



# Lithium Silicate Pellets for CO<sub>2</sub> Capture at High Temperature

Monica Puccini\*, Maurizia Seggiani, Sandra Vitolo

Department of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino 1, 56122 Pisa, Italy  
m.puccini@diccism.unipi.it

In this study, lithium orthosilicate-based pellets were developed and characterized as potential regenerable high-temperature CO<sub>2</sub> sorbents. A mechanical method was used for pelletization of the powdered materials, namely K<sub>2</sub>CO<sub>3</sub>-doped lithium silicate (Li<sub>4</sub>SiO<sub>4</sub>) with cellulose fibres. Different amounts of cellulose fibres (20, 30 and 40 wt%) were added to powdered doped-sorbent in order to identify the optimal amount to ensure an adequate porosity to the produced pellets. The CO<sub>2</sub> sorption properties of the produced pellets were investigated at high temperature (500 - 600 °C) by using a thermal gravimetric analyzer (TGA) at low CO<sub>2</sub> partial pressure with repeated calcination/carbonation cycles.

Compared to the pure K<sub>2</sub>CO<sub>3</sub>-doped lithium silicate pellets, the sorbents prepared using cellulose fibres showed greater CO<sub>2</sub> capture capabilities, which were ascribed to the higher porosity developed as a result of thermal degradation of cellulose. At 580 °C and a CO<sub>2</sub> partial pressure of 0.04 atm, the uptake of CO<sub>2</sub> in pellets prepared with 20 % of cellulose fibres reached about 20 wt% within 120 min corresponding to a Li<sub>4</sub>SiO<sub>4</sub>-conversion of 57 %. During multiple sorption/desorption cycles, a decay of the sorption capacity of the pellets was observed due to a partial sintering of the materials. This suggested that an appropriate binder should be added in order to improve the cyclic stability and the strength of the produced pellets.

## 1. Introduction

Fossil-fueled power plants are responsible for roughly 40 % of total anthropogenic CO<sub>2</sub> emissions (Yang et al., 2008). If fossil fuels, in particular coal, are to continue being used, CO<sub>2</sub> capture from such large stationary sources is necessary to stabilize the atmospheric concentration of CO<sub>2</sub> in order to reduce the severity of future climate change effects. The goal of any fossil fuel CO<sub>2</sub> capture process is to produce a concentrated CO<sub>2</sub> stream which can be transported and stored in geological formations (depleted oil and gas fields, saline formations, unmineable coal seams) (Soundararajan and Gundersen, 2012). Currently, the absorption process using aqueous amino solution is the most common and available for industrial applications for the post-combustion CO<sub>2</sub> capture (Moioli and Pellegrini, 2013). However, this amino-based process involves significant energy penalty due to the low operating temperatures (40-150 °C) and the high energy requirement for solvent regeneration. In recent years, separation systems operating at high temperature (450-750 °C) are being investigated (Pannocchia et al., 2007), among which solid sorbents based on lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) doped with carbonates (Seggiani et al., 2011). Such sorbents have shown promise for CO<sub>2</sub> capture at high temperature and low carbon dioxide concentration as alternatives to low-temperature absorption system (Puccini et al., 2013).

Lithium orthosilicate-based looping cycles, which utilize reversible carbonation and calcination reactions (Eq.1), offer a promising technology to separate CO<sub>2</sub> from flue gases. The Li<sub>4</sub>SiO<sub>4</sub> looping cycle concept can be realized using a dual fluidized bed system, where solid sorbents are continuously cycled between the two reactors, a carbonator (where the forward reaction occurs at lower temperature) to absorb CO<sub>2</sub> from the flue gases and a calciner (reverse reaction at a higher temperature) to release absorbed CO<sub>2</sub> from the sorbent (which regenerates the sorbent).



The CO<sub>2</sub> looping cycle technology is interesting owing to its potential advantages: the use in a mature technology such as large-scale circulating fluidized beds (CFB) and the application for enhanced production of hydrogen from shift reactors.

Looping cycles involving solid Li<sub>4</sub>SiO<sub>4</sub>-based sorbents require that the sorbent must be used several times for CO<sub>2</sub> capture after regeneration. The most substantial challenge for these processes is the loss of sorbent activity with increasing numbers of reaction cycles caused by sintering (Seggiani et al., 2013). Carbonation is affected by changes in sorbent porous structure related to the formation of a molten carbonate layer, due to the presence of K<sub>2</sub>CO<sub>3</sub> used as promoter to improve the CO<sub>2</sub> diffusion into sorbent particle. The methods for cyclic sorption enhancement are mainly based on producing changes in sorbent morphology.

In this study, pellets of Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were developed for CO<sub>2</sub> capture at high temperature and low concentration, in view of industrial applications. A mechanical method was used for pelletization of the powdered materials, namely lithium silicate (Li<sub>4</sub>SiO<sub>4</sub>) doped with carbonates and cellulose fibres. The CO<sub>2</sub> sorption properties of the obtained pellets were investigated by using a thermal gravimetric analyzer (TGA) in a controlled gas flow environment at low CO<sub>2</sub> partial pressure (0.04 atm). Scanning electron microscopy (SEM) was used to characterise the prepared sorbents and to understand the relationship between the sorbent structure and CO<sub>2</sub> sorption properties. Besides, the cyclic stability of the pellets was investigated by carrying out multiple cycles of CO<sub>2</sub> sorption/desorption.

## 2. Experimental section

### 2.1 Sorbent preparation and characterization

Li<sub>4</sub>SiO<sub>4</sub> powders were prepared by the solid state method. Starting materials were reagent-grade Li<sub>2</sub>CO<sub>3</sub> and ZrO<sub>2</sub> (from Sigma-Aldrich) in a 2:1 molar ratio. The materials were weighed, mixed, and ground in an agate mortar with a suitable amount of water. Then, the mixtures were dried and calcined in air at 900 °C for 4 h. Both temperature increase and decrease ramping rates were set to 60 °C/h. The resulting powders were ground by agate mortar to break down any agglomeration and then sieved to produce Li<sub>4</sub>SiO<sub>4</sub> particles with size below 10 µm. Promoted Li<sub>4</sub>SiO<sub>4</sub>-based sorbent, named LiK, was prepared mixing 30 wt% of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) with the previously synthesized pure Li<sub>4</sub>SiO<sub>4</sub> powder.

Pellets were prepared using the powdered sorbent, LK, mixed with 20, 30 and 40 wt% (by weight of LK) of cellulose fibres (sample LK-C2, LK-C3 and LK-C4, respectively). Cylindrical pellets were produced by using a mechanical press, operating at 5 bar pressure applied for 3 min. Three pellet sizes were prepared, with diameter of 6 mm and length of 3.5, 2.5 and 1.5 mm (named S1, S2 and S3).

The sample morphology was observed with a JEOL 5600 LV scanning electron microscope (SEM).

### 2.2 CO<sub>2</sub> sorption test

Carbon dioxide adsorption on the prepared pellets was studied using a thermogravimetric analyzer (TGA Q500 TA Instrument). Pellets were placed in a sample pan and heated (at a heating rate of 10 °C/min) in 100 % N<sub>2</sub> to the operating temperature (580 °C). Then, the N<sub>2</sub> flow was switched to air flow in order to thermally degrade the cellulose for developing porosity in the pellets. When the sample weight became stable, the air flow was switched to a mixture CO<sub>2</sub>/N<sub>2</sub> containing 4 vol% of CO<sub>2</sub>. The total feed gas flow rate was maintained at 100 mL/min at atmospheric pressure. The weight increase due to CO<sub>2</sub> sorption was recorded as a function of time during the adsorption process lasted 120 min. Besides, to assess the stability of the pellets fifteen adsorption/desorption cycles were carried out. The adsorption of CO<sub>2</sub> was carried for 60 min at the desired temperature in 4 vol% CO<sub>2</sub> flow. Afterwards, the feed gas stream was switched to a pure N<sub>2</sub> flow (100 mL/min) and the temperature was raised to 700 °C with heating rate of 20 °C/min. The sample was kept to the regeneration temperature until it was completely regenerated. The regeneration process lasted about 15 min. After that, a new cycle was carried out.

## 3. Results and discussion

Different ratios of cellulose and powered LK sorbent, between 20 and 40 wt%, were used in order to identify the optimal amount of cellulose fibres to ensure good hardness and a porous structure to the pellets. An amount of binder exceeding 40 wt% has not been considered appropriate since reduces the amount of active sorbent.

Cellulose fibres were mainly used to make porous the structure: during the heating to operating temperature (580 °C) the cellulose degradation takes place and, consequently, there is the formation of cavities into the pellet structure, as shown in Figure 1. The SEM micrographs display the morphology of the section of the sample LK-C2 before and after the cellulose decomposition: in the picture (a) the cellulose fibres dispersed

around the doped-orthosilicate particles are visible, in the picture (b) the fibres have been replaced by holes and cavity.

Figure 2 shows the weight increase of the pellets as a result of CO<sub>2</sub> sorption from a 4 vol% CO<sub>2</sub> stream at temperature of 580 °C. As it can be seen, the samples LK-C showed higher CO<sub>2</sub> sorption capacities compared to LK sample.

Since the promoter (K<sub>2</sub>CO<sub>3</sub>) and the residual cellulose fibres (after thermal degradation in air) showed no affinity for the CO<sub>2</sub> capture but contributed to the sorbent weight, the conversion of Li<sub>4</sub>SiO<sub>4</sub>,  $X_{\text{Li}_4\text{SiO}_4}$ , was used to compare the sorption performance of the pellets. The percentage conversion  $X_{\text{Li}_4\text{SiO}_4}$  was calculated by using the equation (2):

$$X_{\text{Li}_4\text{SiO}_4}(\%) = \frac{\Delta W}{F_{\text{Li}_4\text{SiO}_4} \cdot r_s} \quad (2)$$

where  $\Delta W$  is the percentage weight change of the sorbent during sorption,  $F_{\text{Li}_4\text{SiO}_4}$  is the weight fraction of Li<sub>4</sub>SiO<sub>4</sub> in the sorbent and  $r_s$  is the stoichiometric uptake of CO<sub>2</sub> by Li<sub>4</sub>SiO<sub>4</sub>, which is about 0.36 g of CO<sub>2</sub>/g of Li<sub>4</sub>SiO<sub>4</sub>. Table 1 reports the percentage conversion of the pellets produced with 20, 30 and 40 wt% of cellulose fibres. It can be seen that for the pellets LK, the conversion was significantly lower than the other pellets. As shown, the use of cellulose fibres enhanced the CO<sub>2</sub> uptake: the adsorbed amount of CO<sub>2</sub> after 2 h was nearly 15 wt% of the starting material corresponding to a 55 % conversion of Li<sub>4</sub>SiO<sub>4</sub>. This results can be attributed to the different morphology of the pellets: the porosity created as a result of the cellulose degradation increased the surface area of the pellets and, consequently, their sorption capacity increased.

However, at the end of the first regeneration, a deformation was observed for the pellets at higher starting amounts of cellulose fibres (LK-C3 and LK-C4). This can be attributed to the cellulose degradation process before the CO<sub>2</sub> uptake. Gases evolved during the air/cellulose reactions can modify the original structure of the pellet. Although the samples were able to achieve high sorption performance (see Table 1), this behavior makes the LK-C3 and LK-C4 samples unsuitable for the use in multiple cycles and fluidized bed systems. On the other hand, the shape and morphology of the LK-C2 pellet did not change after the first capture-regeneration cycle, as shown in Figure 3. After the first cycle, the sorbent still presents a porous structure that makes it suitable for application in multiple cycles.

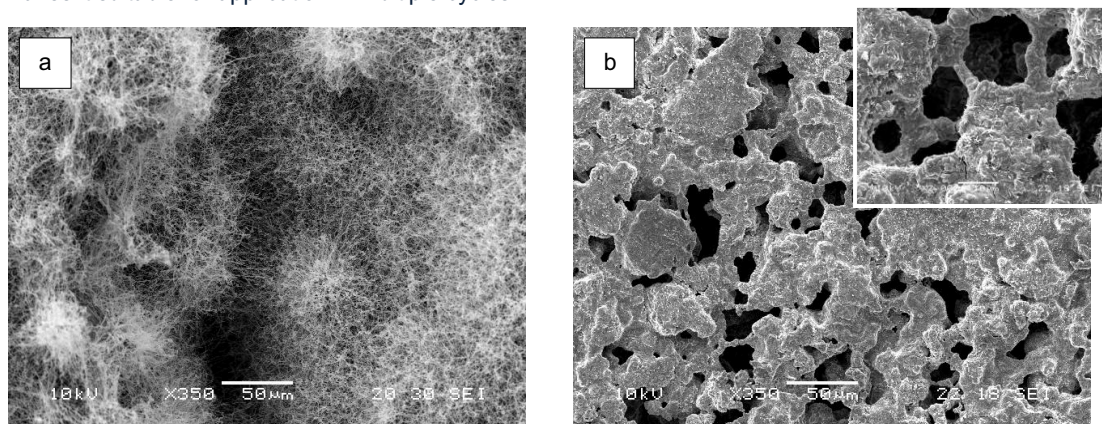


Figure 1: SEM images of cross-section of a LK-C2 pellet (size: S1): (a) before and (b) after cellulose degradation.

For the sorbent LK-C2 the effect of particle size on CO<sub>2</sub> uptake was investigated. Figure 4 shows the CO<sub>2</sub> sorption profiles at 580 °C of the pellets LK-C2 with the three different size. No significant variation on CO<sub>2</sub> adsorption capacity was observed. All the pellets showed a conversion of Li<sub>4</sub>SiO<sub>4</sub> nearly 57 % at an adsorbed amount of carbon dioxide after 2 hours.

The cyclic stability of the sorbents LK and LK-C2 with size S1 and S3 was investigated by carrying out 15 CO<sub>2</sub> sorption/desorption cycles (Figure 5). The pellet produced without cellulose fibres (LK) showed a remarkable decay in CO<sub>2</sub> absorption capacity after the first cycle: the conversion dropped off from 32 % to 13 % and remained essentially constant during the subsequent cycles. The other pellets, produced using 20 wt% of cellulose fibres, showed a different behavior: the sorption capacity remained nearly constant after the first 5 cycles and then it decreased slowly. Also in this case, no significant variation related to pellet size was

observed. Thus, cellulose fibres are able to enhance the sorption performance of the  $\text{Li}_4\text{SiO}_4$ -based pellet, but it seems do not affect the cyclic stability.

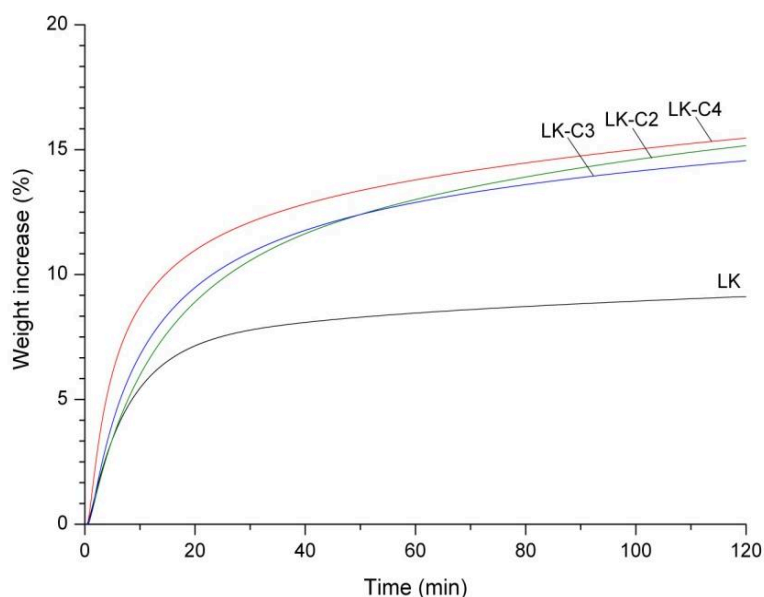


Figure 2:  $\text{CO}_2$  sorption profiles on the different pellets (size: S1) in 4 vol%  $\text{CO}_2$  stream at 580 °C.

To better understand the cyclic performance of the sample LK-C2 (size S1), the morphology of the used sample was analyzed by SEM. SEM images of fifteen used LK-C2 sample are shown in Figure 6. By comparison the image of the initial sorbent (Figure 1b), it can be seen that the morphology significantly changed during the sorption/desorption cycles. Also compared with the SEM image of the one-cycle (Figure 3), the structure of 15-cycle used LK-C2 pellet appears denser in many parts, indicating that partial sintering took place. This gave rise to a reduction in surface area which in turn slowed down the  $\text{CO}_2$  diffusion and subsequently reduced the absorption capacity within the defined absorption time (60 min).

Table 1: Percentage conversion of  $\text{Li}_4\text{SiO}_4$

Pellets	$X_{\text{Li}_4\text{SiO}_4}$ (%)
LK	32.3
LK-C2	54.8
LK-C3	51.5
LK-C4	54.7

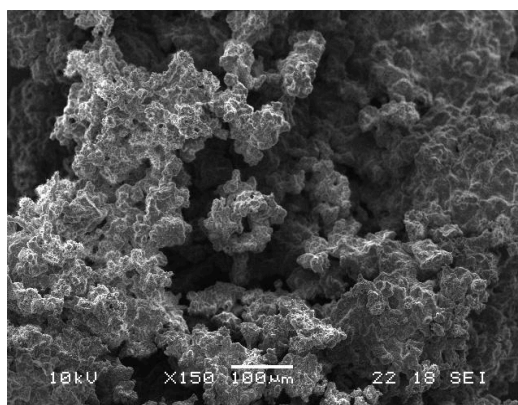


Figure3: SEM image of cross-section of LK-C2 pellet after the first capture-regeneration cycle

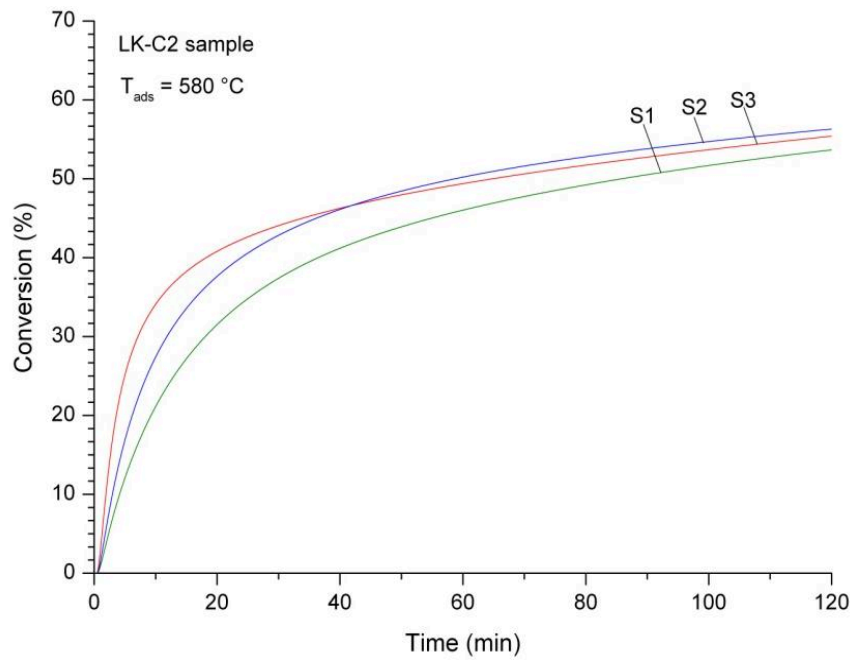


Figure 4: Effect of the pellet size on sorption performance of the sample LK-C2

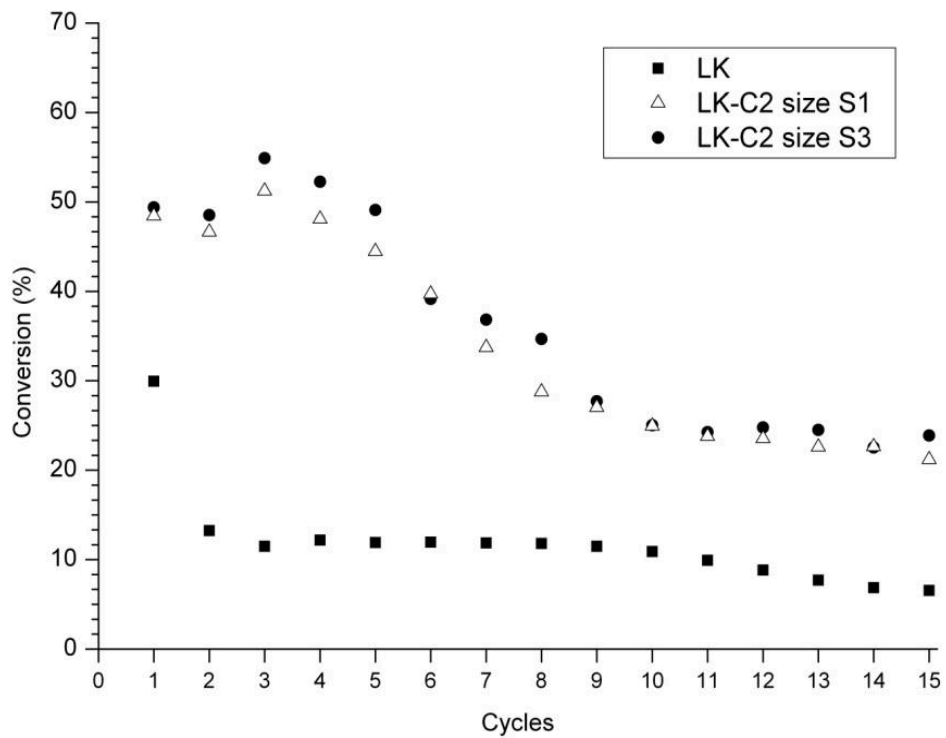


Figure 5: Multiple cycles of CO<sub>2</sub> sorption/desorption on pellets LK (size S1) and LK-C2 (size S1 and S3)



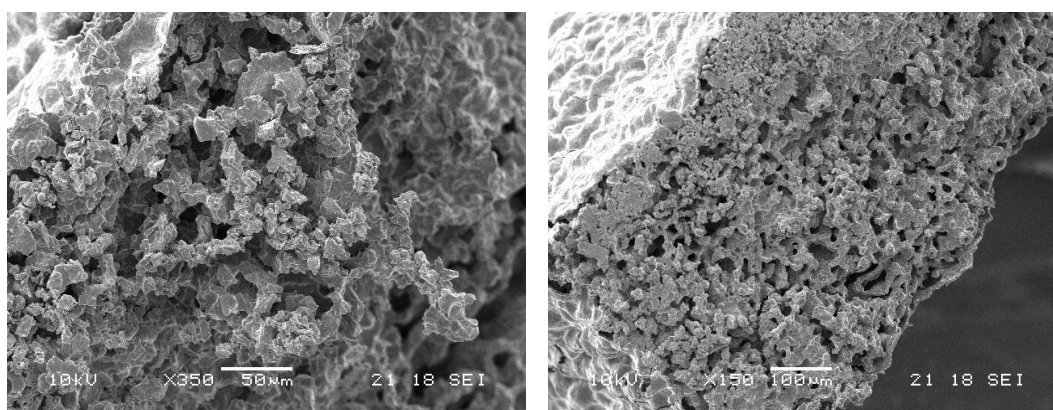


Figure 6: SEM images of the section of the LK-C2 pellet after 15 sorption/desorption cycles

#### 4. Conclusions

The objective of this work was the development of novel  $\text{Li}_4\text{SiO}_4$  based-sorbents in form of pellets for  $\text{CO}_2$  capture at high temperature (500 - 600 °C) and low concentration. A mechanical method was used for pelletization of the powdered materials, namely lithium silicate ( $\text{Li}_4\text{SiO}_4$ ) doped with carbonates and different amounts of cellulose fibres. Cellulose fibres were used to make porous the structure as evidenced by the morphology of the produced pellets. The  $\text{CO}_2$  sorption properties of the pellets were investigated by using a thermal gravimetric analyzer (TGA). The curves uptake revealed that the use of cellulose fibres enhanced the  $\text{CO}_2$  sorption capacity of the  $\text{Li}_4\text{SiO}_4$ -based pellets. At 580 °C and under a 4 vol%  $\text{CO}_2$  flow the  $\text{CO}_2$  sorption capacity for the pellets (diameter 6 mm and length 3.5 mm) produced using 20 wt% of cellulose fibres was about 200 mg  $\text{CO}_2/\text{g}$  sorbent after 2 hours corresponding to a 57 % conversion of  $\text{Li}_4\text{SiO}_4$ . These results can be attributed to the different morphology of the pellets: the porosity created by the cellulose degradation in air (before the first sorption run) increased the surface area of the pellets and, consequently, their sorption capacity. No significant variation on  $\text{CO}_2$  adsorption capacity was observed in relation to the investigated pellet sizes.

During 15  $\text{CO}_2$  sorption/desorption cycles, the sorption capacity of the pellets remained nearly constant only for the first 5 cycles and, then, decreased markedly because of a partial sintering of the material, as shown by SEM morphological analysis. Future work will focus on the use of an appropriate inert binder for the pelletization process in order to improve the cyclic stability and the mechanical resistance of the produced pelletized  $\text{Li}_4\text{SiO}_4$ -based sorbents.

#### References

- Moioli S., Pellegrini L., 2013, Regeneration section of  $\text{CO}_2$  capture plant by MEA scrubbing with a rate-based model, *Chemical Engineering Transactions*, 32, 1849-1854.
- Pannocchia G., Puccini M., Seggiani M., Vitolo S., 2007, Experimental and modelling studies on high temperature capture of  $\text{CO}_2$  using lithium zirconate based sorbents, *Ind. Eng. Chem. Res.* 46, 6697-6706.
- Puccini M., Seggiani M., Vitolo S., 2013,  $\text{CO}_2$  capture at high temperature and low concentration on  $\text{Li}_4\text{SiO}_4$  based sorbents, *Chemical Engineering Transactions*, 32, 1279-1284.
- Seggiani M., Puccini M., Vitolo S., 2011, High-Temperature and Low Concentration  $\text{CO}_2$  Sorption on  $\text{Li}_4\text{SiO}_4$  based Sorbents: Study of the used silica and doping method effects, *Int. J. Greenh. Gas Con.* 5, 741-748.
- Seggiani M., Puccini M., Vitolo S., 2013, Alkali promoted lithium orthosilicate for  $\text{CO}_2$  capture at high-temperature and low concentration, *Int. J. Greenh. Gas Con.* 17, 25-31.
- Soundararajan R., Gundersen T., 2012, Coal based power plants using oxy-combustion for  $\text{CO}_2$  capture: pressurized coal combustion to reduce capture penalty, *Chemical Engineering Transactions*, 29, 187-192.
- Yang H., Xu Z., Fan M., Gupta R., Slimane R.B., Bland A.E., Wright I., 2008, Progress in carbon dioxide separation and capture: A review, *J. Environ. Sci.* 20, 14-27.