

Development of Na and K-Based Sorbents for CO₂ Capture from Flue Gas

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Abstract

This paper describes the dry regenerable sorbent technology, one of the cost-effective and energy-efficient technologies for CO₂ capture from flue gas. The purpose of this work is to prepare alkali metal-based sorbents, especially focused on the high attrition resistance and high CO₂ sorption capacity applicable to fluidized-bed and/or fast transport-bed CO₂ capture process. With spray-drying techniques the several formulations (Sorb NH, NX30, and KX35) each contained 20 ~ 35 wt% of either Na₂CO₃ or K₂CO₃ were successfully spray-dried in 15 ~ 30 kg scale. Both Sorb NX30 and Sorb KX35 sorbents satisfied most of the physical requirements for a commercial fluidized-bed reactor process. They have spherical shape, average size of 100 μm, size distribution of 40-300 μm, and bulk density of near 1g/ml. The attrition indices (AI) of sorbents by ASTM D 5757 (10 slpm) reached below 5% compared to about 20% of commercial fluidized catalytic cracking (FCC) catalysts. The TGA CO₂ sorption capacities of them were 8-10 wt% (>80% sorbent utilization) in the simulated flue gas condition (14.4% CO₂, 5.4% O₂, 5-10% H₂O, and N₂ balance) compared to 6 wt% of 30 wt% MEA solution (33% sorbent utilization). All Sorbents showed the near complete regeneration below at 120°C with the possible regeneration window of 80-150°C. The Sorb NX30 sorbent after tested for 20 h in a fluidized-bed reactors at KIER was maintained its initial performance of the TGA reactivity. Some excellent features of sprayed-sorbents are superior attrition resistance and high CO₂ sorption capacity along with their high bulk density. These characteristics are most important parameters for the compact design of process to reduce total capital and operating costs.

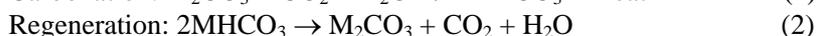
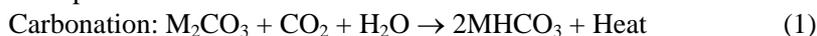
1. Introduction

Carbon dioxide, the major “greenhouse gas” of concern in possible climate change, is produced in large part as a result of fossil fuel use including electric power generation. Fossil fuel-fired power plants dominates electricity generation in Korea taking 65 % of the total generation (59.2 GW) as of 2004, which is equivalent to 39.4 MMtC (0.1151 kgC/kWh) and coal-fired power plants alone take about 20% of total amount of carbon dioxide released customarily in Korea. With the projected increase in energy, CO₂ emission in 2017 from fossil fuel-fired power plants will reach to 46.7 MMtC (0.1022 kgC/kWh) even with more use of nuclear power generation and renewable energies.

To cap atmospheric CO₂ concentrations at less than 550 ppm, a global average emission rate of less than 0.055 kgC/kWh would have to be achieved by the latter half of the 21st century. The current rates in PC and NGCC power plants in Korea are 0.2244 and 0.1097 kgC/kWh, respectively and it will remain by 2017 without any significant change (0.2227 and 0.1162 kgC/kWh) [1]. To meet such harsh criteria it is necessary to have diverse approaches such as efficiency improvement, fuel switching to less carbon intense fuel and carbon dioxide capture and sequestration. The application of a carbon capture technology, if it is economically viable, is the obvious first step directly to cut down the CO₂ emission rate from fossil-fuel conversion system instead of mere dilution of the emitted CO₂ by the energy mix.

Much attention has been recently directed towards cost-effective and energy-efficient process - anthropogenic CO₂ capture and sequestration techniques aimed at capturing CO₂ released from fossil fuel-fired power plants. There are many techniques available to capture CO₂ emissions with different advantages and limitations. One of the advanced concepts for capturing CO₂ is an absorption process with dry regenerable sorbents [2]. A critical review on this subject was appeared in the recent literature [3].

Thermodynamic analyses on various possible materials of dry regenerable sorbents showed that alkali metal carbonates were suitable to use flue gas temperatures of below 200°C [4]. The dry, regenerable sorbent CO₂ capture process consists of two reactors, carbonation and regeneration reactor. The following reaction proceeds in each reactor:



Where M is Na or K and the reaction enthalpy of (1) for Na and K is -31.69 and -33.74 kcal/mol, respectively.

We have considered a fast transport reactor as a carbonator and a bubbling fluidized-bed reactor as a regenerator to accommodate massive flue gas treatment from fossil fuel-fired power plants and other industrial boilers. Since flue gas is atmospheric pressure, such a process could be an energy-efficient process for CO₂ capture compared with other processes. The dry regenerable sorbent CO₂ capture process of fluidized-bed/transport reactor has several potential advantages over other processes. These advantages include better gas contact with smaller sorbent particle, ease of sorbent refill and removal, ease control of exothermic carbonation reaction temperature, and continuous steady operation.

Primary issues for the fluidized-bed/transport reactor process are high attrition resistant sorbent, its high sorption capacity and regenerability, durability, and cost. It requires a sorbent maintaining structural integrity during the repeated use since attrition of sorbent can result from both physical attrition (i.e., friction by movement) as well as chemical transformations (volume change caused by reaction) in nature. Thus a sorbent must have the high attrition resistance, the high sorption capacity within reasonable contact time (2-8 s), and the good flow characteristic (high bulk density). It must be also regenerable over multicycle use and be competitively priced [5-6].

This work described an efficient technique with spray drying for shaping alkali metal-based sorbents that showed the high attrition resistance and high CO₂ sorption capacity, which is uniquely suited for a transport/fluidized-bed process for capturing CO₂ from flue gas.

2. Experimental

The sorbent forming was done with a spray drying technique that is easily scalable to commercial quantity [6]. A spray drying process of sorbent includes the selection of raw material, the comminution of raw materials and colloidal slurry preparation, a spray drying, and calcination steps. Sorbents were calcined at 500~750°C under air atmosphere. About 15~30 kg batch scale sorbent was routinely spray-dried in our lab and is provided to a process developer. With NaHCO₃, Na₂CO₃, or K₂CO₃ as an active ingredient, three formulations contained about 30 wt% active material were designated to Sorb NH, NX30, and KX35 sorbents.

Physical properties of fresh sorbents prepared by spray-dried technique were characterized by the routine analytical methods [6]. The attrition resistance of catalysts or sorbents for fluidized-bed application was measured with a modified three-hole air-jet attrition tester based on the ASTM D 5757-95. The attrition index (AI) was determined at 10 slpm over 5h as described in the ASTM method.

The attrition index is the percent fines generated over 5h:

$$AI = \text{total fined collected for 5h} / \text{amount of initial sample (50 g)} \times 100.$$

The corrected attrition index (CAI) is the percent fines generated only over 4 h, that is, the fines generated over the first 1h was subtracted from a total fine generated over 5h and from a total amount of sample used initially:

$$CAI = (\text{total fine collected for 5h} - \text{fine collected for first 1h}) / (\text{amount of initial sample} - \text{fine collected for first 1h}) \times 100.$$

Chemical reactivity of sorbents was assessed using a simultaneous thermal analyzer (Rheometric Scientific STA 1500) that has dual functions of thermogravimetric analysis and differential scanning calorimetry. Amount of samples used for tests were about 10 mg scale. Carbonation were done at 50 ~ 100°C and regeneration at 80 ~ 160°C. The simulated flue gas compositions for Na-based sorbents were 14.4 vol% CO₂, 5.4 vol% O₂, 10 vol% H₂O, and N₂ balance. Gas composition for K-based sorbents was similar to that of the Na-based sorbents except of 7 vol% H₂O. Regeneration gas was a neat N₂ gas. A total flow rate for carbonation and regeneration was 60 ml/min (standard). To investigate the effect of water vapor concentration, the water content varied in the range of 5-15vol% H₂O with corresponding the dry flow rates of 57 - 51 std ml/min. To quantitatively supply water vapor to sample, it is necessary to prevent water condensation along the gas supply line. So the temperature of gas stream from the port of

syringe pump to near the assembly cup inside the furnace was kept higher than the carbonation temperature of the sample.

Figure 1 illustrated the overall schematic diagram of TGA gas supply system and heating configuration in this work.

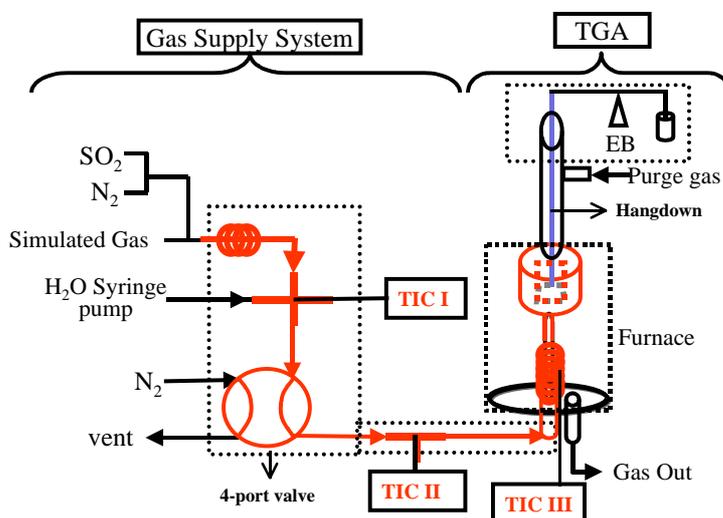


Figure 1. Schematic Diagram of TGA Gas Supply System. TIC: temperature indicator and control, EB: electronic balance.

Table 1. Physical & Chemical Properties of Spray-dried Sorbents

	Sorb NH	Sorb NX30	Sorb KX35
Avg. particle size/ μm	140	89	92
Size distribution/ μm	45 – 303	40-250	38-250
Bulk density/g/ml	0.4-0.6	0.8-1.0	1.1
BET/ m^2/g	40	> 50	> 30
BET pore volume/ml/g	-	0.132-0.346	0.112-0.196
Hg porosity/%	70-80	80	50-60
Attrition index at 10slpm/%			
AI	60-80	<5	< 0.1
CAI	40-70	<2.5	< 0.1
TGA CO_2 sorption capacity/wt%	7-14	8-12	4-9

3. Result and discussion

3.1 Basic Physical Properties:

During the sorbent screening with alkali metal carbonate, M_2CO_3 as active component and matrix, the several formulations were successfully spray-dried, which designated Sorb NH, Sorb NX30, and Sorb KX35 sorbents. All of which have semi-spherical shape, average particle size of about $100\mu\text{m}$, size distribution of 40-300 μm range and high specific surface area (BET). Although microstructural parameters are very sensitive to the calcination temperature, the calcination of spray-dried green body would be good enough to warrant the other performances in the temperature range of 500-700°C. Table 1 summarized the basic physical properties of three sorbents. It is important to note that all three sorbents have high surface area and pore volume closely relating to the chemical reactivity of sorbents and high bulk density. Particularly, the fluidized-bed or transport reactor is designed based on the volume of sorbent it holds not the weight of the sorbent. Thus the higher the bulk density of the sorbent, the faster and easier the sorbent circulation can be achieved between the two reactors.

3.2 Attrition resistance

Attrition resistance is one of the critical parameters in the development of sorbent because any attrition of sorbent causes frequent refill of the sorbent inventory as well as additional filtration and plugging in the downstream process. It also affects the fluidization and solid circulation properties [7]. The AI (CAI) of fresh Akzo and Davison FCC catalysts as references are 22.5(18)% and 18.4(13.1)% at the same conditions, respectively. It would be acceptable in a fast fluidized-bed CO₂ capture process that solid sorbent have an AI of 30 % or less. A lower value of attrition index (AI or CAI) indicates better attrition resistance of bulk particles.

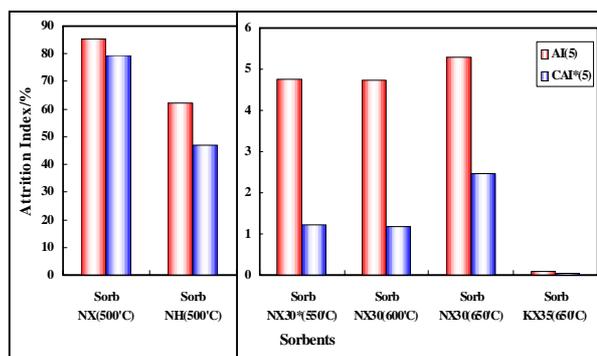


Figure 2. Attrition Resistance of Spray-dried Sorbents [AI (red) and CAI (blue)] (right: enlarged scale for Sorb NX 30 & KX35 Sorbents)

Figure 2 showed attrition index (AI) of sorbents calcined at different temperature indicated in the parenthesis. The Sorb NX and NH sorbents, which calcined at 500 °C, showed the promising attrition resistance but not enough to warrant to be used in fluidized-bed process. With modification of binder matrix, we have spray-dried two sorbent formulations, designated to Sorb NX30 and Sorb KX 35, which showed the superior attrition resistance with high bulk density of about 1 g/ml. The high attrition resistance of sorbent, which is even superior to commercial fluidized catalytic cracking (FCC) catalysts, provides less amount of refill of additional sorbent in a fluidized-bed CO₂ removal. In addition of the basic physical properties, the high attrition resistance with high bulk density of Sorb NX30 and KX35 sorbents offers considerable advantages for process developer to investigate parameter studies and feasibility test of dry regenerable sorbent technology to remove CO₂ from flue gas.

3.3. TGA chemical reactivity of Sorbent

In carbonation reaction, active component, M₂CO₃, need at least stoichiometric amount of water to proceed the forward reaction in Equation (1). Thus spray-dried sorbents must have a water sorption capacity in the reaction conditions like flue gas stream. Figure 3 illustrates the typical profile of water sorption by spray-dried sorbents. The three solid sorbents constantly absorbed 2-5wt% H₂O under the same carbonation conditions with 5-15 vol% H₂O.

Figure 4 showed the carbonation temperature effects on CO₂ sorption capacity of 500°C calcined Sorb NH sorbent. To access net CO₂ sorption capacity from CO₂ + H₂O absorption by solid alkali carbonate-based sorbent, The TGA test was used to divide into three different sequential regions: The region I is just baseline with neat N₂ gas. The H₂O + N₂ mixture gas was introduced at the onset of the region II until there was no more TGA weight gain by H₂O adsorption. It usually took more than 30 min. At the beginning of the region III, a simulated flue gas was introduced to proceed the normal TGA experiment where active component mostly reacts with stoichiometric amount of CO₂ and H₂O.

Figure 4 also demonstrates that with constant 10vol% H₂O, the net TGA CO₂ sorption capacity increases as the carbonation temperature decrease. The sorption capacity of sodium-based sorbents became negligible above 70 °C carbonation temperature. However, the net CO₂ sorption capacity at higher temperature could increase by introducing more water vapor [7b].

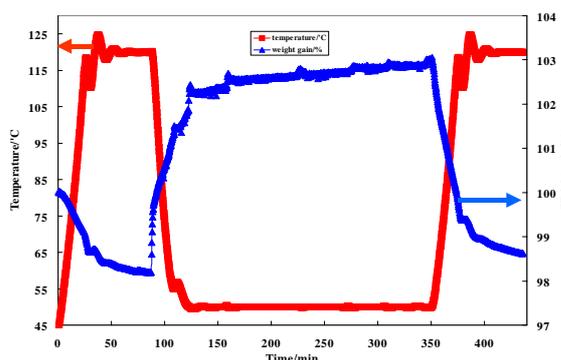


Figure 3. H₂O Vapor Sorption Capacity of Sorb NH Sorbent under same carbonation and regeneration conditions

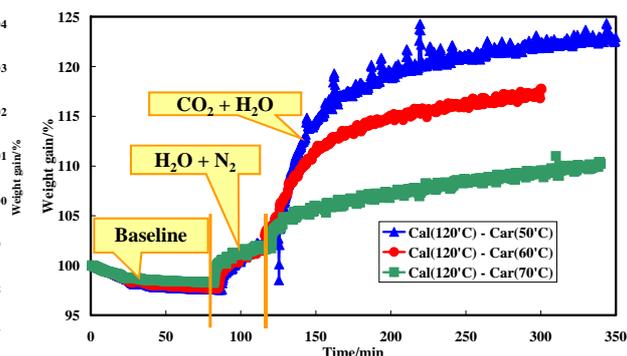


Figure 4. CO₂ Sorption Profiles of Sorb NH Sorbents

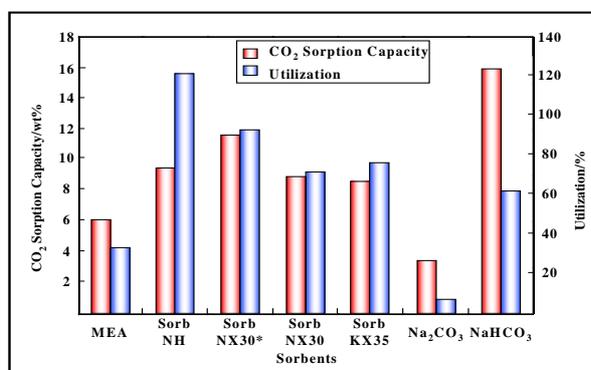


Figure 5. CO₂ Sorption Capacity & Utilization of Sorbents

Figure 5 summarized the results of TGA chemical reactivity of sorbents developed here. This figure included 30.3wt% MEA solution, pure Na₂CO₃ and NaHCO₃ for comparison purpose. MEA solution is one of the well known commercial wet scrubbing method to capture CO₂ in industry and its CO₂ sorption capacity is 6 wt% and sorbent utilization is 33%. We have used these values as our reference target for developing solid sorbents. Pure Na₂CO₃ and NaHCO₃ solids show about 3.2 wt% and 16 wt% CO₂ sorption capacities and 8% and 60% sorbent utilization, respectively. The carbonation temperature of Na-based sorbents was 50°C and 10vol% H₂O in the baseline test. The carbonation temperature of K-based sorbent was 70°C with 7 vol% H₂O. All the sorbents developed in this work showed the higher sorption capacity (> 8 wt%) as well as the higher sorbent utilization (> 70%) compared to those of the well-known MEA (30.3 wt% solution) [8].

The sodium-based sorbents showed the fast CO₂ sorption rate with 7 wt% within 20 min. The Sorb KX35 sorbent showed even better CO₂ sorption rate with 6.7 wt% with 10 min. The sodium-based sorbents showed that regeneration nearly completed at 120°C or below. The potassium-based sorbent also showed similar regeneration behavior but usually higher temperature (<150°C) was needed (see Figure 6). The thermal stability of solid sorbents developed here, if needed, offers some advantages to regenerate the CO₂ absorbed sorbent even at higher temperature up to 500°C without any adverse effect.

The ceramic supported K₂CO₃ sorbents studied by our subcontractor claimed that the much higher regeneration temperature be require to complete the regeneration reaction, especially with Al₂O₃ and MgO support and it may attribute to side products such as KM(CO₃)(OH)₂ or KM(CO₃)₂ identified by X-ray powder patterns where M = Al or Mg etc. On the other hand, active carbon supported K₂CO₃ sorbent showed near complete regeneration about 120°C.

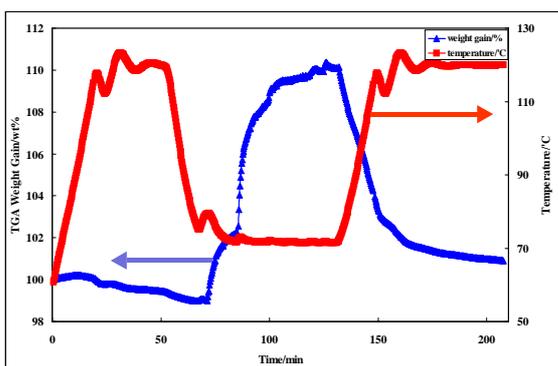


Figure 6. The 1.5 Cycle TGA Chemical Reactivity of Sorb KX35 Sorbent showing near complete regeneration below 120°C

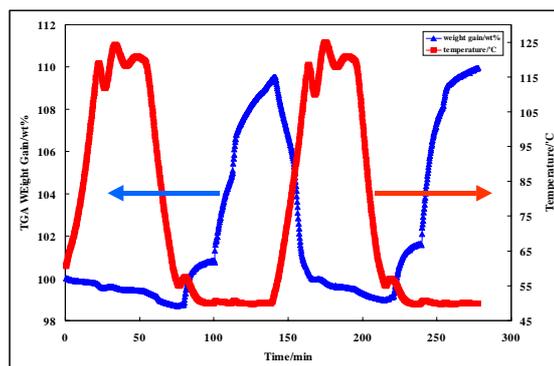


Figure 7. The 1.5 Cycle TGA Chemical Reactivity of Used Sorb NX30 Sorbent after 20h Continuous Run in Fluidized-bed Reactor at KIER

The scale-up version of Sorb NX 30 sorbent (about 25 kg) was supplied to the process developer at KIER for evaluation and feasibility test. The preliminary test results were very promising showing that near complete removal of CO₂ was achievable in continuous solid circulating fluidized-bed mode. Other BSU tests for Sorb NX35 sorbent are already underway in the continuous solid circulation mode between a transport reactor for carbonation and a fluidized-bed reactor for regeneration, showing the promising removal efficiency of CO₂ under simulated flue gas conditions.

The 1.5 cycle TGA test was performed with the Sorb NX 30 sorbent used for about 20h in continuous solid circulating fluidized-bed mode. As shown in Figure 7, it maintains its initial performance of TGA reactivity without any significant signs of degradation or deactivation.

4. Conclusion

With spray-drying techniques the several formulations each contained 20 ~ 35 wt% of either Na₂CO₃ or K₂CO₃ were successfully spray-dried in 15 ~ 30 kg scale. Both Sorb NX 30 and Sorb KX 35 sorbents have almost all the requirements for a commercial fluidized-bed reactor process in the initial lab scale tests. Some excellent features of them are superior attrition resistance and high CO₂ sorption capacity along with their high bulk density. These characteristics are most important parameters for the compact design of process to reduce total capital and operating costs. This work clearly shows that dry regenerable sorbent technology will be one of the viable methods for cost-effective and energy-efficient CO₂ capture from flue gas.

Sorbent development work will continue with particular emphasis on the development of sorbents for bulk CO₂ removal, improved regeneration, scale-up, and commercialization of dry regenerable sorbent technology based on this work.

Acknowledgement

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References

- [1] EPRI, (2003), "Electric Technology Roadmap"
- [2] H. Gupta, et al, (2002), "Separation of CO₂ from Flue Gas by High Reactivity Calcium Based Sorbents," in the Proceedings of 19th Ann. Int'l Pittsburgh Coal Conference (PCC), Sep 23-27, Pittsburgh, PA, USA, CD-ROM.
- [3] C. M. White, et al, H. W., J. Air & Waste Management Assoc., 53, (2003) 645-715.
- [4] Hoffman, J. S.; Pennline, H. W., (2000), "Investigation of CO₂ Capture Using Regenerable Sorbents," in the 17th Annual Int'l Pittsburgh Coal Conference, Pittsburgh, PA, U.S.

- [5] R. P. Gupta, et al, (1997), "Desulfurization Sorbents for Transport-Bed Applications", in the Proceedings of the Advanced Coal-Based Power and Environmental Systems '97 Conference, July 22-24, Pittsburgh, PA, U.S.
- [6] a) C. K. Ryu, et al, (2003), "Dry Regenerable Sorbents for CO₂ Capture from Flue Gas" in the Proceedings of 20th Ann. Int'l PCC, Sep 15-19, Pittsburgh, PA, USA, CD-ROM. b) C. K. Ryu, et al, (2004), "Characterization of Sodium-Based Sorbents for CO₂ Capture from Flue Gas," in the Proceedings of 21st Ann. Int'l PCC, Sep 15-19, Osaka, JP, CD-ROM.
- [7] R. Zhao, J. G. Goodwin Jr., R. Oukaci, Appl. Catal. A, 189, (1999) 99-116.
- [8] J. T. Cullimane et al, (2004), "Aqueous Piperazine/Potassium Carbonate for Enhanced CO₂ Capture," in the Proceeding of 7th International Conference on Greenhouse Gas Control Technology, Vancouver, Canada.