurements has been discussed. Instrument used monolithic pellets and equipment used for packed bed adsorption was reported. Effect of composition, synthesis methods, pellet size, crushing strength, surface area and binders are analyzed for CC. XRD (X-ray Diffraction), SEM (Scanning electron Microscope) and break through curves were discussed for further analysis and CC. Kinetic parameter estimation was calculated for the best performing adsorbent.

II. EXPERIMENTAL METHOD

Experimental schematic of the laboratory packed bed reactor setup for high temperature CO₂ capture is shown in Fig. 2. The experimental setup is used for user defined composition of CO₂+ N₂ gas mixture with mass flow controllers. Solid adsorbents of limestone doped flyash in the form of monolithic pellets could be placed in packed bed quartz reactor.

The quartz reactor has dimensions of 25mm ID with 550mm length and sustainable upto 1200°C at atmospheric pressure. Gas leakages at high temperatures could be avoided with graphite gaskets with quartz wool. The set value and the process value parameters difference must be below 50°C for temperature controllers to avoid any further damage to the electronic circuits inside the experimental setup.

The monolithic pellet sizes of 3mm and 5mm with an aspect ratio (ratio of thickness to diameter) must always be equal to 1. Monolithic pellets made with pelletizer shown in Fig. 3. The pellets sizes are shown in Fig. 4 and Fig. 5. It is to have optimal strength to the pellet for minimal attrition loss during the cyclic process of carbonation and calcination in the pecked bed reactor. The monolithic pellets made of freeze granulation(FZ) method by dropping into liquid nitrogen.

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Mechanical mixing(MM) is through physical mixing of composition with binder. Dispersion method(DM) is done through the adsorbent composition and binder is mixed and then dispersed in polymer of poly ethylene glycol polymer (400m.wt). The design of experiment is explained in Table I. The best performing adsorbent is chosen based on CC at 650°C, 1atm, 250cm³/minute flowrate,60minutes carbonation, (33%CO₂+67%N₂) gas mixture and with a sample size of

10gm during the 1st cycle CO₂ capture. 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(NO₃)₂:NaHCO₃: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.

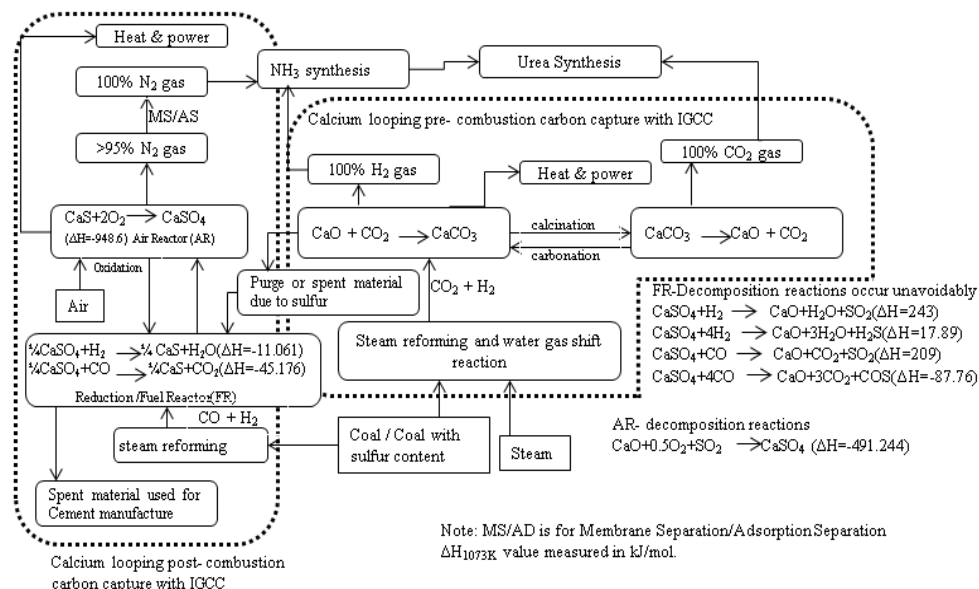


Fig. 1. Limestone based adsorbent used in calcium looping for pre-combustion and post combustion CC.

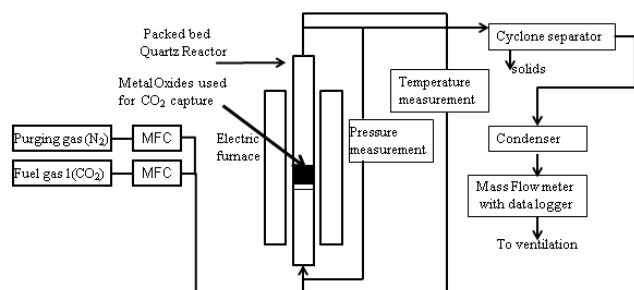


Fig. 2. Schematic of experimental setup used.



Fig. 5. 5mm x 5mm monolithic pellet size.



Fig. 3. Monolithic pelletizer.



Fig. 4. 3mm x 3mm monolithic pellet size.

III. RESULTS AND DISCUSSION

A. Effect of Composition

The fresh sample compositions of CaO:Mg(NO₃)₂:NaHCO₃:FA in combination of dispersion method and nitric acid binders were shown better CO₂ captures than remaining combinations of binders and synthesis methods. Further improvement of cyclic carbonation and calcinations adsorbents were shown better capture capacities up to three cycles. Beyond third cycle the CC values remains constant and stable. The composition with CaO:Mg(NO₃)₂:NaHCO₃:FA (40:20:10:30) shown better CC of 7.5mmolCO₂/g. As this is equivalent to the active material conversion capacity of >50% and this gets increased to 9.5mmolCO₂/g after the 3rd cycle carbonation. But, the reported MgO+CaO adsorbent gave a CC of 15.9 mmolCO₂/g_{ads}, 750°C, 100% CO₂ using TGA [6].

B. Effect of Crushing Strength

The adsorbent compositions of

CaO:Mg(NO₃)₂:NaHCO₃:FA with weight ratios of 30:10:30:30 and 30:10:40:20 performed better strengths with a value of 15N/cm² and 20N/cm² respectively. The strength could be enhanced by sintering longer times of >10hr at 1050°C. But, Surface area and porosity may affect and results in lower CC capacity. The strength is retained up to 3rd cycle for A2 and A4 sample. The sample A2 with 1mm pellet size performed a CC capacity of 7.5, 7.51 and 7.6 mmolCO₂/g_{ads} in 1st, 2nd and 3rd cycle respectively. It is observed that the CC capacities for A2 sample after 3rd cycle for 1mm, 3mm and 5mm pellet size are 7.6, 6.82 and 7.1mmolCO₂/g_{ads} respectively. The CC capacities for sample A4 with 1mm, 3mm and 5mm pellet sizes are 6.1, 6.2 and 5.9 respectively. The maximum CC achieved after 3rd cycle for selected samples of A2 (1mm size) and A4 (3mm size) were reported with nitric acid as binder using dispersion method of synthesis are 7.6 and 6.2 mmolCO₂/g_{ads} respectively. It was reported that the pellet form with CC of 0.52mmolCO₂/g_{ads} and the optimal pellet size in the range of 2-5mm for effective CO₂ adsorption [7]. MgCO₃ starts decomposing from 300°C and re-carbonation also favors between 300°C to 900°C [8]. Calcium and magnesium silicates present in flyash decompose into alkaline carbonates while sintering the carbonated adsorbent of sample A2 and A4. Emitted CO₂ from CaCO₃ decomposition would accelerates the decomposition of Ca and Mg silicates into carbonates and then to alkaline oxides and silicon dioxides [9]-[11].

TABLE I: EXPERIMENTAL DESIGN BY TAGUCHI METHOD

Run No.	Sample name	Synthesis method	Binders	Granule size (mm)	CC (mmolCO ₂ /g _{ads})
1.	A1	FZ	Acetic Acid	1	4.6
2.	A1	MM	Acetone	3	3.2
3.	A1	DM	Nitric Acid	5	7.2
4.	A2	FZ	Acetone	3	3.8
5.	A2	MM	Acetic Acid	5	3.5
6.	A2	DM	Nitric acid	1	5.2
7.	A3	FZ	Nitric Acid	5	5.2
8.	A3	MM	Acetone	3	5.1
9.	A3	DM	Acetic Acid	1	7.5
10.	A4	FZ	Nitric Acid	1	5.4
11.	A4	DM	Acetone	5	3.9
12.	A4	MM	Acetic Acid	3	4.4

C. 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°C) these nitrates decomposes into active sites of metal oxides giving better CC at 650°C. the carbonation at this high temperature is due to chemical adsorption made of covalent bonding of carbon dioxide with metal oxide compound [12]-[14]. Presence of calcium and magnesium in flyash making the adsorbent resistant to agglomeration.

D. 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 CO₂ capture due to higher alkalinity at the standard optimal operating conditions. It is reported that addition of alkaline metals and flyash enhances the carbonation and also alkaline silicates decomposition also contributes for enhancement along with synthesis methods for accelerated carbonation [12]-[15].

E. Effect of Surface Area

It has been observed that the surface area and CO₂ capture increases proportionately to carbonation-calcination cycle number. After 3rd cycle of carbonation (it is up to 3rd cycle), the CC has nearly reached to constant value. Calcined adsorbent is me so 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 from 7.5 to 8.1 mmolCO₂/g_{ads} (S.A increased from 3.2 to 11.5m²/g for 1st to 3rd cycle) of carbonation from 1st cycle to 3rd cycle. It is observed that the CC capacities for A1 sample after 3rd cycle for 1mm, 3mm and 5mm pellet size are 8.1, 8.3 and 8.2mmolCO₂/g_{ads} respectively. 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 m²/g_{ads} respectively. The CC capacities for sample A3 with 1mm, 3mm and 5mm pellet sizes are 9.5, 9.2 and 9 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 m²/g_{ads} respectively. The surface areas of A1 and A3 sample (with pellet size of 1mm) increased from 3.2 - 11.5m²/g and 4.6 - 11.3 m²/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 4.8-11.5m²/g respectively. Similarly the CC capacities enhanced from 7.2-8.2 and 7.5-9mmolCO₂/g_{ads} for samples with 5mm pellet sizes of A1 and A3 respectively

F. Analysis of XRD and SEM

The XRD graphs revealed that there is significant increase in the peaks corresponding to the calcination of fresh sample to that of 3rd cycle calcination after carbonation. The selected sample with CaO:Mg(NO₃)₂:NaHCO₃:FA (40:20:10:30) gets converted into CaO and MgO after each cycle with enhanced crystallinity. Some of the silicates of calcium and magnesium present in flyash get carbonated and results in the CO₂ capture increase by the adsorbent.

G. Breakthrough Curves and Kinetics

The carbonation and calcination cycles performed with 60 minutes interval each. The carbonation is performed for 60 minutes and the calcination is for 60 minutes to make sure the maximum conversion is achieved.

IV. CONCLUSIONS

The monolithic pellets which are performing better CC were not having better crushing strength. The monolithic

pellets compositions (CaO:Mg(NO₃)₂:NaHCO₃:FA) of 30:10:40:20 and 30:10:30:30 are showing better crushing strength in the range of 15-20N/cm² or 0.15-0.2MPa. Addition of NaHCO₃ with 30-40wt% showing better pellet strength in CaO+MgO+Flyash. Pellet based adsorbent makes this more suitable to multicycle capture capacities used in packed bed reactor with higher pressure drops. Pellet sizes of <5mm with sufficient strength comparable to cement based bricks to be improved. Suitable acid treatments of such as HNO₃ research need to be done to improve surface area of high temperature carbon capture to be used pre-combustion carbon capture. Additional amount of NaHCO₃ contributing enhanced pellet strength. Presence of MgO and CaO are not showing any agglomeration after the 3rd cycle.

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