

Study on the Interaction between CaO-based Sorbents and Coal Ash in Calcium Looping Process

Donglin He^a, Changlei Qin^{a,}, Vasilije Manovic^b, Jingyu Ran^a, and Bo Feng^c*

^a Key Laboratory of Low-grade Energy Utilization Technologies and Systems of Ministry of Education, College of

Power Engineering, Chongqing University, Chongqing 400044, China

^b Combustion and CCS Centre, Cranfield University, Cranfield, Bedfordshire MK43 0AL, United Kingdom

^c School of Mechanical and Mining Engineering, The University of Queensland, St Lucia, Queensland 4072,

Australia

Published by Elsevier. This is the Author Accepted Manuscript issued with:
Creative Commons Attribution Non-Commercial No Derivatives License (CC-BY-NC-ND 3.0).
The final published version (version of record) is available online at <http://dx.doi.org/10.1016/j.fuproc.2016.09.017>
Please refer to any applicable publisher terms of use.

* Corresponding author:

Tel.: +86-23-65103114. Email: c.qin@cqu.edu.cn.

ABSTRACT

Calcium looping (CaL), implemented via cyclic carbonation and calcination of calcium-based sorbents, is a novel and promising technology in reducing emissions of CO₂ into the atmosphere. The reactivity of CaO is important in calcium looping, but its CO₂ sorption will be affected by the presence of ash deriving from coal combustion in the calciner. We report here, the investigation of influence of coal-derived ash on CaO-based sorbents using a thermogravimetric analyzer and a combination of other techniques. As a result of this work, our understanding of the role of several key variables (sorbent type, ash content and its particle size, the calcination conditions) and how they interact during repeated cycles of CO₂ sorption and desorption, has been greatly enhanced. Furthermore, an attempt was made to explain the interaction mechanism between sorbents and coal-derived ash. It is proposed that the blockage of pores blow 3 nm due to ash deposition and subsequent grains agglomeration are the main reason for CaO-based sorbents' loss in CO₂ carrying capacity.

Key words: calcium looping; CO₂ capture; cyclic carbonation and calcination

1. INTRODUCTION

The mitigation of anthropogenic CO₂ emission has become a major concern due to the well-known problem of global warming. CO₂ capture and sequestration (CCS) is an option for reducing emissions of CO₂ into atmosphere, especially via its implementation on fossil fuel-fired power plants. These plants are large stationary CO₂ emission sources and inherently possess the technical potential for CO₂ capture due to the relatively high CO₂ concentration (10-15 vol. %) [1-4]. However, separation of CO₂ from power plants via conventional methods imposes severe energy penalties, and reduces the net electricity output by as much as 13-37% [5-7]. Thus, a more technically and economically feasible CO₂ separation process is required.

Calcium looping (CaL) is an emerging CO₂ capture technology based on the reversible reaction between CaO and CO₂, and appears to be suitable for controlling CO₂ emissions from fossil fuel-fired power plants. A schematic representation of CaL process for CO₂ capture in a power plant is shown in Figure 1. CO₂ in flue gas is sequestered through a carbonation reaction in a carbonator, then the sorbent containing CO₂ is transported into a second reactor (calciner) and regenerated in an atmosphere of nearly pure CO₂, producing a highly enriched stream of CO₂. Repeated cycles the above processes results in sequestration of CO₂ from the plant's flue gas. Comparing CaL to other CO₂ capture technologies, calcium looping is particularly competitive due to (a) the abundant use of an inexpensive raw material (limestone) as sorbents, (b) the superior theoretical CO₂ carrying capacity, (c) implementation using large-scale demonstrated fluidised-bed technology, and (d) the potentially wide application in both pre- and post-combustion CO₂ capture systems. As a result, the calcium looping process has attracted great interest and had a rapid development in various areas worldwide. For example, various strategies including: hydration or thermal pretreatment of limestone-derived CaO, development of sintering-resistant pure CaO, and dispersion of active CaO on inert matrix etc., have been proposed to resolve the well-known loss-in-capacity problem of

CaO-based sorbents [8-19]. Additionally, a number of pilot plants using the technology have been constructed [20-25], and the latest validation and operation of these facilities can be found in the scientific literature [26-29].

Figure 1. Schematic representation of calcium looping for CO₂ capture from power plant flue gas.

Practically, the decomposition of CaCO₃ is a highly endothermic reaction. To allow the collection of concentrated CO₂ from calciner, combustion of coal with pure oxygen should be used to supply the large amount of energy required. However, direct contact between sorbents and coal ash would necessarily occur as a result of the simultaneous coal combustion and CaCO₃ decomposition in the calciner. It is known that adhesion of coal ash to the surface of CaO-based sorbents under high temperature can affect characteristics of CaO for CO₂ capture during repeated cycles of carbonation and calcination [30-34]. In the operation of a pilot-scale dual-fluidised bed for CO₂ capture with oxygen-combustion in the calciner, Lu et al.[4] and Hughes et al.[35] observed the distribution of fine grains or a thin shell on the surface of calcined limes, which was attributed to ash deposition. Conversely, the work of Fan et al.[34] showed that CO₂ sorption stability of the mixed limestone and coal ash was qualitatively similar to that of pure limestone with the cycle number. Kuramoto et al.[36] also investigated the effect of coal-derived minerals on CO₂ sorption performance of CaO-based sorbents, but their focus was on the carbonation reaction with elevated pressure, which was specifically suitable for hydrogen production from coal gasification. While similar performance between CaCO₃ and CaCO₃/ash was demonstrated in the calcination/carbonation cycle, solid-solid interaction between the materials was observed to be largely enhanced by an intermediate hydration treatment. It was suggested that a proper choice of coal particle size and reaction conditions may reduce the interaction.

Based on the above results, it is known that the presence of coal ash can limit the CO₂ capture by CaO-based sorbents. However, no consensus has been reached on when and how coal-derived ashes are involved; i.e., whether the characteristics of CaO-based sorbents would be a key factor for the sorption performance with the addition of coal-derived ash. On the other hand, the interaction mechanism of ash on the sorption process of sorbents is still unclear. Therefore, purpose of the work was to evaluate the impacts of different coal ashes on CO₂ sorption by both natural and synthetic CaO-based sorbents under various testing conditions, and then understand the interaction mechanism between coal ashes and CaO-based sorbents.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation

In this work pure lime and a synthetic sorbent (SolGel) were used as both sorbents and components in the mixtures with coal ash. The lime (denoted as “L” in the mixture with coal ash) was prepared by calcining a natural limestone from Dujiangyan, China, at 950 °C for 30 min; its mass loss during calcination was equal to 39.64%. The fresh lime was sieved to obtain a sample with particles size smaller than 0.1 mm. SolGel (denoted as “S” in the mixture), consisting of 75 wt. % CaO and 25 wt. % MgO, was synthesized from analytical reagents of calcium nitrate tetrahydrate ($\geq 99.0\%$), magnesium nitrate hexahydrate ($\geq 99.0\%$), and citric acid monohydrate ($\geq 99.5\%$) following procedures described in Ref. [8]. Firstly, predetermined amounts of Ca(NO₃)₂·4H₂O, Mg(NO₃)₂·6H₂O, and citric acid were added into deionized water at a water to metal ions molar ratio of 40:1 and a citric acid to metal ions molar ratio of 1:1. Then, the mixed solution was continuously stirred at 80 °C for 7 h to form a well-dispersed sol. Thirdly, the sol was kept at room temperature for 18 h to form wet gel, followed by a two-stage drying of 5 h at 80 °C and 12 h at 110 °C in an oven. Finally it was calcined at 900 °C for 30 min and sieved to be smaller than 0.1 mm in particle

size. Both natural lime and synthetic SolGel were stored in a desiccator before using.

Two different ashes were obtained by burning a bituminous coal from Xunyang (denoted as X) and an anthracitic coal from Yaan (denoted as Y) at 950 °C for 4 h. Afterwards they were sieved into five particle size ranges of <0.1 mm, 0.1-0.2 mm, 0.2-0.3 mm, 0.3-0.4 mm and 0.4-0.5 mm before mixing with the lime and SolGel.

To study interaction characteristics between the CaO-based sorbent and coal ash, these materials were fully mixed for 30 min in a mechanical agitator. The mixtures were denoted using abbreviations of CaO-based sorbents and coal ashes, followed by the mass content of ash and its particle size range. For example, “LY30_0.1-0.2” represents the mixture of lime and Yaan coal ash with a coal ash content of 30 wt. % and ash particle size of 0.1 to 0.2 mm.

2.2. Sorption Test and Materials Characterisation

CO₂ carrying capacity of samples was evaluated using a NETZSCH Simultaneous Thermal Analyser (STA 409 PC). In a typical test under mild calcination conditions, a small (around 12 mg) sample was placed in a quartz pan and heated up to 900 °C at a rate of 25 °C/min under a flow of 85 mL/min N₂; the calcination temperature was held for 10 min. Then the sample was cooled to 650 °C at a rate of -25 °C/min. Once carbonation temperature was reached, a CO₂ flow of 15 mL/min was introduced into the STA. Thus, the carbonation reaction was performed in an atmosphere containing 15 vol. % CO₂ and 85 vol. % N₂. After 10 min carbonation, the flow of CO₂ was stopped, completing one cycle of calcination and carbonation. The calcination/carbonation cycle was repeated 15 times for each sample. Some tests were carried out under more severe calcination condition, i.e. at 950 °C in an atmosphere of pure CO₂, but the other testing conditions were kept unchanged.

CO₂ carrying capacity of CaO in the samples was expressed in the form of carbonation conversion. It was calculated from the continuously monitored weight changes during reactions, assuming mass change was only caused by the formation and decomposition of CaCO₃.

Table 1. Chemical composition of calcined limestone and coal ashes.

X-ray Fluorescence (XRF) measurements were used to determine the chemical composition of raw materials (Table 1). It was seen that both coal ashes have a similar chemical composition of the main components namely SiO_2 , Al_2O_3 , and Fe_2O_3 ; on the contrary the lime was almost pure CaO (96.56 wt. %). A X-ray Diffractometer (XRD) was used over the angular range $10\text{-}90^\circ$ in 0.02° step size and 0.3 s per step at 40 kV, 150 mA. Sample phases morphologies were observed by a scanning electron microscope (TESCAN VEGA3) at an acceleration voltage of 10 kV. The surface area, pore volume and pore size distribution of materials were determined using a Micromeritics ASAP 2020 instrument. Prior to N_2 adsorption/desorption analysis at approximately -196°C , materials were outgassed at 350°C for 4 h. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models were used to calculate the specific surface area and pore size distribution, respectively.

3. RESULTS AND DISCUSSION

3.1. Cyclic CaO Carbonation in Presence of Ash

The investigation of interactions between coal ash and CaO -based sorbent was conducted by varying the type of both coal-derived ash and sorbent; it was expressed in terms of carbonation conversion as a function of cycle number under mild calcination conditions (Figure 2). Carbonation as a function of time for the 1st and 15th cycle was shown in Figure 3. The particle size of coal ash was below 0.1 mm and its content in the mixture was kept constant at 30 wt. %. For comparison, the performance of pure lime and SolGel for CO_2 capture were also shown. As it can be seen, SolGel showed the highest initial carbonation conversion (0.64), compared to that for pure lime (0.54). However, as cycles progressed, carbonation conversion of both sorbents decreased, and after 15

cycles the residual value was 0.27 and 0.20, respectively. The average decay rate of the conversion with cycle number was 2.48% and 2.25% per cycle for SolGel and lime, respectively. Influence of coal-derived ash on the cyclic carbonation was demonstrated to be different for SolGel and lime. Though carbonation conversion of LY30_<0.1 is below that of pure lime for the entire test, deviation of their conversion values is comparatively small. In contrast, carbonation conversion of SolGel-mixed-Yaan coal ash was approximately 0.59 initially, being 8.54% lower than that without the addition of coal ash; moreover, its conversion decreased to around 0.22, thus 20.4% lower at the end of 15 cycles of calcination/carbonation. The results indicate that the addition of coal ash can reduce carbonation conversion of SolGel to a more pronounced extent. Xunyong (X) coal ash was also mixed into the two sorbents in a test of their CO₂ sorption performance. It was clear that Xunyong coal ash demonstrated a detrimental impact on sorbent reactivity identical to Yaan coal ash. An examination of the above results led us to conduct further experiments only on Yaan (Y) coal ash.

Figure 2. Repeated cycles of carbonation in presence of coal-derived ash (carbonation at 650 °C in 15 vol. % CO₂ for 10 min, and calcination at 900 °C in pure N₂ for 10 min).

Figure 3. Carbonation as a function of time in the 1st and 15th cycle of CaO-based sorbents with/without coal ash at 650 °C in 15 vol. % CO₂.

3.2. Effect of Ash Content on Carbonation

Samples composed of different contents of coal ash (Y) and SolGel or lime were prepared for investigating its influence on CaO reactivity in CO₂ capture. Carbonation conversion of samples containing coal ash amounts ranging from 15 wt. % to 60 wt. % are plotted in Figure 4. While the change of CaO conversion was small for lime/coal ash with increasing ash content, as shown in

Figure 4 (a), Figure 4 (b) demonstrates an accelerated degradation rate on CaO conversion with the increase of ash content in the mixture prepared using SolGel. It can be observed that SolGel with 15 wt. % coal ash showed the highest CaO conversion in the first carbonation (around 65%), while the initial conversion of SY30_<0.1, SY45_<0.1, and SY60_<0.1 was 59%, 55% and 43%, respectively. After 15 cycles of calcination/carbonation, the same tendency of decreasing carbonation conversion with increasing ash content was still apparent. SolGel containing no coal ash has the highest CaO conversion of 27% at the end of 15 cycles, followed by SY15_<0.1, SY30_<0.1 and SY45_<0.1, and SY60_<0.1, which demonstrated the minimum conversion of 11%, about 59% lower than that of pure SolGel. These results indicate that the pure lime utilised in the work has a superior resistance to the influence of coal ash on its performance for CO₂ sorption during multiple cycles of calcination/carbonation, while the CO₂ sorption reactivity of SolGel can be severely inhibited by coal ash. Therefore, preliminary selection of CaO-based sorbent is important, as adaptability of sorbents in the real application environment could vary extensively. Though ash percentages from 15 wt. % to 60 wt. % were used in this work, it is necessary to know that the content of coal ash should be kept as low as possible in the practical calcium looping system, as more ash means larger heat consumption in the calciner.

Figure 4. Effect of ash content on carbonation. Testing condition: carbonation in 15 vol. % CO₂ at 650 °C, calcination in 100 vol. % N₂ at 900 °C, both for 10 min.

3.3. Effect of Ash Particle Size on Carbonation

The effect of coal ash particle size, ranging from <0.1 mm to 0.4-0.5 mm, on CaO conversion was investigated and the experimental data are shown in Figure 5. As expected, the difference on CaO conversion for pure lime and its mixtures with changing particle size of coal ash was small, and all

showed a continuous decrease of conversion with cycle number. Turning now to carbonation conversion of mixtures consisting of SolGel and coal-derived ash (Y), the reduction of CaO conversion caused by the addition of coal ash can still be seen. However, it was interesting to find a decreasing detrimental effect of ash on the reactivity of CaO as particle size of coal ash increasing from <0.1 mm to 0.4-0.5 mm. CaO conversion of SY30_<0.1 was 0.22 in the 15th carbonation reaction, while SY30_0.2-0.3 and SY30_0.4-0.5 showed a carbonation extent of 23% and 26%, respectively. This could possibly be due to a more uniform solid-solid contact between the coal ash with smaller size and the sorbent. These results suggest that suitable particle size of coal ash could reduce the occurrence of its inhibition on the carbonation of CaO with CO₂. Fortunately, ash with smaller size is relatively easier to be separated from the fluidised bed reactor through the cyclone, in comparison with larger particles [37].

Figure 5. Effect of particle size of coal ash on carbonation conversion of CaO. Testing conditions: carbonation in 15 vol. % CO₂ at 650 °C, calcination in 100 vol. % N₂ at 900 °C, both for 10 min.

3.4. Effect of Severe Calcination on Carbonation

Regeneration of CaO-based sorbents should occur at temperatures much higher than 900 °C in a relatively pure CO₂ stream if the calcium looping process is operated to separate CO₂ from flue gas. Therefore, a series of experiments with pure lime, SolGel, and their mixtures with coal ash were conducted under calcination conditions of 950 °C and 100% CO₂ atmosphere. Figure 6 demonstrates the change of carbonation conversion with cycle number under the severe calcination conditions. For comparison, testing results under mild calcination conditions are also presented. The initial carbonation conversion of pure lime was 0.37 under severe calcination conditions, indicating a degradation of 31% from 0.54 measured under mild calcination. The degradation of carbonation

conversion tends to become smaller in the following cycles and a reduction of only 18% (0.2 vs. 0.16) was observed after 15 cycles. Additionally, CaO conversion of lime and the lime/coal ash mixture had almost identical profiles as a function of cycle number, regardless of the mild or severe calcination implemented. SolGel, by contrast, demonstrated a more pronounced impact in the shifting from mild to more severe calcination conditions, and the reduction of carbonation conversion caused by coal ash addition can be observed from the 1st to the last cycle. The results imply that calcination condition was not a major factor affecting the interaction between coal ash and CaO-based sorbents for CO₂ capture during cyclic calcination and carbonation.

Figure 6. Carbonation conversion of sorbents under mild and severe calcination conditions. Testing conditions: carbonation in 15 vol. % CO₂ at 650 °C, mild calcination in 100% N₂ at 900 °C while severe calcination in 100% CO₂ at 950 °C, all for 10 min.

3.5. Characterisation and Discussion

The results described above clearly demonstrated that coal-derived ash can affect CO₂ sorption performance of sorbents during cyclic reactions of calcination and carbonation, but the extent of impact varied according to the sorbents. The interaction between coal ash and CaO-based sorbents may occur in chemical or physical aspect. To investigate the potential chemical interactions, XRD results of five samples were presented in Figure 7. It shows that CaO and Ca(OH)₂ are the main compounds in lime and beyond those, there is MgO in SolGel. The strongest peak demonstrated in coal ash is SiO₂, and other compounds of Ca₃Al₂O₆ and Ca₂(Al(AlSi)O₇) are observed as well. In the sorbent-ash mixtures, however, no new compounds is detected under the conditions studied. Therefore, here we speculate that chemical consumption of active CaO is not the dominant reason for the different resistance of sorbents to coal ash, basing on the facts: (1) coal ashes are measured to

have no CO₂ sorption capacity, though experimental results are not presented; (2) the main difference between lime and SolGel is that the latter contains 25 wt. % MgO. However, no chemical reactions between MgO and the components from coal ash are found in Figure 7, which agrees with the results in the literature [33, 38-40].

Figure 7. XRD patterns of selected samples after 10 min calcination at 900 °C.

To understand the physical interactions between coal ash and sorbents, N₂ adsorption/desorption was utilised to measure structural parameters of freshly calcined lime, SolGel, their mixtures containing 60 wt. % Yaan (Y) coal ash, and ash Y. The BET surface area, the BJH desorption (cumulative) of pores, the average pore diameter, and the pore diameter distribution are summarised in Figures 8 and 9. From Figure 8, it can be seen that BET surface area and BJH pore volume of pure lime are 22.32 m²/g and 0.1146 cm³/g, respectively. It is well known that calcination of natural limestone usually yields a porous structure due to CO₂ diffusion following the disintegration of calcite crystals into small lime crystals [41]. BET surface area of the lime used in the work is very close to the commonly reported data of calcined limestone, ranging from around 3 to just above 20 m²/g [11, 42-46], while SolGel exhibits a superior surface area of 56.14 m²/g. By comparing BET surface area of two sorbents, ash Y and their mixtures, it is clear that the presence of coal ash results in a large loss in the BET surface area of both initial sorbents and ash, implying there should be a synergy effect between the CO₂ sorbent material and coal ash. Figure 9 shows that both the lime and SolGel have two main types of pores. Pores named type 1 are very small, with a diameter between 3-8 nm for lime, while is mainly <4 nm for SolGel. Pores type 2 are approximately 50-80 nm in diameter. With 60 wt. % coal ash in LY60_<0.1, its pore diameter distribution curve is similar to that of the original lime, but there is a loss of approximately 60-70% of the surface area and pore volume,

as shown in Figure 8 and 9. In contrast, the pores with a diameter <3 nm all disappeared for SolGel mixed with the same amount of coal ash, resulting a more pronounced decay (higher than 80%) in surface area and pore volume, which are $4.71 \text{ m}^2/\text{g}$ and $0.0207 \text{ cm}^3/\text{g}$ for SY60_ <0.1 . Therefore, the pores <3 nm is believed to be the most important factor for the interaction between coal ash and CaO-based sorbents.

Figure 8. Pore structure parameters of five samples after calcination for 10 min at 900°C .

Figure 9. Pore diameter distribution of calcined lime, SolGel and their mixtures with coal ash (Y).

Variation in sorbent morphological structure as a result of ash addition was further investigated by SEM (Figure 10). It can be seen that freshly calcined lime has a well-defined, homogeneous distribution of spherical grains close to 200 nm in diameter. Adding coal ash into lime caused only minimal grain growth. Compared to pure lime, SolGel grains were smaller but very close to each other. Moreover, the addition of coal ash resulted in a significant change of SolGel's morphology. Though few small grains with good porosity could still be observed, more of them disappear through mergence with the production of a more coarse and heterogeneous structure.

Figure 10. SEM images showing morphology of calcined sorbents with and without coal ash.

Figure 11. Schematic representation of pore-and-grain variation of lime and SolGel with the existence of coal ash.

Based on the above results, a schematic representation of the physical interaction between coal ash and CaO-based sorbents is proposed, as shown in Figure 11. It is known that the introduction of coal ash can change porous structure of CaO-based sorbents with the decline in surface area and pore

volume. However, the variation of type 1 pores especially those below around 3 nm is thought to play the most critical role, as these pores are the main contributor for the surface area and pore volume of a material. Once coal ash is presented, the majority of micro-pores in SolGel is blocked, which largely reduces the accessibility of CO₂ to active sorbent sites and the subsequent internal diffusibility, thus resulting in a more pronounced CaO reactivity loss than the lime. Additionally, ash deposition is also able to cause grain agglomeration along the surrounding sorbent and ash because of its adhesive properties. CaO grains in lime are characterised with more regular spherical shape and better separation from each other. Conversely, SolGel grains were observed to be connected and agglomerated with less obvious individuality than that of the lime. After the blockage of the micro-pores, the grains in SolGel can be easily bridged together in clumps with smooth surface and evident loss in porosity while there is coal ash with propensity of melting and adhesivity. Similar changes in morphological structure have also been reported in the literature [35].

The impact of coal-derived ash on calcium looping should be of concern. Even though its inhibition on CO₂ sorption of sorbents can be minimised by a careful selection of both coals and sorbents, transportation of ash with sorbents in the interconnected fluidised bed, which was proposed to be the best candidate for calcium looping, and temperature maintenance of the large amount of needless material would lead to consumption of a large amount of energy. Therefore, it would be interesting to investigate the optimum combination of particles of sorbents and coals, aiming to realize an efficient separation of coal ash from the main stream of solid sorbents using a cyclone.

4. CONCLUSIONS

Calcium looping is a technically and economically competitive approach in mitigating CO₂ emissions from coal-fired power plants. The long-term stability in sorption capacity of CaO-based sorbents is a key parameter determining the operating efficiency of the CO₂ capture system, which

can be easily affected by the ash from coal combustion in the calciner. In this work, we investigated the impact and role of several variables (sorbent type, ash content, particle size of ash, and the calcination conditions) on CO₂ sorption capacity in cyclic calcination and carbonation via a thermogravimetric analyzer. The resistance to ash's negative impact is observed to be very different, largely depending on the type of sorbent used (natural or synthetic sorbent). However, the increase of ash content in sorbents and the reduction in particle size of coal ash resulted in a generally lower carbonation conversion; thus, the influence of calcination conditions on the interaction between coal ash and CaO-based sorbents could be ignored. Physical blockage of pores (especially those with a diameter <3 nm, probably due to ash deposition and subsequent agglomeration) is thought to be the main contributor for the inhibition of CaO-based sorbents with respect to their CO₂ carrying capacity.

ACKNOWLEDGEMENTS

The authors are grateful to the financial supports from the National Natural Science Foundation of China (No. 51606018), China Postdoctoral Science Foundation (No. 2015M572448), Chongqing Postdoctoral Funding Project (No. Xm2015002), the Fundamental Research Funds for the Central Universities (No. 106112015CDJXY140005), Key Laboratory of Low-grade Energy Utilization Technologies and Systems of Ministry of Education (No. LLEUTS-2016004, LLEUTS-201411), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

REFERENCES

- [1] N. Rodriguez, R. Murillo, J.C. Abanades, CO₂ capture from cement plants using oxyfired precalcination and/or calcium looping, *Environ. Sci. Technol.* 46 (2012) 2460-2466.

- [2] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-Combustion CO₂ Capture Using Solid Sorbents: A Review, *Ind. Eng. Chem. Res.* 51 (2011) 1438-1463.
- [3] S. Dobner, L. Sterns, R.A. Graff, A.M. Squires, Cyclic Calcination and Recarbonation of Calcined Dolomite, *Ind. Eng. Chem. Process Des. Dev.* 16 (1977) 479-486.
- [4] D.Y. Lu, R.W. Hughes, E.J. Anthony, Ca-based sorbent looping combustion for CO₂ capture in pilot-scale dual fluidized beds, *Fuel Process. Technol.* 89 (2008) 1386-1395.
- [5] L.S. Fan, L. Zeng, W.L. Wang, S.W. Luo, Chemical Looping Processes for CO₂ Capture and Carbonaceous Fuel Conversion-Prospect and Opportunity, *Energy Environ. Sci.* 5 (2012) 7254-7280.
- [6] M. Zhao, A.I. Minett, A.T. Harris, A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO₂, *Energy Environ. Sci.* 6 (2013) 25-40.
- [7] A.B. Rao, E.S. Rubin, A Technical, Economic, and Environmental Assessment of Amine-Based CO₂ Capture Technology for Power Plant Greenhouse Gas Control, *Environ. Sci. Technol.* 36 (2002) 4467-4475.
- [8] C. Luo, Y. Zheng, C. Zheng, J. Yin, C. Qin, B. Feng, Manufacture of calcium-based sorbents for high temperature cyclic CO₂ capture via a sol-gel process, *Int. J. Greenhouse Gas Control* 12 (2013) 193-199.
- [9] Y. Wu, V. Manovic, I. He, E.J. Anthony, Modified lime-based pellet sorbents for high-temperature CO₂ capture: Reactivity and attrition behavior, *Fuel* 96 (2012) 454-461.
- [10] C. Qin, W. Liu, H. An, J. Yin, B. Feng, Fabrication of CaO-Based Sorbents for CO₂ Capture by a Mixing Method, *Environ. Sci. Technol.* 46 (2012) 1932-1939.
- [11] R. Sun, Y. Li, S. Wu, C. Liu, H. Liu, C. Lu, Enhancement of CO₂ capture capacity by modifying limestone with propionic acid, *Powder Technol.* 233 (2013) 8-14.
- [12] R. Koirala, G.K. Reddy, P.G. Smirniotis, Single Nozzle Flame-Made Highly Durable Metal Doped Ca-Based Sorbents for CO₂ Capture at High Temperature, *Energy Fuels* 26 (2012) 3103-3109.
- [13] Y. Hu, W. Liu, J. Sun, M. Li, X. Yang, Y. Zhang, M. Xu, Incorporation of CaO into novel Nd₂O₃ inert solid

support for high temperature CO₂ capture, Chem. Eng. J. 273 (2015) 333-343.

- [14] A. Akgornpeak, T. Witoon, T. Mungcharoen, J. Limtrakul, Development of synthetic CaO sorbents via CTAB-assisted sol–gel method for CO₂ capture at high temperature, Chem. Eng. J. 237 (2014) 189-198.
- [15] T. Witoon, T. Mungcharoen, J. Limtrakul, Biotemplated synthesis of highly stable calcium-based sorbents for CO₂ capture via a precipitation method, Appl. Energy 118 (2014) 32-40.
- [16] A.M. Kierzkowska, L.V. Poulikakos, M. Broda, C.R. Müller, Synthesis of calcium-based, Al₂O₃-stabilized sorbents for CO₂ capture using a co-precipitation technique, Int. J. Greenhouse Gas Control 15 (2013) 48-54.
- [17] H. Chen, C. Zhao, Development of a CaO-based sorbent with improved cyclic stability for CO₂ capture in pressurized carbonation, Chem. Eng. J. 171 (2011) 197-205.
- [18] H. Chen, C. Zhao, Y. Yang, Enhancement of attrition resistance and cyclic CO₂ capture of calcium-based sorbent pellets, Fuel Process. Technol. 116 (2013) 116-122.
- [19] C. Luo, Y. Zheng, J. Yin, C. Qin, N. Ding, C. Zheng, B. Feng, Effect of Support Material on Carbonation and Sulfation of Synthetic CaO-Based Sorbents in Calcium Looping Cycle, Energy Fuels 27 (2013) 4824-4831.
- [20] R.W. Hughes, D.Y. Lu, E.J. Anthony, A. Macchi, Design, Process Simulation and Construction of An Atmospheric Dual Fluidized Bed Combustion System for In Situ CO₂ Capture Using High-Temperature Sorbents, Fuel Process. Technol. 86 (2005) 1523-1531.
- [21] W. Wang, S. Ramkumar, S. Li, D. Wong, M. Iyer, B.B. Sakadjian, R.M. Statnick, L.S. Fan, Subpilot Demonstration of the Carbonation–Calcination Reaction (CCR) Process: High-Temperature CO₂ and Sulfur Capture from Coal-Fired Power Plants, Ind. Eng. Chem. Res. 49 (2010) 5094-5101.
- [22] S. Koppatz, C. Pfeifer, R. Rauch, H. Hofbauer, T. Marquard-Moellenstedt, M. Specht, H₂ rich product gas by steam gasification of biomass with in situ CO₂ absorption in a dual fluidized bed system of 8 MW fuel input, Fuel Process. Technol. 90 (2009) 914-921.
- [23] A. Charitos, N. Rodríguez, C. Hawthorne, M. Alonso, M. Zieba, B. Arias, G. Kopanakis, G. Scheffknecht, J.C. Abanades, Experimental Validation of the Calcium Looping CO₂ Capture Process with Two Circulating

- [24] N. Rodríguez, M. Alonso, J.C. Abanades, Experimental Investigation of A Circulating Fluidized-Bed Reactor to Capture CO₂ with CaO, *AIChE J.* 57 (2011) 1356-1366.
- [25] M.H. Chang, C.M. Huang, W.H. Liu, W.C. Chen, J.Y. Cheng, W. Chen, T.W. Wen, S. Ouyang, C.H. Shen, H.W. Hsu, Design and Experimental Investigation of Calcium Looping Process for 3-kW_{th} and 1.9-MW_{th} Facilities, *Chem. Eng. Technol.* 36 (2013) 1525-1532.
- [26] B. Arias, M.E. Diego, J.C. Abanades, M. Lorenzo, L. Diaz, D. Martínez, J. Alvarez, A. Sánchez-Biezma, Demonstration of steady state CO₂ capture in a 1.7 MW_{th} calcium looping pilot, *Int. J. Greenhouse Gas Control* 18 (2013) 237-245.
- [27] V. Materić, R. Symonds, D. Lu, R. Holt, V. Manović, Performance of Hydration Reactivated Ca Looping Sorbents in a Pilot-Scale, Oxy-fired Dual Fluid Bed Unit, *Energy Fuels* 28 (2014) 5363-5372.
- [28] D.P. Hanak, E.J. Anthony, V. Manovic, A review of developments in pilot-plant testing and modelling of calcium looping process for CO₂ capture from power generation systems, *Energy Environ. Sci.* 8 (2015) 2199-2249.
- [29] J. Ströhle, M. Junk, J. Kremer, A. Galloy, B. Epple, Carbonate looping experiments in a 1 MW_{th} pilot plant and model validation, *Fuel* 127 (2014) 13-22.
- [30] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell, The calcium looping cycle for large-scale CO₂ capture, *Prog. Energy Combust. Sci.* 36 (2010) 260-279.
- [31] B.R. Stanmore, P. Gilot, Review--calcination and carbonation of limestone during thermal cycling for CO₂ sequestration, *Fuel Process. Technol.* 86 (2005) 1707-1743.
- [32] Y. Wu, V. Manovic, I. He, E.J. Anthony, Reuse of Spent Sorbents from FBC for SO₂ Capture by Simultaneous Reactivation and Pelletization, *Energy Fuels* 27 (2013) 82-86.
- [33] H. Katalambula, A. Bawagan, S. Takeda, Mineral attachment to calcium-based sorbent particles during in situ desulfurization in coal gasification processes, *Fuel Process. Technol.* 73 (2001) 75-93.

- [34] F. Fang, Z.-s. Li, N.-s. Cai, CO₂ capture from flue gases using a fluidized bed reactor with limestone, Korean J. Chem. Eng. 26 (2009) 1414-1421.
- [35] R.W. Hughes, A. Macchi, D.Y. Lu, E.J. Anthony, Changes in Limestone Sorbent Morphology during CaO-CaCO₃ Looping at Pilot Scale, Chem. Eng. Technol. 32 (2009) 425-434.
- [36] K. Kuramoto, S. Shibano, S. Fujimoto, T. Kimura, Y. Suzuki, H. Hatano, L. Shi-Ying, M. Harada, K. Morishita, T. Takarada, Deactivation of Ca-Based Sorbents by Coal-Derived Minerals during Multicycle CO₂ Sorption under Elevated Pressure and Temperature, Ind. Eng. Chem. Res. 42 (2003) 3566-3570.
- [37] J. Bao, Z. Li, N. Cai, Interaction between iron-based oxygen carrier and four coal ashes during chemical looping combustion, Appl. Energy 115 (2014) 549-558.
- [38] J.E. Readman, R. Blom, The use of in situ powder X-ray diffraction in the investigation of dolomite as a potential reversible high-temperature CO₂ sorbent, PCCP 7 (2005) 1214-1219.
- [39] C. Qin, J. Yin, W. Liu, H. An, B. Feng, Behavior of CaO/CuO Based Composite in a Combined Calcium and Copper Chemical Looping Process, Ind. Eng. Chem. Res. 51 (2012) 12274-12281.
- [40] W. Liu, B. Feng, Y. Wu, G. Wang, J. Barry, J.C.D.D. Costa, Synthesis of Sintering-Resistant Sorbents for CO₂ Capture, Environ. Sci. Technol. 44 (2010) 3093-3097.
- [41] J.M. Valverde, Ca-based synthetic materials with enhanced CO₂ capture efficiency, Journal of Materials Chemistry A 1 (2013) 447-468.
- [42] W. Wu, C. Zhao, Q. Li, W. Zhou, Experimental investigation on calcination/sulphation characteristics of limestone modified by acetic acid solution in O₂/CO₂ atmosphere, Proceedings of the Combustion Institute 33 (2011) 3455-3462.
- [43] F. Donat, N.H. Florin, E.J. Anthony, P.S. Fennell, Influence of high-temperature steam on the reactivity of CaO sorbent for CO₂ capture, Environ. Sci. Technol. 46 (2012) 1262-1269.
- [44] H. Chen, Z. Zhao, X. Huang, K. Patchigolla, A. Cotton, J. Oakey, Novel Optimized Process for Utilization of CaO-Based Sorbent for Capturing CO₂ and SO₂ Sequentially, Energy Fuels 26 (2012) 5596-5603.

- [45] M.J. Al-Jeboori, M. Nguyen, C. Dean, P.S. Fennell, Improvement of Limestone-Based CO₂ Sorbents for Ca Looping by HBr and Other Mineral Acids, *Ind. Eng. Chem. Res.* 52 (2013) 1426-1433.
- [46] Y. Li, H. Liu, S. Wu, R. Sun, C. Lu, Sulfation behavior of CaO from long-term carbonation/calcination cycles for CO₂ capture at FBC temperatures, *J. Therm. Anal. Calorim.* 111 (2013) 1335-1343.

TABLES

Table 1. Chemical composition of calcined limestone and coal ashes.

Compound, wt. %	Lime	Ash X	Ash Y
CaO	96.56	3.55	2.02
SiO ₂	1.70	51.35	56.37
Al ₂ O ₃	0.60	26.17	27.74
Fe ₂ O ₃	0.47	10.52	5.30
SO ₃	0.33	2.45	0.31
TiO ₂	0.13	2.91	2.16
SrO	0.13	0.21	0.04
P ₂ O ₅	0.03	0.14	0.21
K ₂ O	0.03	1.02	2.61
MgO	0.00	0.73	2.31
Na ₂ O	0.00	0.43	0.62
ZrO ₂	0.00	0.24	0.08
BaO	0.00	0.10	0.00
MnO	0.00	0.04	0.05
Cr ₂ O ₃	0.00	0.04	0.04
CuO	0.00	0.03	0.03
Y ₂ O ₃	0.00	0.02	0.01
ZnO	0.00	0.02	0.04
NbO	0.00	0.02	0.00
NiO	0.00	0.02	0.03
Co ₂ O ₃	0.00	0.00	0.02
Rb ₂ O	0.00	0.00	0.02
Total	100.00	100.00	100.00

FIGURES

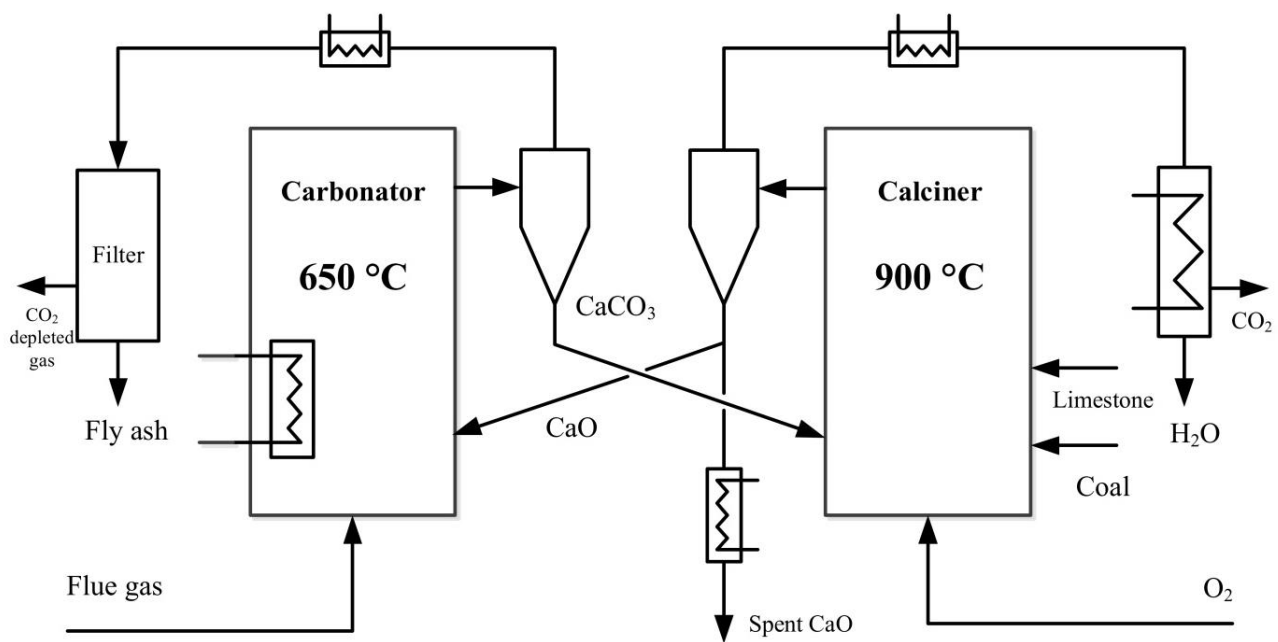


Figure 1. Schematic representation of calcium looping for CO₂ capture from power plant flue gas.

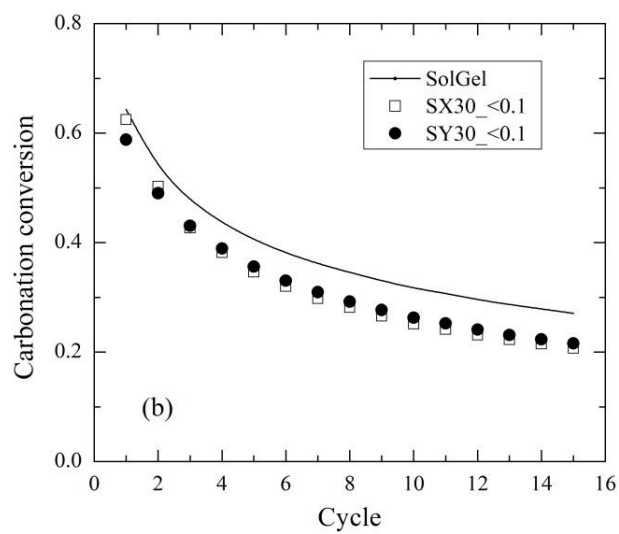
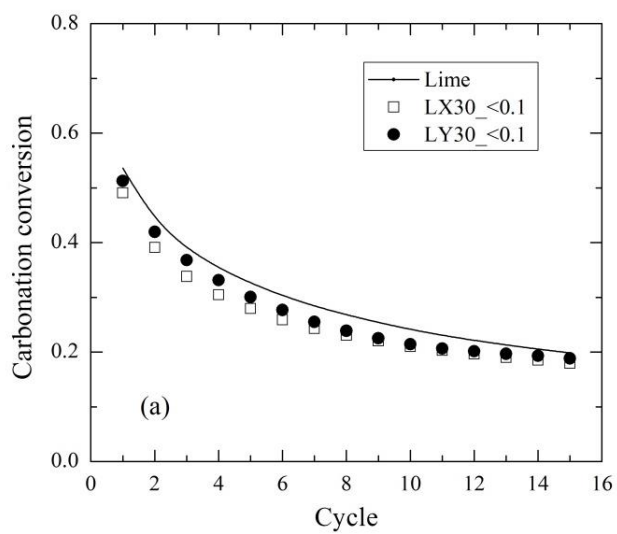


Figure 2. Repeated cycles of carbonation in presence of coal-derived ash (carbonation at 650 °C in 15 vol. % CO₂ for 10 min, and calcination at 900 °C in pure N₂ for 10 min).

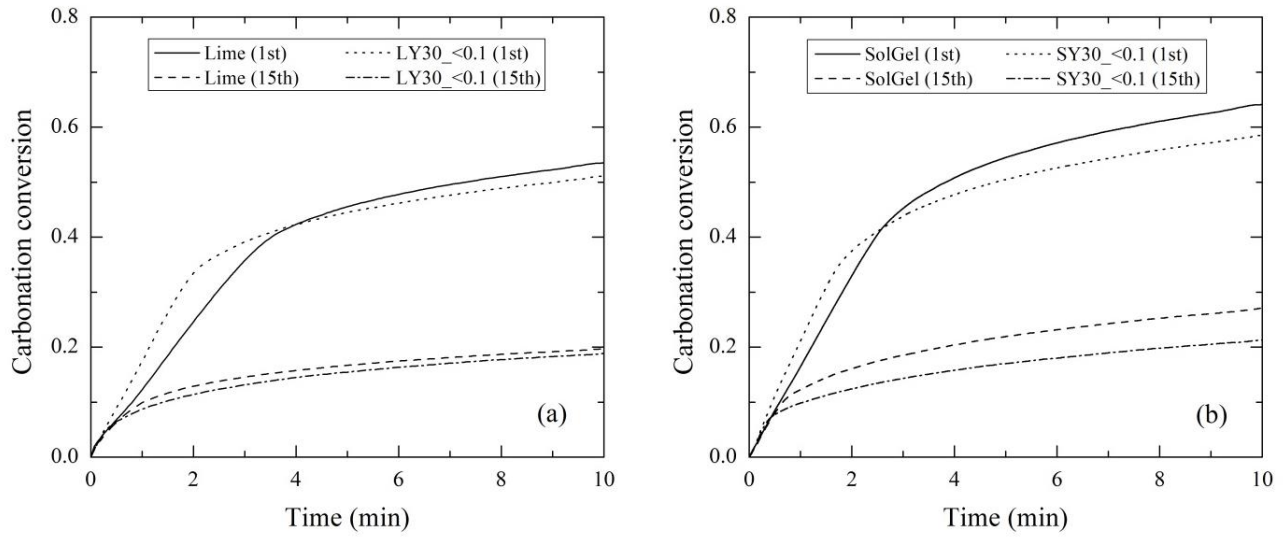


Figure 3. Carbonation as a function of time in the 1st and 15th cycle of CaO-based sorbents with/without coal ash at 650 °C in 15 vol. % CO₂.

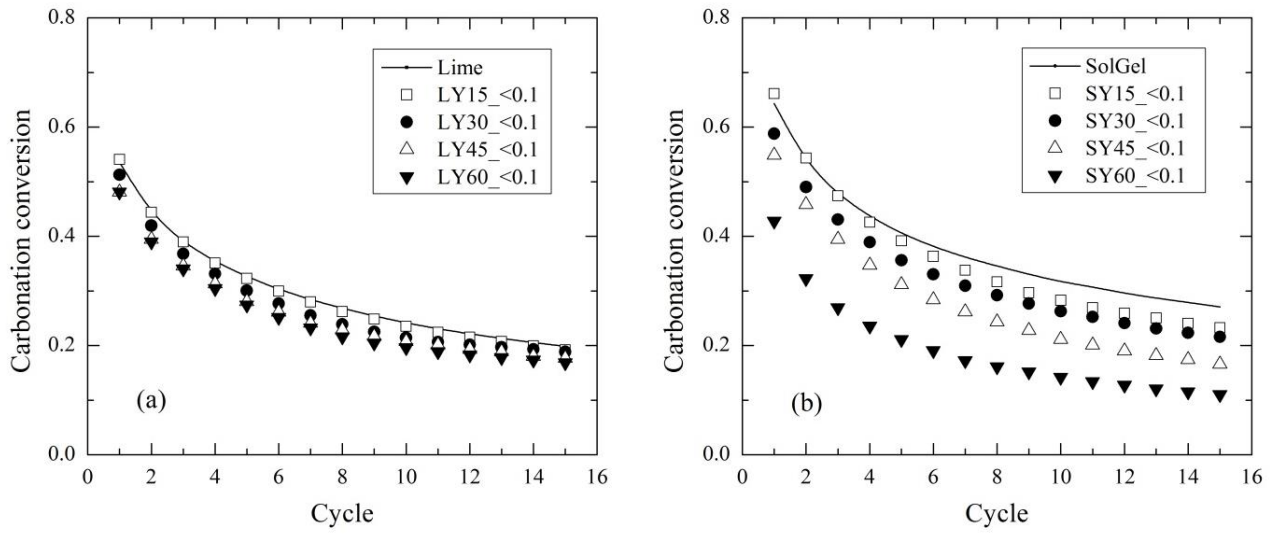


Figure 4. Effect of ash content on carbonation. Testing condition: carbonation in 15 vol. % CO₂ at 650 °C, calcination in 100 vol. % N₂ at 900 °C, both for 10 min.

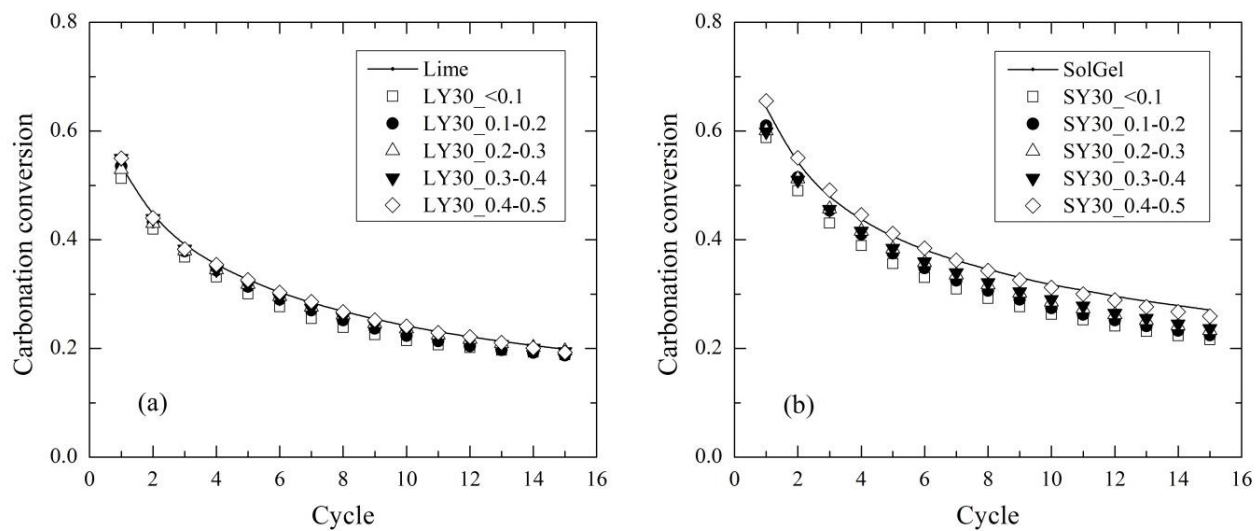


Figure 5. Effect of particle size of coal ash on carbonation conversion of CaO. Testing conditions: carbonation in 15 vol. % CO₂ at 650 °C, calcination in 100 vol. % N₂ at 900 °C, both for 10 min.

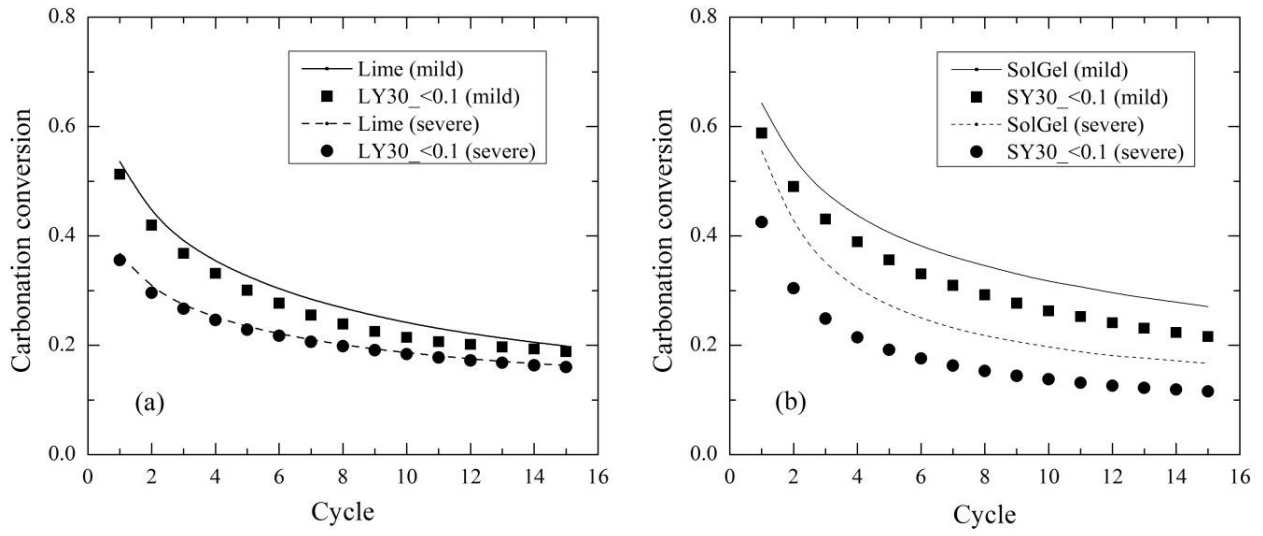


Figure 6. Carbonation conversion of sorbents under mild and severe calcination conditions. Testing conditions: carbonation in 15 vol. % CO₂ at 650 °C, mild calcination in 100% N₂ at 900 °C while severe calcination in 100% CO₂ at 950 °C, all for 10 min.

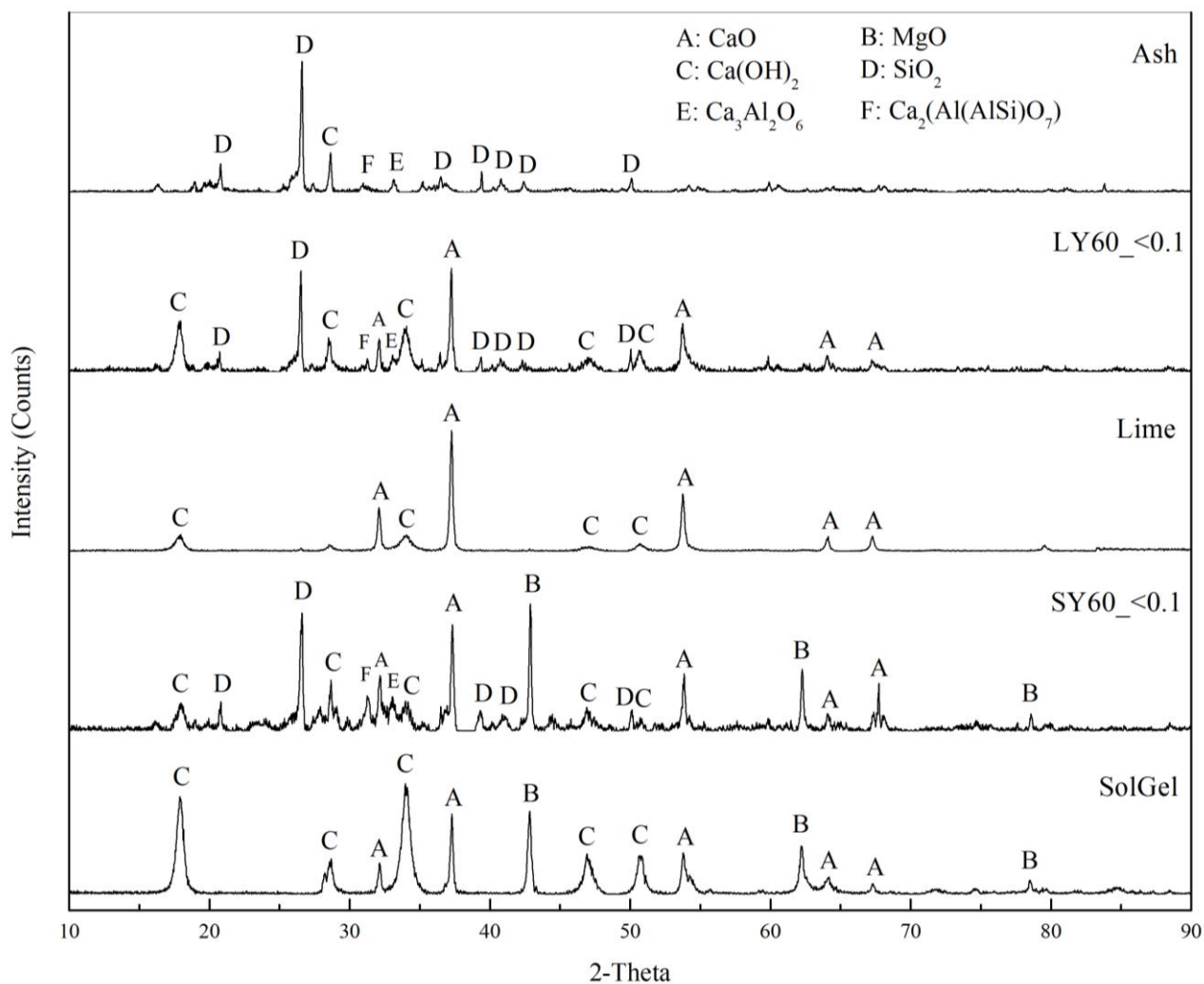


Figure 7. XRD patterns of selected samples after 10 min calcination at 900 °C.

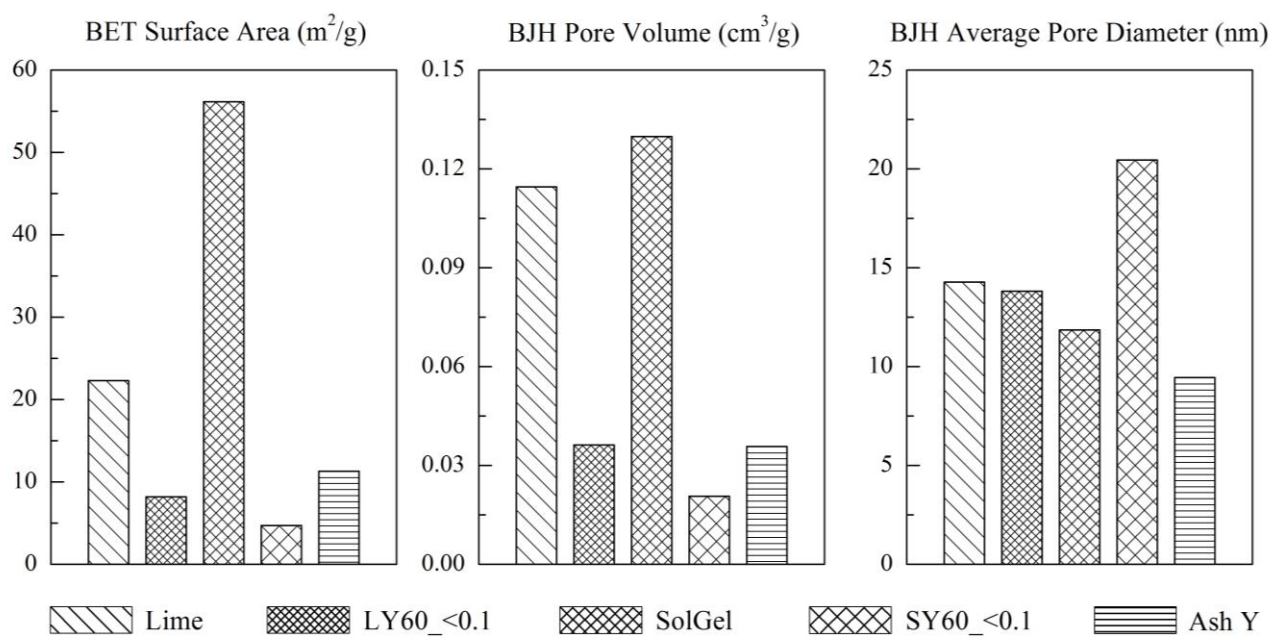


Figure 8. Pore structure parameters of five samples after calcination for 10 min at 900 °C.

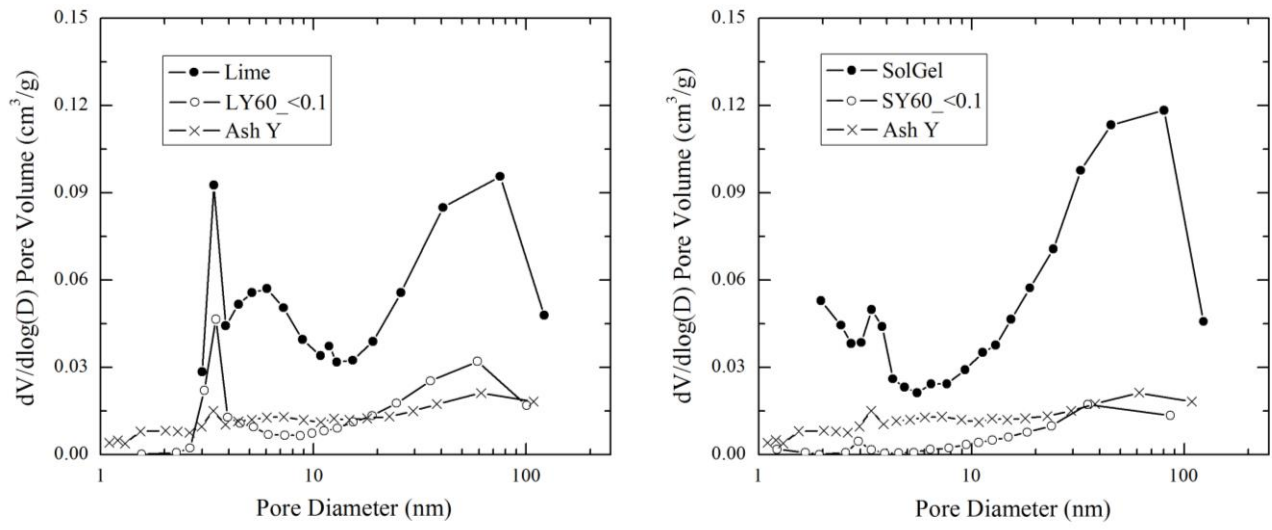


Figure 9. Pore diameter distribution of calcined lime, SolGel and their mixtures with coal ash (Y).

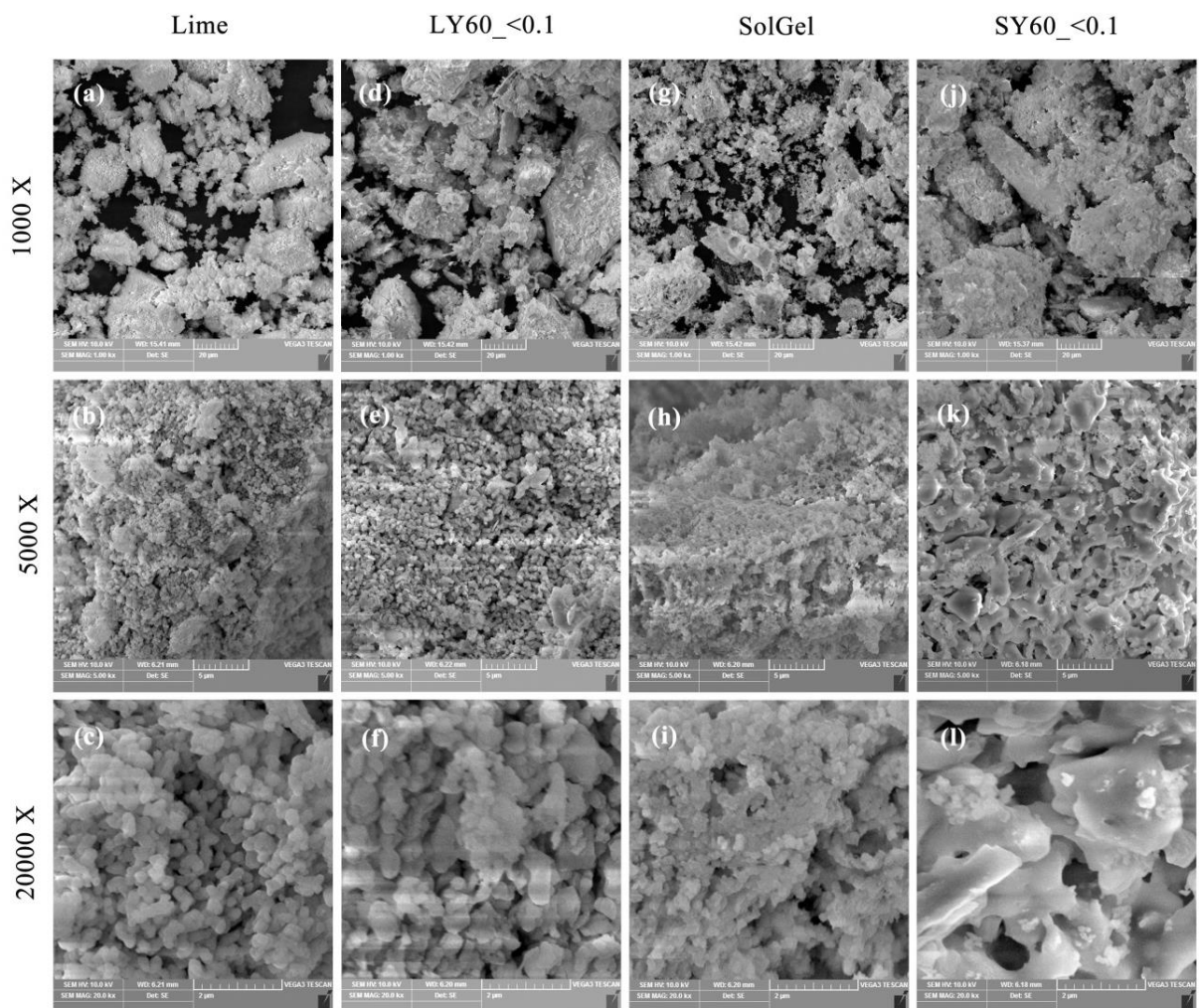


Figure 10. SEM images showing morphology of calcined sorbents with and without coal ash.

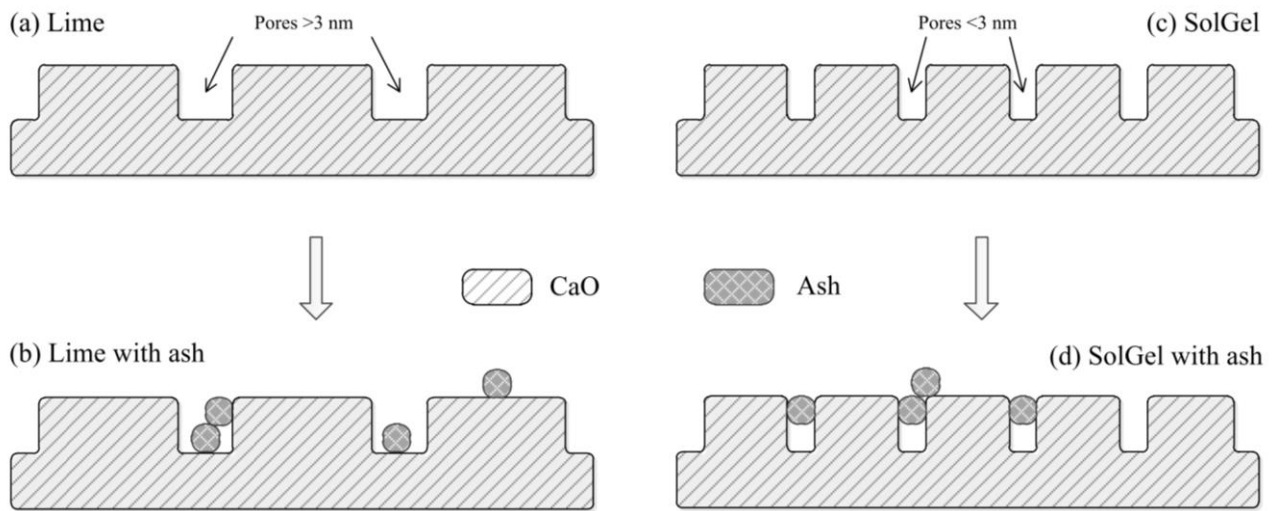


Figure 11. Schematic representation of pore-and-grain variation of lime and SolGel with the existence of coal ash.

Study on the interaction between CaO-based sorbents and coal ash in calcium looping process

He, D.

2016-09-21

Attribution-NonCommercial-NoDerivatives 3.0 International

He D, Qin C, Manovic V, Ran J, Feng B, Study on the interaction between CaO-based sorbents and coal ash in calcium looping process, Fuel Processing Technology, Volume 156, February 2017, pp.339-347

<http://dx.doi.org/10.1016/j.fuproc.2016.09.017>

Downloaded from CERES Research Repository, Cranfield University