

# The Effect of Flue Gas Contaminants on CO<sub>2</sub> Capture at High Temperature by Li<sub>4</sub>SiO<sub>4</sub>-Based Sorbents

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In this study, high-temperature CO<sub>2</sub> capture by solid sorbent based on lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) was investigated in the presence of gas contaminants, such as NO and SO<sub>2</sub>. Simulated flue gas containing CO<sub>2</sub> (4 vol%), SO<sub>2</sub> (up to 2,000 ppm), and NO (up to 1,000 ppm) was used during the CO<sub>2</sub> capture process. The CO<sub>2</sub> sorption properties of the sorbent were investigated at high temperature (580 °C) by a thermal gravimetric analyzer (TGA).

The tested sorbent showed high CO<sub>2</sub> sorption capacity (210 mg CO<sub>2</sub>/g sorbent) along with high absorption rates, and lower regeneration temperature than other solids such as calcium oxide. The results also showed that the solid sorbent is inert with respect to NO. Instead, the presence of SO<sub>2</sub> resulted in a negatively effect on the sorption capacity of the sorbent, due to an irreversible reaction with the adsorbent. Thus, industrial application would require desulfurization of flue gas prior to contacting the sorbent.

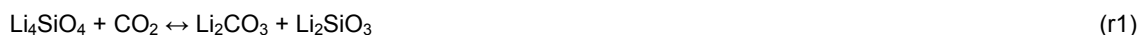
## 1. Introduction

The emission of carbon dioxide (CO<sub>2</sub>), one of the major greenhouse gases, has raised great concerns about the relationship between anthropogenic CO<sub>2</sub> and global warming: the CO<sub>2</sub> emission may have contributed to urban smog, acid rain, and health problems. The development of efficient technologies for the capture and sequestration of carbon dioxide produced by existing point sources, such as fossil-fuel power plants, will prove vital in controlling the environmental impact of anthropogenic emissions (Leperi et al., 2014). In order for these technologies to be economically viable, carbon capture and sequestration (CCS) systems must curb the energy penalty associated with CO<sub>2</sub> capture and sorbent regeneration, and operate effectively in realistic conditions.

Processes based on aqueous amine absorbents represent the best, currently available, and practically applied technology for CO<sub>2</sub> capture, but regeneration requires substantial heat input, 63–84 kJ/mol CO<sub>2</sub>, resulting in plant inefficiencies and high costs, even though recent efforts have achieved some cost and energy reductions (Quinn et al., 2012). An alternative approach to reduce the energy penalty is by using dry solid sorbents that are able to reversibly react with CO<sub>2</sub> at elevated temperatures. An industrial process also requires an absorbent material that maintains a high CO<sub>2</sub> capacity in the presence of the numerous impurities found in coal-fired power plant flue gas. A typical flue gas contains 0.05–0.2 vol% of SO<sub>2</sub>, 0.015–0.1 vol% of NO<sub>x</sub>, with trace quantities of other compounds such as HCl, arsenic, mercury, and selenium (Czyzewski et al., 2013). Such species could have a significant impact on the reversible absorption of CO<sub>2</sub> leading to a decrease in capacity with time, as observed for high-temperature absorbents such as CaO (Sun et al., 2007).

A screening effort involving solid sorbents was conducted to identify viable candidates for post combustion CO<sub>2</sub> capture: a lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>)-based sorbent was found to have very favorable properties (Seggiani et al., 2011), and it holds promise for a practical CO<sub>2</sub> capture process (Puccini et al., 2013a). Main advantages of this material are their high CO<sub>2</sub> capture capacity at low CO<sub>2</sub> concentration (Seggiani et al., 2013), lower regeneration temperatures (< 750 °C) compared to other high-temperature sorbents, such as CaO, and their excellent stability that allow operation over a significant number of cycles without losing their sorption capacity (Puccini et al., 2013b).

Lithium orthosilicate can theoretically adsorb CO<sub>2</sub> in amounts up to 0.36 g CO<sub>2</sub>/g sorbent, according to the following reaction r1:



In practice, CO<sub>2</sub> capacities up to 35 wt % have been reported at a temperature of 700 °C in pure CO<sub>2</sub> (Kato et al., 2005). Considering the potential applications of these sorbents for carbon dioxide capture from exhaust gas in thermal power plants (low CO<sub>2</sub> concentrations), the requested temperature range is between 450 and 600 °C.

The aim of the present work is to study the sorption properties of the Li<sub>4</sub>SiO<sub>4</sub>-based sorbent under realistic conditions, by exposing the solid sorbents to gases with low CO<sub>2</sub> concentration and containing typical contaminants of flue gas (CO<sub>2</sub>, SO<sub>2</sub>, and NO). The CO<sub>2</sub> sorption properties of the sorbent were investigated at high temperature (580 °C) by a thermal gravimetric analyzer (TGA), and by exposure to gas mixtures containing CO<sub>2</sub> (4 vol%), SO<sub>2</sub> (up to 2000 ppm) and NO (up to 1000 ppm).

## 2. Experimental

### 2.1 Sorbents preparation and characterization

Lithium silicate powder was prepared by the solid state method. Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>, reagent-grade, Sigma-Aldrich) and silicon dioxide (SiO<sub>2</sub>, quartz type, Sigma-Aldrich) were mixed and ground in an agate mortar in a 2:1 molar ratio (with a suitable amount of water). Then, the mixture was 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 powder was 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. The Li<sub>4</sub>SiO<sub>4</sub>-based sorbent was prepared mixing 30 wt% of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, reagent-grade, Sigma-Aldrich) with the previously synthesized pure Li<sub>4</sub>SiO<sub>4</sub> powder.

Powder X-ray diffraction (XRD) characterization of Li<sub>4</sub>SiO<sub>4</sub> sorbent after the sorption tests was conducted using a Philips PW 1050/25 X-ray diffractometer with Cu-Kα radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The XRD patterns were recorded over a 2θ range between 15 ° and 70 °. Phase identification was verified by comparison against the corresponding Joint Committee Powder Diffraction Standards (JCPDS).

### 2.2 Experimental procedure

Carbon dioxide adsorption on prepared powders was studied using a thermogravimetric analyser (TGA Q500 TA Instrument). About 20 mg of sample were placed in a sample pan and, prior to CO<sub>2</sub> sorption testing, the sample was pre-conditioned and dried in a nitrogen flow (100 mL/min) elevating the temperature (at 10 °C/min) to the operating temperature (580 °C), till sample weight became stable. Then, the N<sub>2</sub> flow was switched to a mixture CO<sub>2</sub>/N<sub>2</sub>, containing 4 vol% of CO<sub>2</sub>, with and without NO (up to 1,000 ppm) or SO<sub>2</sub> (up to 2,000 ppm). 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 optimized sorbent twenty-five adsorption/desorption cycles were carried out. The adsorption of CO<sub>2</sub> was carried for 60 min at 580 °C 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.

Since the promoters 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 assess and compare the effect of the different promoters used on the CO<sub>2</sub> sorption reaction. The percentage conversion  $X_{\text{Li}_4\text{SiO}_4}$  was calculated by using the Eq(1):

$$X_{\text{Li}_4\text{SiO}_4} (\%) = \frac{\Delta W}{F_{\text{Li}_4\text{SiO}_4} \cdot r_s} \quad (1)$$

where ΔW is the percentage weight change of the sorbent during the adsorption,  $F_{\text{Li}_4\text{SiO}_4}$  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>.

## 3. Results and discussion

The uptake of CO<sub>2</sub> on Li<sub>4</sub>SiO<sub>4</sub>-based sorbent was investigated over one cycle of absorption and desorption, and a repetitive series of adsorption/desorption steps, at a fixed temperature (580 °C).

Carbon dioxide sorption/desorption profile obtained at 580 °C under 4 vol% CO<sub>2</sub> flow is reported in Figure 1. The sorbent exhibits a sorption capacity of 210 mgCO<sub>2</sub>/g sorbent after 2 h. Afterwards, during the regeneration the CO<sub>2</sub> is desorbed completely, confirming that the reaction between Li<sub>4</sub>SiO<sub>4</sub> and CO<sub>2</sub> is reversible on the microstructural level during the CO<sub>2</sub> sorption/desorption process. Furthermore, the stability of the sorbent undergoing several cycles of CO<sub>2</sub> sorption and desorption was tested. In particular, Figure 2 shows CO<sub>2</sub> uptake and release of the sorbent during 25 cycles of sorption and desorption. It can be seen that no differences are noticed in terms of sorption capacity among different cycles, and therefore the sorbent appears fully stable.

Although CO<sub>2</sub>, and N<sub>2</sub> constitute 95% or more of typical flue gas, the minor components as SO<sub>2</sub> and NO<sub>x</sub> can play a major role in affecting adsorption process. Among nitrogen oxides, NO and NO<sub>2</sub> are the major components and NO represents 90 to 95 % of total NO<sub>x</sub> in power plant flue gases.

The effect of NO on adsorption capacity as function of NO concentration in the gas stream is reported in Table 1. Results show that adsorption capacity does not change when the concentration of NO rises from 0 to 1,000 ppm: varying the NO gas content, the adsorbed amount of CO<sub>2</sub> after 2 hours remained constant, about 21 wt% of the starting material corresponding to a 73% conversion of lithium orthosilicate. As expected, the solid sorbent is inert with respect to NO, thus nitrogen monoxide does not represent a poison for Li<sub>4</sub>SiO<sub>4</sub>-based sorbent.

Figure 3 shows the time-dependent capture profiles of the sorbent using different SO<sub>2</sub> content in the gas stream. In all these cases, the weight change during the adsorption step is higher than the weight change during the desorption step. This result can be attributed to the adsorption of both SO<sub>2</sub> and CO<sub>2</sub> during the sorption process, and only CO<sub>2</sub> desorption during the desorption step.

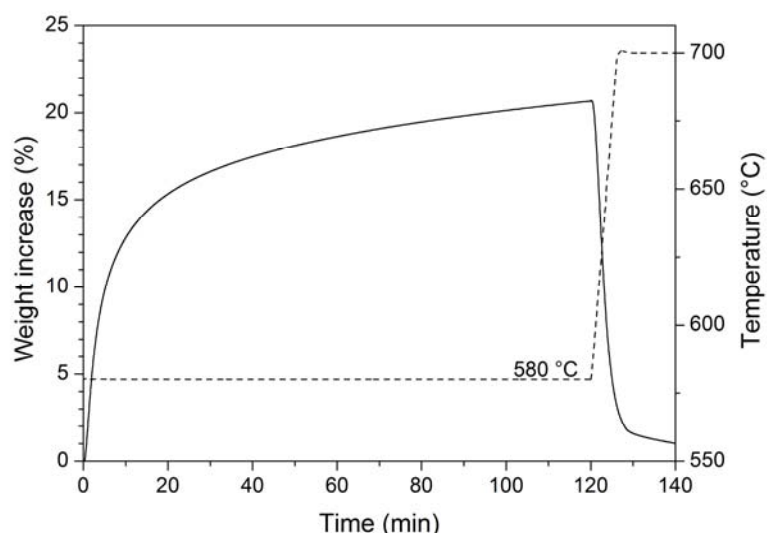


Figure 1: CO<sub>2</sub> sorption and regeneration on Li<sub>4</sub>SiO<sub>4</sub>-based sorbent (at 580 °C in 4 vol% CO<sub>2</sub>).

Table 1. Effect of NO on percentage conversion of Li<sub>4</sub>SiO<sub>4</sub>-based sorbent during CO<sub>2</sub> capture process.

[NO] (ppm)	Conversion (%)
0	73.1
250	72.9
500	73.5
750	71.0
1000	73.4

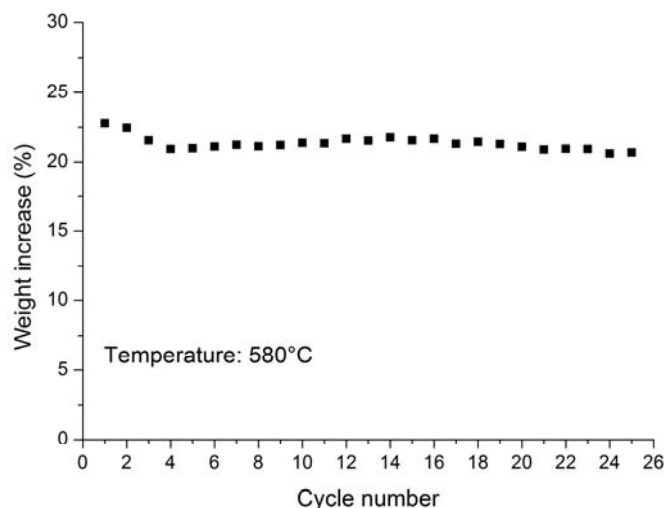


Figure 2: Multiple cycles of CO<sub>2</sub> sorption (60 min at 580 °C in 4 vol% CO<sub>2</sub>) on Li<sub>4</sub>SiO<sub>4</sub>-based sorbent

Therefore, SO<sub>2</sub> reactivity in the absence of CO<sub>2</sub> was evaluated by exposing the sorbent for 2 h to a gas containing 2,000 ppm of SO<sub>2</sub> (in N<sub>2</sub>) followed by the regeneration step. As shown in Figure 4, SO<sub>2</sub> exposure resulted in a weight increase of the sample (about 21 %), and regenerating the SO<sub>2</sub>-loaded sorbent with nitrogen at 700 °C resulted no desorption of sulfur dioxide. This indicates that SO<sub>2</sub> reacts irreversibly with the lithium orthosilicate at these conditions, preventing the regeneration of the sorbent and, as a consequence, its use in a CO<sub>2</sub> sorption/desorption cyclic process.

Thus, SO<sub>2</sub> appears to be irreversibly absorbed by the sorbent, and its presence negatively impacts the CO<sub>2</sub> capacity. The above experimental results show that SO<sub>2</sub> reacts readily with the sorbent, and it supposes that sulfur dioxide reacts with Li<sub>4</sub>SiO<sub>4</sub> via chemistry analogous to CO<sub>2</sub> (see reaction r1) with formation of lithium sulfite (Li<sub>2</sub>SO<sub>3</sub>) and lithium metasilicate (Li<sub>2</sub>SiO<sub>3</sub>), as in reaction r2:

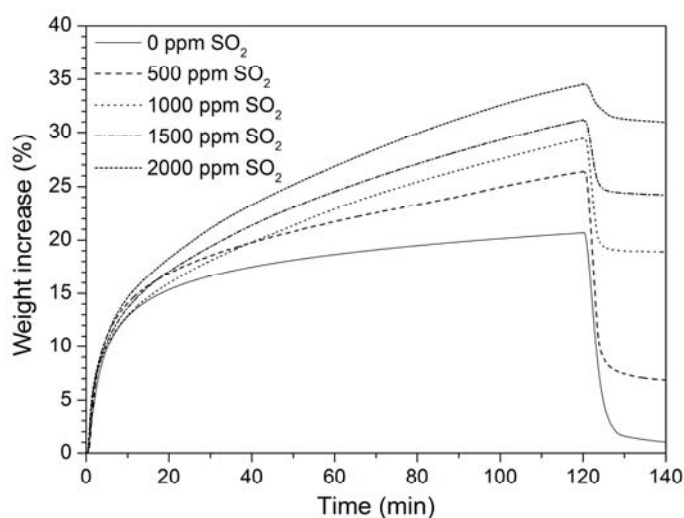


Figure 3: Effect of SO<sub>2</sub> concentration on CO<sub>2</sub> capture capacity of the sorbent at 580 °C

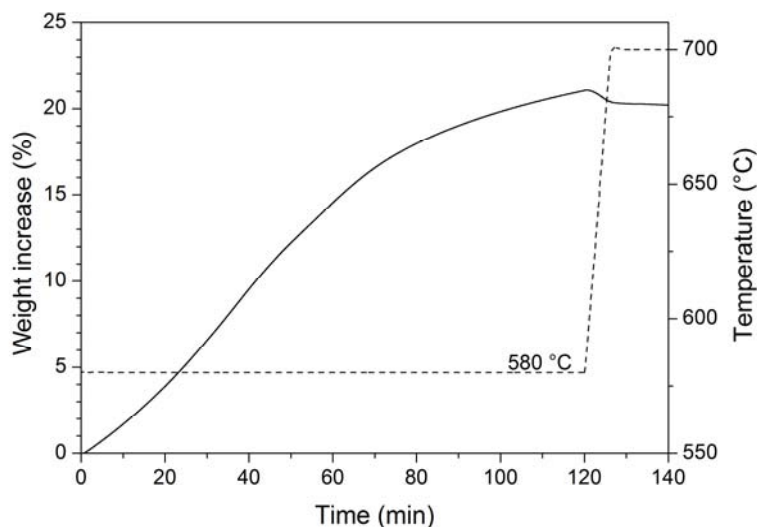


Figure 4:  $\text{SO}_2$  uptake at 580 °C (2,000 ppm  $\text{SO}_2$ )

In order to establish elemental and phase composition of the products, and thereby shed light on the reaction chemistry, analysis of the exposed sorbent samples was carried out. Figure 5 shows, by means of X-ray analysis, the microstructure changes of the  $\text{Li}_4\text{SiO}_4$ -based sorbent after  $\text{CO}_2$  sorption process by using the gas stream with and without  $\text{SO}_2$  (2,000 ppm). XRD pattern of the sorption products shows the peaks associated with  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{SiO}_3$ , as expected, indicating that during the  $\text{CO}_2$  sorption process  $\text{Li}_4\text{SiO}_4$  reacts with  $\text{CO}_2$  to become lithium carbonate and lithium metasilicate. XRD also shows the peaks associated with  $\text{Li}_2\text{SO}_3$  and  $\text{Li}_2\text{SO}_4$  as  $\text{SO}_2$  adsorption reaction products. Even for exposure to  $\text{SO}_2$  in absence of  $\text{CO}_2$ , the sulfur containing-phase  $\text{Li}_2\text{SO}_4$  was identified by XRD.

The presence of  $\text{Li}_2\text{SO}_4$  in the  $\text{SO}_2$ -exposed sorbent was unexpected. It could perhaps be attributed to oxidation upon exposure to air after removal from the balance. This was thought to be unlikely because oxidation is expected to be quite slow at room temperature. Alternatively, it could be supposed that lithium metasilicate reacts with  $\text{SO}_2$ , following the reaction r3:

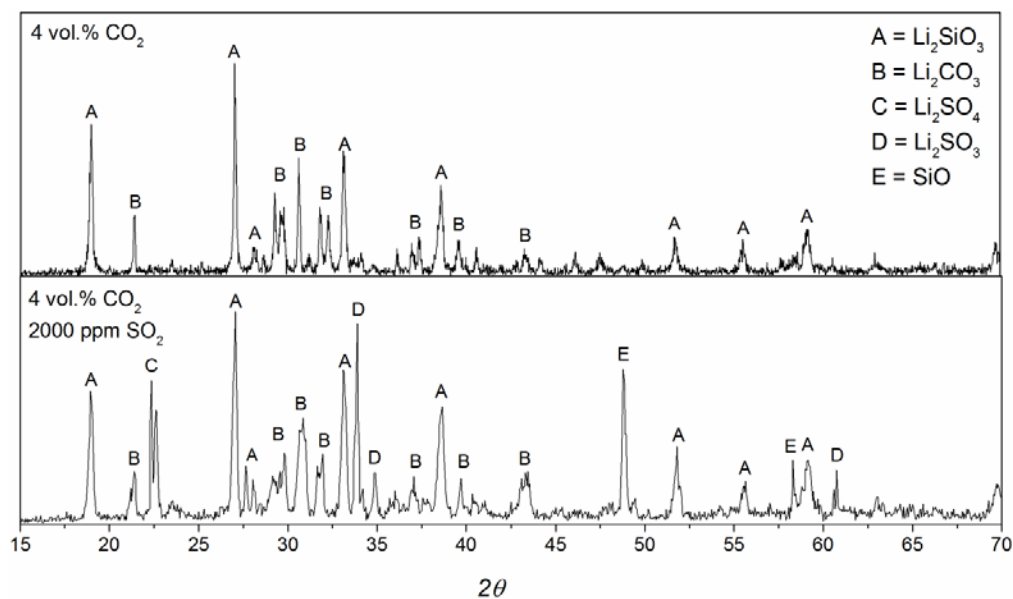


Figure 5: XRD patterns of products of the sorption process

This theory is supported by the XRD pattern of SO<sub>2</sub>-exposed sorbent (see Figure 5) that also shows some peaks attributable to silicon monoxide (Schnurre et al., 2004). Furthermore, it was noticed that the reaction products of SO<sub>2</sub>-exposed sorbent had a yellowish-brown color, proper to the solid silicon monoxide.

The resulting formation of Li<sub>2</sub>SO<sub>4</sub> during the CO<sub>2</sub> capture process prevents the regeneration of the SO<sub>2</sub> exposed sorbent. Such material will need to be replaced with fresh absorbent. In practice, removal of SO<sub>2</sub> from flue gases may be necessary. In this regard, the Li<sub>4</sub>SiO<sub>4</sub>-based sorbent is no different than any other material that chemically absorbs CO<sub>2</sub>. All such materials will have a higher affinity for SO<sub>2</sub> than CO<sub>2</sub>, and some desulfurization of flue gas prior to contacting the adsorbent will be required

#### 4. Conclusions

The CO<sub>2</sub> capture capacity of the Li<sub>4</sub>SiO<sub>4</sub>-based sorbent at high-temperature (580 °C) in the presence of NO and SO<sub>2</sub> was investigated in this study.

Li<sub>4</sub>SiO<sub>4</sub> offers excellent CO<sub>2</sub> sorption characteristics in terms of large CO<sub>2</sub> sorption capacity after 2h at 580 °C (about 210 mg of CO<sub>2</sub>/g sorbent corresponding to a conversion of 73 %), infinite CO<sub>2</sub>/N<sub>2</sub> selectivity, and good reversibility. Besides, the sorbent maintained its sorption properties after 25 sorption/desorption cycles, displaying a good prospect for application in the separation at high temperatures of CO<sub>2</sub> from fuel-fired power stations as well as in the in situ removal of CO<sub>2</sub> produced in some reactions such as SMR and WGS reactions to enhance hydrogen production.

The sorption properties of sorbent were also investigated by exposure to gas stream containing CO<sub>2</sub> (4 vol%), SO<sub>2</sub> (up to 2,000 ppm) and NO (up to 1,000 ppm). Results showed that the solid sorbent is inert with respect to NO, thus nitrogen monoxide does not represent a poison for Li<sub>4</sub>SiO<sub>4</sub>-based sorbent. Instead, the presence of SO<sub>2</sub> in the flue gas significantly affects the CO<sub>2</sub> sorption properties of the sorbent. Results indicate that SO<sub>2</sub> reacts irreversibly with the lithium orthosilicate, with formation of Li<sub>2</sub>SO<sub>3</sub> and Li<sub>2</sub>SO<sub>4</sub>. Thus, removal of SO<sub>2</sub> from flue gases may be necessary prior to contacting the sorbent.

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