Utilization of CO_2 from flue gases for Waste ONP and OCC Papers

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Abstract: In this paper we reported the utilization of CO2 instead of storage existing from coal power plants. The typical flue gas composition of coal combustion flue gases are of O_2, CO_2, N_2, SO_2 gases. CO_2 is the major flue gas emitted from coal power plants. This CO_2 could be directly neutralized using fly ash particles because flue gas is acidic and fly ash is alkaline. We investigated the effect of accelerated carbonation for the power plant real flue gases and fly ash particles and we demonstrated the feasibility of direct mineralization of flue gas CO_2 without separation. Accelerated carbonation is simple, novel, economical and ecofriendly process and this process can help sustain the coal and power industry by producing clean energy. It can also protect the air quality from coal-fired power plants. Finally, the accelerated carbonation process is applicable not only to coal-fired power plants, but also to processes that produce flue gas and ash particles. In the present work, we report a novel microstructure of synthesized scalenohedral PCC (precipitated calcium carbonate) without any additives by a simple and ecofriendly carbonation process carried out in a liquid-gas system on the crystal growth of the scalenohedral calcite phase. Especially, the process parameters of $Ca(OH)_2$ concentration and CO_2 flow rates were investigated to enhance the sensitivity of the process. The highest average length of the scalenohedral calcite was obtained at pH 6.0, temperature 45^0C, $Ca(OH)_2$ concentration 0.2M, CO_2 flow rate 80mL/min, and total volume 1L. The utilization of flue gas-derived CO_2 from coal fired power plants could be a form of carbon capture and storage using carbonation reaction with scalenohedral PCC. Finally, the synthesized scalenohedral PCC was used as a filer for ONP recycling. We demonstrated all these experiemnts at semi pilot plant scale. This precipitated calcium carbonates used as a filer for ONP/OCC recycling.

Index Terms: Utilization, CO_2, flue gases, Old newspapers, old corrugated containers

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I. INTRODUCTION

In the present trend, environmentally benign accelerated carbonation process is attractive method for CO_2 precipitation process. Accelerated carbonation of lime binders in presence of 20% atmosphere CO_2 leads to the formation of cracked/corroded scalenohedral calcite crystals. This morphology obtained due to excess of CO^{3-} ions by dissolution-reprecipitation process. Initial precipitation of amorphous calcium carbonate (ACC) turns transformation of scalenohedral calcite under excess of Ca^{2+} ions in presence of CO_2. During carbonation, precipitation of lime paste under different experimental conditions had been evaluated. Among the various morphologies of calcite, scalenohedral calcite is an important as a filler material in the paper industry because it can improve the optical properties of hand sheets. Scalenohedral calcite shows higher optical effect than conventional ground calcium carbonate. Surface strength of coated paper with scalenohedral PCC (precipitated calcium carbonate) shows higher than rhombohedral calcite PCC and orthorhombic aragonite PCC.

Current domestic greenhouse gas emissions constitute 1.8% of global emissions and it is highly probable that Korea will be classified as a greenhouse gas reduction mandatory subject for the 2nd commitment period (2013-2017). The coal fired plants status, current and future presented in Figure.1[1]. USC plants have been operated in Europe and Japan. Recently, most advanced plants in China have reached the steam condition. Further R&D effort to commercialize higher efficiency plant like A-USC, IGCC is important.

The most established precipitation methods are available for precipitation process i.e i) kraft pulping method, ii) mixing of solutions and iii) carbonation process. In kraft pulping method, in liquid-liquid system, fast addition of Na_2CO_3 favored the formation of scalenohedral phase. From mixed solution methods, both continuous and liquid-solid method scalenohedral formation is possible. The higher content of $Ca(OH)_2$ in solid-liquid-gas system leads to obtain CaO by hydrating from industrial process favored to scalenohedral calcite[2]. Semicontinuous process of slaked lime carbonation is possible for the synthesis of different morphologies of calcite pcc (rhombhohedral, truncated prismatic, scalenohedral, spheroidal or chain-like agglomerates, colloidal shape) by controlling the process parameters like temperature, mixture gas flow rates (20% CO_2 and 80% N_2)[3]. During carbonation, precipitation of lime paste under different experimental conditions had been evaluated. Among the various morphologies of calcite, scalenohedral calcite is an important as a filler material in the paper industry because it can improve the optical properties of hand sheets. Scalenohedral calcite shows higher optical effect than conventional ground calcium carbonate. Surface strength of coated paper with scalenohedral PCC (precipitated calcium carbonate) shows higher than rhombohedral calcite PCC and orthorhombic aragonite PCC. The scalenohedral morphology is favored in most applications. Calcium carbonates can be synthesized by several methods[4-8] they play important roles as fillers[9-11], coating agents[12] and waste water sorbing material[13].

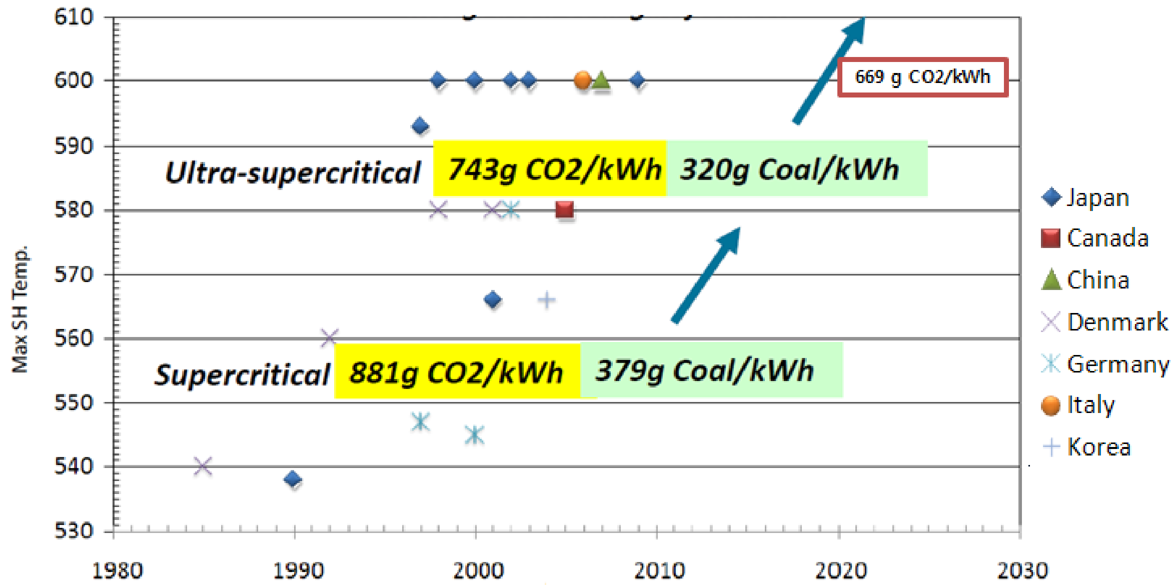

Figure 1. Global trend of coal fired plants status-past and future

The main objective this research to utilize the flue gases from coal fired power plants to control the greenhouse gas emissions reduction. Coal combustion flue gas CO_2 could be directly mineralized using scalenohedral PCC synthesis. We investigated the effect of accelerated carbonation for the power plant real flue gas and we demonstrated the feasibility of direct mineralization of flue gas CO_2 without separation. We can directly mineralize flue gas CO_2 (without separation) into carbonate minerals using scalenohedral PCC synthesis. Accelerated carbonation is simple, novel, economical, and eco-friendly process and this process can help sustain the coal and power industry by producing clean energy. The utilization of flue gas-derived CO_2 for mineral carbonation can be a form of carbon capture and storage. Therefore, this synthesized PCC used as a filer for ONP recycling. We demonstrated all these experiemnts at semi pilot plant scale.

II. MATERIAL AND METHOD

Synthesis of scalenohedral PCC

Slaked lime ($Ca(OH)_2$) was obtained from Sigma-Aldrich, Sourth Korea (95% Purity assay). Pure CO2 gas was supplied by Jeil Gas Company, South Korea. The 0.2M $Ca(OH)_2$ slurry was prepared in a glass reactor using commercial $Ca(OH)_2$ and 1000mL of high-purity water with electrical resistivity of 18.2 MΩ. 1000mL of freshly prepared $Ca(OH)_2$ slurry transferred into the double jacket glass reactor heated to 45°C with a heating system attached to the reactor. When the slaked lime temperature was reached, CO_2 was bubbling into the reactor at different flow rate from 20 to 100mL/min during reaction time of 1.30 hrs in order to evaluate the precipitation (or production) rate, and we measured the pH value in a range of 12.0 ~6.0. The carbonation reaction was completed when the slaked lime slurry reached pH 6.0. The homogenization of the system was fixed at stirring rate of 600 rpm. The experiments were also carried out at different $Ca(OH)_2$ concentration from 0.01 to 0.2M. Figure 2 shows the flow chart of scalenohedral PCC synthesis. For a particle size analysis, approximately 20 ml of the suspension was sampled after the calcite precipitation.

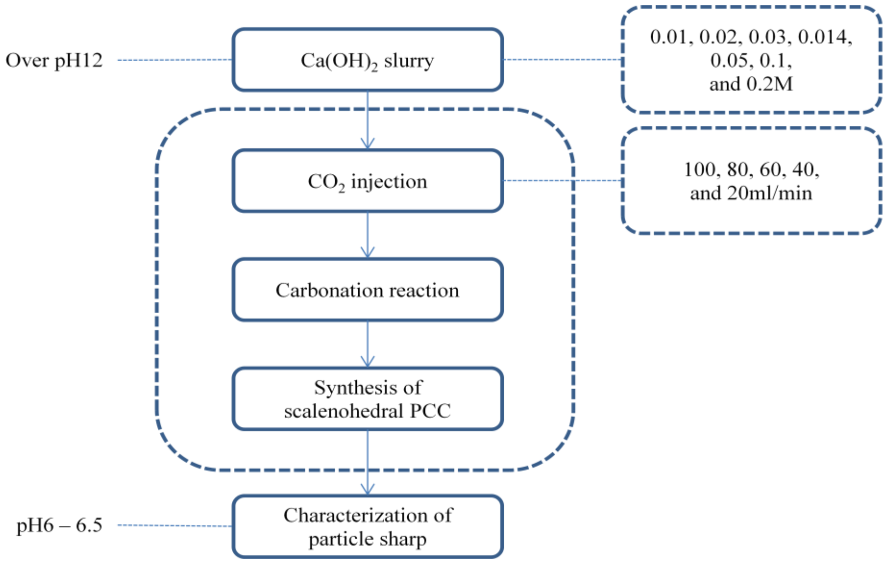

Figure 2. Schematic diagram of carbonation process for scalenohedral PCC.

Synthesized PCC used as a filer for ONP recycling

The recycled old newspaper pulp (ONP) used in this study was kindly supplied by the H. paper mill, located in Daejeon, Korea. The ONP pulp used in the research was supplied after completing the deinking process. Reactor with 2000mL was used to form the in-situ aragonite. The reactor was surrounded by an open water bath to keep the reaction temperature at 45^{o}C, with a two-wing paddle-type impeller rotating at 400rpm. ONP furnish was added to a calcium hydroxide slurry, and CO_2 gas (99.9%) was injected to this mixture slurry for 1 hr through porous glass with 70mL/min flow rate. The pH of $Ca(OH)_2$ slurry decreases to 6-6.5 by carbonation reaction with CO_2.

RESULTS AND DISCUSSION

Crystal growth of calcite by carbonation process with CO_2 gas

The general reaction mechanism of carbonation precipitation followed several factors, such as reaction temperature, $Ca(OH)_2$ concentration, and CO_2 flows rates. The basic aqueous carbonation of $Ca(OH)_2$ with CO_2 described in the following reaction.

$$[CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-}] \quad (1)$$

$$[Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^-] \quad (2)$$

$$[Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3] \quad (3)$$

The effect of temperature on supersaturation is complex. Increasing temperature negatively affects the morphology of scalenohedral PCC. The SEM image in figure 4(a) shows that needle-shaped scalenohedral PCC with a particle size in a range of about 3-7 um were synthesized. In contrast lower temperature positively affects the morphology and is favourable for the higher precipitation of $CaCO_3$. In case of $Ca(OH)_2$ concentration factor, the effects of different concentrations (i.e. from 0.01 M – 0.2 M) of $Ca(OH)_2$ on the scalenohedral PCC growth rate. The optimum $Ca(OH)_2$ concentration was determined to be 0.2 M is and this was more suitable for obtaining scalenohedral PCC. At this concentration the particle size was more than 5 µm (Figure 3).

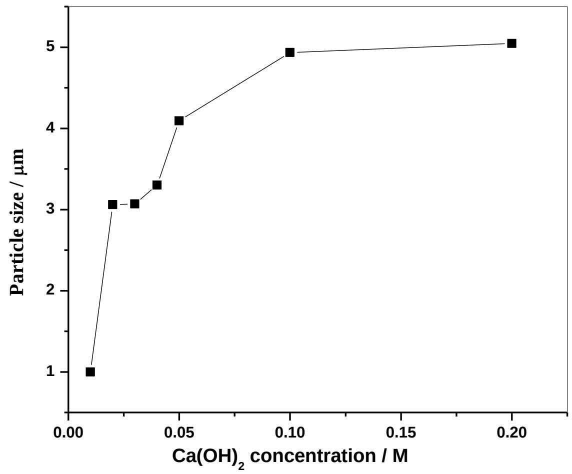

Figure 3. Scalenohedral PCC particle size at different $Ca(OH)_2$ concentrations (a) 0.01M (b) 0.02M (c) 0.03M (d) 0.04M (e) 0.05M (f) 0.1M and (g) 0.2M

In addition, we checked different CO_2 gas flow rates in a range of 20 mL/min to 100mL/min at 45^{0}C. However, after a certain limit, increasing the flow rate no longer had any effect. This was due to the higher mobility of CO_2 molecules with respect to water, resulting in CO_2 bypassing the solution. At a lower CO_2 gas flow rate of 20 mL/min, the unreacted calcium hydroxide crystals were embedded and another calcium carbonate polymorph aragonite phase appeared. In Figure 4 shows the particle size analysis of scalenohedral PCC at different CO_2 flow rates.

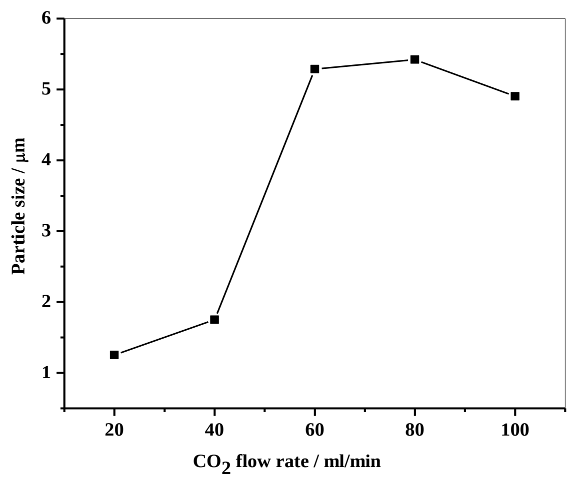

Figure 4. Particle size analysis of scalenohedral calcite pcc at different CO_2 flow rates on the morphology of (a) 100mL/min (b) 80mL/min (c) 60mL/min (d) 40mL/min (e) 20mL/min

Utilization in old newspaper waste

We investigated Since most mineral fillers are considerably cheaper than fibers, fillers can be loaded in paper to reduce the manufacturing cost and thus improve process economics. Fillers are incorporated into paper i) to reduce the cost of paper making; ii) to modify certain properties of the paper as desired by the manufacturer; iii) to improve the surface characteristics in relation to printing grades; iv) to improve brightness, opacity, whiteness, etc.; v) to improve color; vi) to increase dimensional stability; an vii) as an aid to produce special paper quality, e.g. controlled rate of burning.

The addition of filler to printing or writing papers (up to 72% of the total global use of PCC) generally enhances the opacity, brightness, smoothness, writing suitability, touch, and printability of the paper by increasing the dispersion of light. The optical and mechanical properties of paper are strongly affected by the particle size distribution and particle shape. The particle shape of precipitated calcium carbonate (PCC) is controlled by the reaction conditions. Moreover, scalenohedral calcite can be readily used as a new advanced functional filler material in place of existing paper fillers such as kaolin and talc. Scalenohedral PCC can be a collection of discrete particles or a cluster of individual crystals arranged in a rosette or starbust pattern. The latter morphology is commonly used in paper filling because this unique shape scatters light efficiently, which significantly enhances paper opacity. Large size scalenohedral PCC particles also increase bulk in filled papers.

The rhombohedral and prismatic forms are useful in paper coating applications and as strength enhancers in polymer matrixes. In filled papers, large prismatic morphologies are useful for improving drainage in the paper machine and providing a bulky finished product. When utilized in applications, large prismatic PCC can help lower the gloss or sheen of the paper surface.

In this present study we synthesized scalenohedral PCC successfully and applied it as filler for recycled old newspaper (ONP) pulp with In-Situ process. Figure 5(b) is confirmed by the SEM image that PCC were synthesized on the ONP pulp surface. The needle-shaped scalenohedral calcite particles were synthesized on the fiber surface and didn’t disturb the interactions between the fibers. Table 1 shows mechanical and optical properties of scalenohedral calcite PCC by in-situ process.

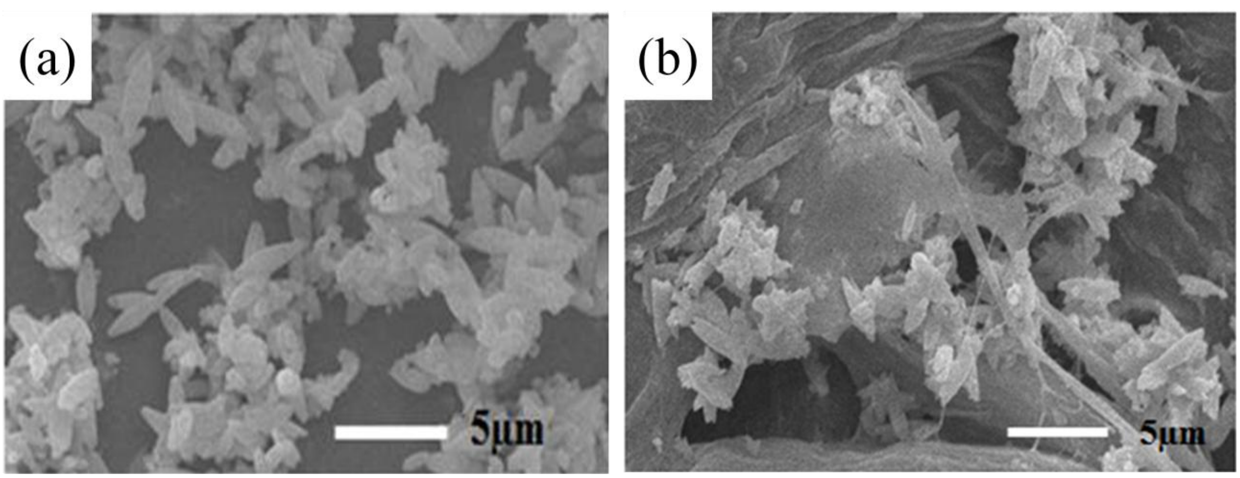

Figure 5. SEM images of synthesized needle-shape scalenohedral PCC (a) and in old news paper (ONP) at In-Situ process (b) by carbonation reaction with CO_2.

Table. 1 Properties of ONP samples before and after synthesized scalenohedral PCC at lab-scale equipment

No.	Conditions	Brightness %	ERIC (PPM)	Breaking length(km)	Bulk (m^3/g)	Ash(%)	Retention Rate(%)
1.	ONP sample	55.85	293.9	2.88	1.94	5.17	
2.	ONP 8g after synthesis	74.8	114.2	0.25	1.67	53.32	72.64
3	ONP 13g after synthesis	72.46	137.9	0.34	1.84	50.84	78.99
4	ONP 18g after synthesis	70.26	161	0.52	1.73	44.58	73.39

Semi-scale pilot plant test

The outline of the semi-scale pilot plant is illustrated schematically in Figure 6. ONP discharged from the paper mill companies and $Ca(OH)_2$ were first pulped in each mixing tank and in-situ tank. The gas including CO_2, which generated from exhaust in incinerator, was injected into in-situ tank with the mixture of ONP and $Ca(OH)_2$ pulpes. The synthesis of scalenohedral PCC in the mixture pulp would take place with stirring. After a certain period of time, the pulp was filtered and the solution phase was separated. Then the mechanical properties of the ONP product including synthesized scalenohedral PCC, such as Figure 5(b). The results are shown in Table 2.

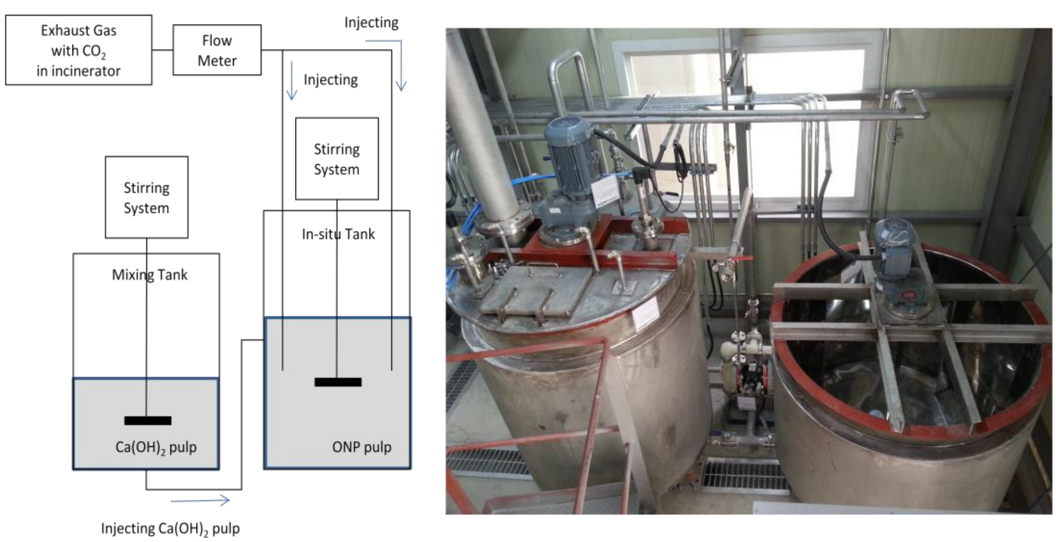

Figure 6. Schematic drawing and picture of the PCC synthesis, with CO_2 injected from exhaust in incinerator, in ONP and $Ca(OH)_2$ mixing pulp.

Table. 2 Properties of ONP samples after Synthesized scalenohedral PCC at semi-scale pilot plant

No.	Conditions	Brightness %	ERIC (PPM)	Breaking length(km)	Bulk (m^3/g)	Ash(%)	Retention Rate(%)
1	ONP 8g after synthesis	72.46	97.7	0.84	2.08	53.39	72.68
2	ONP 13g after synthesis	68.64	125.8	1.1	2	45.32	67.69
3	ONP 18g after synthesis	67.11	149.2	1.48	1.84	38.35	63.71

III. CONCLUSION

The production of precipitated calcium carbonate (PCC) by a carbonation process of slaked lime was performed in a bench-scale glass reactor with the chosen range of process parameters, such as CO_2 gas flow rates and mass concentration of $Ca(OH)_2$ suspension. A experimental analysis of the obtained data suggests that mass concentration of $Ca(OH)_2$ suspension and CO_2 gas flow rates significantly influence the PCC morphology. At obtained parameters, submicrometric PCC can be produced. These results emphasize the role of the liquid - gas phase interface on the physical chemical properties of precipitated calcium carbonate.

In addition, we synthesized scalenohedral calcite PCC successfully and applied it as filler for recycled old newspaper (ONP) pulp with In-Situ process. The needle-shaped scalenohedral calcite particles were synthesized on the fiber surface and didn't disturb the interactions between the fibers. Finally, we devised the outline of the semi-scale pilot plant for recycled ONP with CO_2 gas generated from coal fired power plants, and we obtained the mechanical properties of the ONP product including synthesized scalenohedral PCC.

Acknowledgements

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