Preparation of sintered foam materials by alkali-activated coal fly ash

Yelong Zhao, Junwei Ye, Xiaobin Lu, Mangang Liu, Yuan Lin, Weitao Gong, Guiling Ning*

State Key Laboratory of Fine Chemicals and School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, PR China

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ABSTRACT

Coal fly ash from coal fired power stations is a potential raw material for the production of ceramic tiles, bricks and blocks. Previous works have demonstrated that coal fly ash consists mainly of glassy spheres that are relatively resistant to reaction. An objective of this research was to investigate the effect of alkali on the preparation process of the foam material. Moreover, the influence of foam dosage on the water absorption, apparent density and compressive strength was evaluated. The experimental results showed that homogenous microstructures of interconnected pores could be obtained by adding 13 wt.% foaming agent at 1050 °C, leading to foams presenting water absorption, apparent density and compressive strength values of about 126.5%, 0.414 g/cm^3, 6.76 MPa, respectively.

1. Introduction

With the development of economy, energy needs are increased with years. Then of course many problems come into play. One of them is the utilization of coal fly ash (CFA). The total production of coal fly ash is estimated to exceed 550 Mt per year [1]. Particularly China and India where coal is a major fuel for electricity generation both produce significant quantities of ash. And the increasing number of coal fired power plants means that the large volumes of fly ash will continue to be produced. Efficient disposal of coal fly ash has been a worldwide issue because of the massive amount of ash produced and its harmful effects on the environment [2,3]. Fly ash is generally dumped in landfills. This represents a huge negative environmental impact mainly including the pollution of soils and groundwater.

When coal fly ash was mainly regarded as waste products up until the early-1930s, the use of coal fly ash in concrete started in the US. Gradually, more works on coal fly ash reuse were done. From a power generation's perspective, fly ash is a waste; while from utilization's perspective, coal fly ash is a resource yet to be fully utilized and exploited. Even though many attempts have been made to find new application fields for fly ash such as: construction materials as an additive [4,5], the production of zeolites [6,7], recovery of some elements from coal fly ash [8,9] and the manufacture of geopolymers as raw material [10,11], only a small percentage of coal fly ash is utilized (15% in China) [12].

It is well known that chemically pozzolanic reaction of fly ash occurs readily under thermal treatment creating strong structures with an increase of mechanical strength. Alternatively, Chindaprasirt and Pimraks [4], Taniguchi co-workers [5], Andini et al. [10], Hajimohammadi et al. [11] have proven that aggregates can be obtained by alkali-activated method from coal fly ash. Materials are attractive because excellent mechanical properties and durability can be achieved. But generally speaking, the increasing of strength demands a long period and a mass of coal fly ash dumped in landfills is starved for using. Therefore, the method of sintering was adopted in this study. Furthermore, alkali-activated method was used to enhance the preliminary performance.

Therefore the objective of this work is to convert the coal fly ash into foam materials, which have high water absorption, high specific surface area, low density and long life in severe environments due to their high porosity, well-developed surface pores, and homogenous microstructures of interconnected pores. The use of coal fly ash as a raw material for the foam materials would be beneficial for the environment as well, because of the reduction in mining for raw materials substituted for fly ash and because of the beneficial use for the coal fly ash. In addition, there is the possibility of economic advantages due to the low cost of coal fly ash.

2. Experiment

### 2.1. Characteristic of raw material and sample pre-treatment

The primary components of coal fly ash are silica (SiO_2), alumina (Al_2O_3) and iron oxides (Fe_2O_3) with varying amounts of carbon, calcium, magnesium and sulphur. An empirical formula for fly ash

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Table 1
Composition data for coal fly ash and sheet glass powder (wt.%).

Oxide	Coal fly ash	Sheet glass powder
SiO_2	41.96	67.70
Al_2O_3	24.01	2.78
Fe_2O_3	10.40	0.63
CaO	5.78	8.35
MgO	3.80	3.80
Na_2O	1.05	15.00
TiO_2	2.04	0.06
K_2O	1.50	0.85
SO_3	2.68	0.60
Others	1.28	0.23
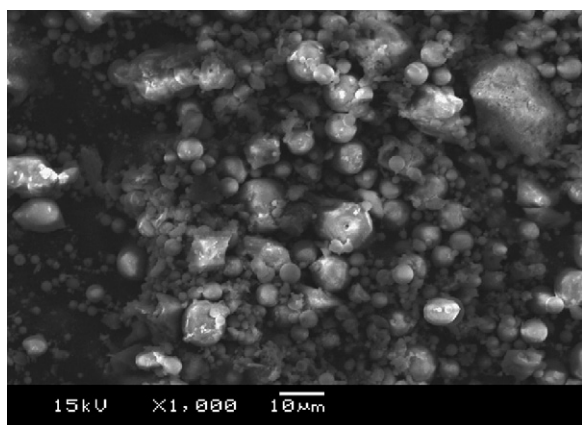
Fig. 1. SEM micrograph of CFA.

based on the dominance of certain key elements has been proposed [13] as

$$Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011}$$
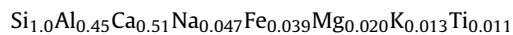
Coal fly ash is considered as pozzolans (substances containing silica and alumina). There are mainly two types of fly ash produced from coal combustion, types F and C. Type F is produced when anthracite, bituminous or sub-bituminous coal is burned and is low in lime (<7%) and contains more silica, alumina and iron oxide. Type C comes from lignite coal and contains more lime (15–30%).

Table 1 gives representative chemical composition data for coal fly ash and sheet glass powder that were used in the experiment. The loss on ignition of coal fly ash was about 5.50 wt.%. As shown in Fig. 1, the coal fly ash is composed primarily of glassy spheres that are relatively resistant to dissolution. In the laboratory the ashes were dried at 100 ± 5 °C for 24 h. The obtained material was homogenized by shaking and kept in polyethylene container. The sheet glass powder was made from sheet glass cullet which was discarded in everyday life and the powder was wet-milled by globe mill. The foaming agent used in our work was a compound of SDBS (sodium dodecyl benzene sulfonate) and glutin.

2.2. Methods of curing

The developed process for the production of material from CFA consists of two stages, making abode and sintering, respectively. Prior making abode, the dried ashes were homogenized by milling with sheet glass powder (~8 wt.%) as fluxing agent. About 30 wt.% sodium hydroxide solution (mass fraction: 10 wt.%) and a small amount of foam by shaking the 10 wt.% aqueous surfactant solution were added after mixing to form slurry. Shaped aggregates were obtained by pouring the slurry in the molds. For the sintering process, the specimens were then dried at 105 °C for 12 h and, following demoulding, were sintered in a muffle at 1050 °C for 2 h. The
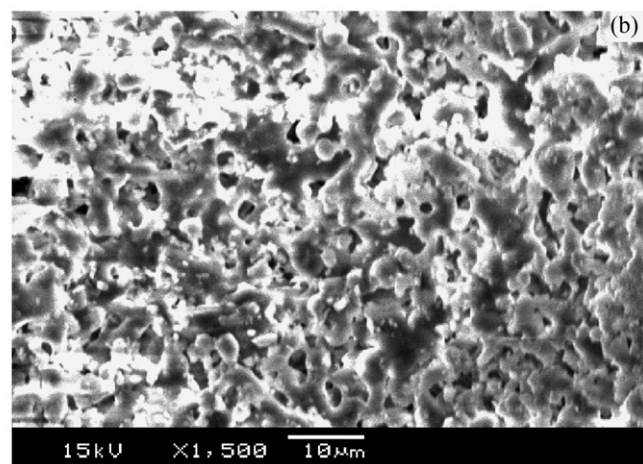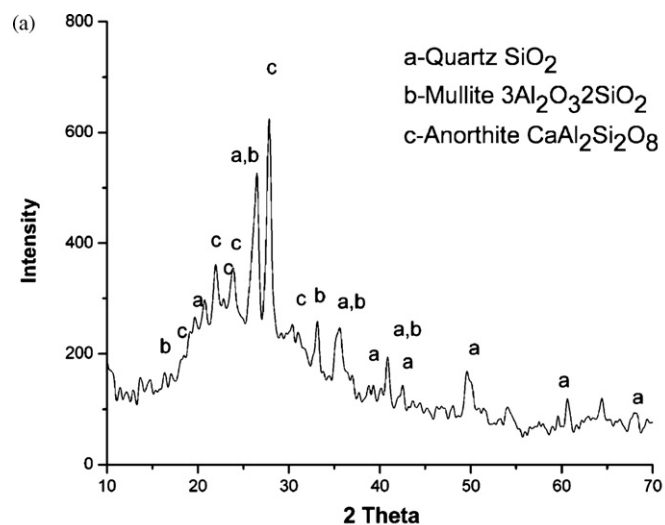
Fig. 2. XRD pattern and SEM micrograph of sintered sample.

samples were heated at a ramp rate of 2–3 °C/min. The muffle was then cooled at approximately 1.5 °C/min. As the silico-aluminates were produced, a strong and porous aggregate was formed.

2.3. Properties evaluated

The apparent density of sintered specimens was determined by the Archimedes method whereas water absorption was deter-

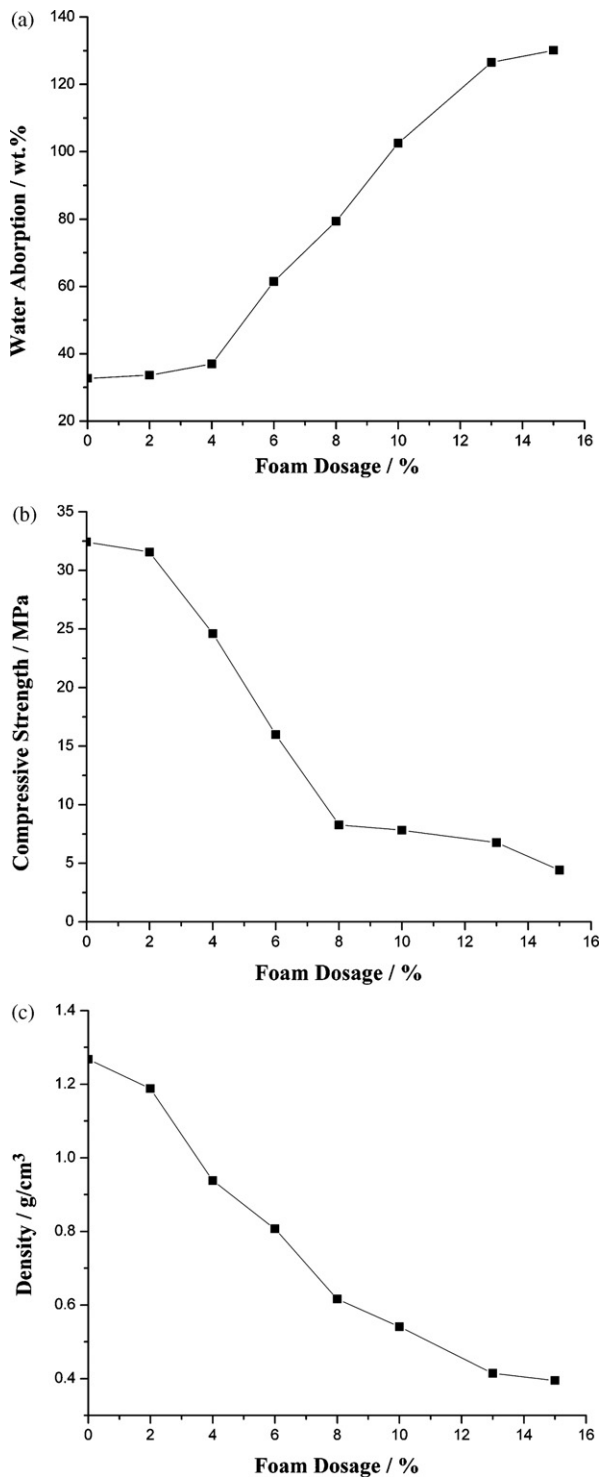**Fig. 3.** Digital photograph of a sample.

Fig. 4. Influence of foam dosage: (a) water absorption; (b) compressive strength; (c) density.

mined by the Chinese National Standard GB 13545-2003 [14]. An oven dried sample was immersed in water for 24 h and then the increased mass of saturated surface dry aggregate was measured. The water absorption using the below mentioned formula is expressed as increase in mass as a percentage of oven dried mass.
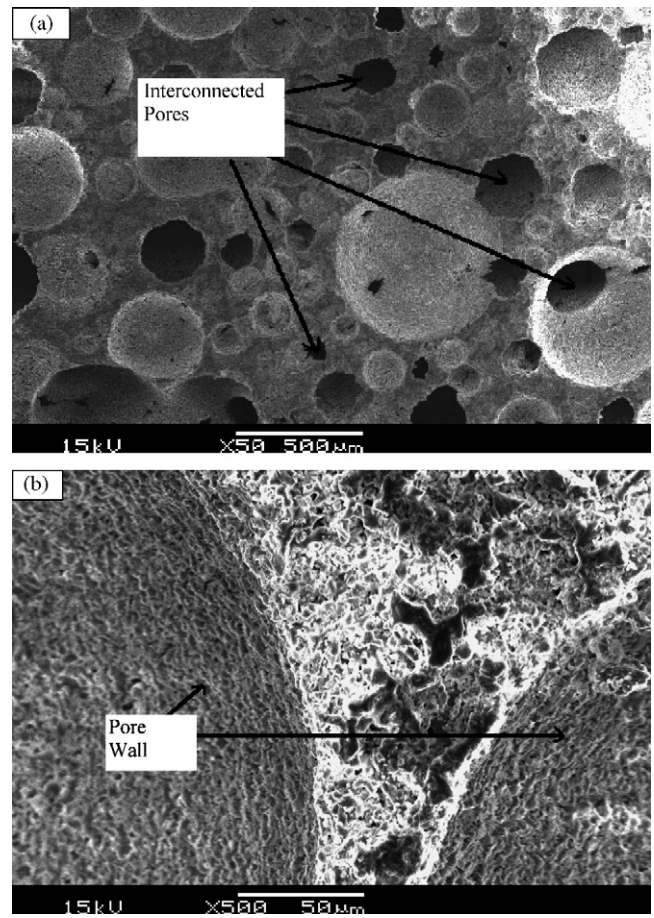
$$Water\ Absorption = \frac{W_2 - W_1}{W_1}$$

Fig. 5. SEM micrograph of a sample.

where W_1 and W_2 are the weight of the sample before and after absorbing water, respectively (in gram).

Fracture surfaces of sintered sample were examined by scanning electron microscopy (SEM, JEOL JSM-5600LV). Mechanical properties were measured on materials fired at their optimal sintering temperature. Compressive strength was also determined by the CNS GB 13545-2003 [14]. Crystalline phase evolutions of powders were analyzed by powder X-ray diffraction (XRD, Rigaku D/max 2400) using a X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.5406\ Å$) at a scanning rate of $0.02°/s$ in the 2θ range from $10°$ to $70°$.

3. Results and discussions

3.1. Mineralogical and micro-structural characteristics of fired samples

3.1.1. Crystalline phase analysis

XRD of the coal fly ash and coal fly ash + 10 wt.% glass powder sintered samples fired at 1050 °C are shown in Fig. 2a. This indicates the presence of quartz (SiO_2), mullite ($3Al_2O_3·2SiO_2$) and anorthite ($CaAl_2Si_2O_8$) in sintered samples. This results in mechanically stronger foam materials. More in particular, sintered sample contains a high content of polycrystalline phases; in this case, due to the high background noise, it is impossible to make a doubtless identification of any specific crystal structure.

3.1.2. Micro-structural analysis

SEM photograph, made on free surfaces of the fired sample, is reported in Fig. 2b. Sample contains polycrystalline grains and
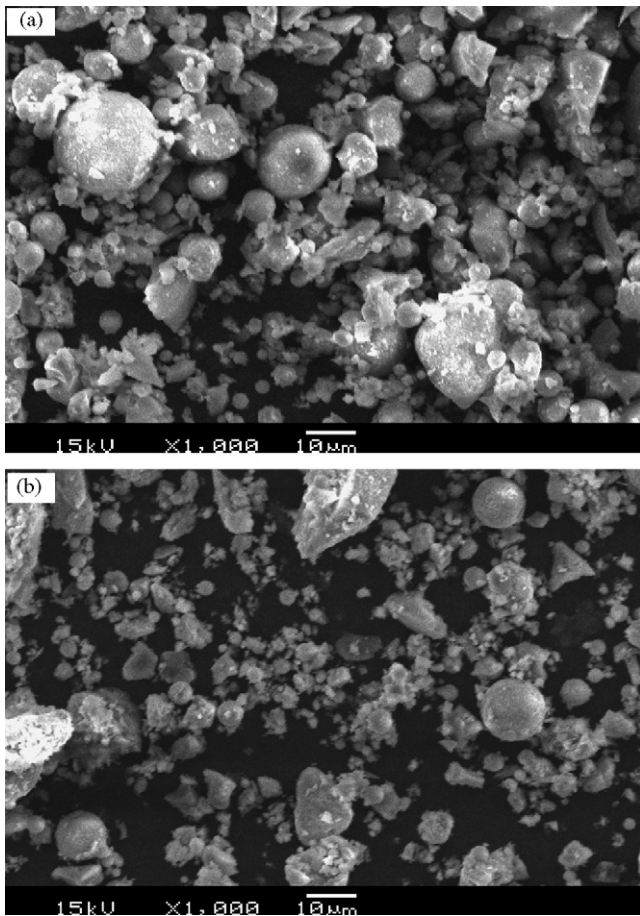
Fig. 6. SEM micrograph of CFA: (a) 24 h after alkali-activation; (b) 48 h after alkali-activation.

Fig. 7. XRD pattern of CFA: (a) original CFA; (b) alkali-activated CFA.

glassy phases. SEM micrograph shows that the vitreous phase is mainly concentrated on the surface of the fired specimens where they are not perfectly defined, being partially hidden by a thin layer of glass. A certain superficial porosity can be observed. All these microstructures are in agreement with water absorption data and XRD analysis. The presence of many elongated grains, probably due to well developed anorthite crystals, explains that anorthite crystals play important roles in the compressive strength of the foam.

3.2. Physical properties

The colour of the sample is brick red and there is a mass of open holes on the surface as shown in Fig. 3. The addition of 10 wt.% glass powder caused significant changes in the sintering behaviour of fly ash, with a reduction in the temperature (approximately 50 °C). As a result of adding glass powder, the apparent density is increased a little but the compressive strength is enhanced from 1.696 MPa to 6.76 MPa. Therefore, the compressive strength of the sample comes up to the standard MU5.0 [14].

The influence of foam dosage was studied at 1050 °C as shown in Fig. 4 and the ratio of the foam was not more than 13 wt.% because excessive foam dosage will lead to the combination of foam. With increasing of foam dosage, the water absorption is enhancive slowly before 4 wt.% and rapid after 4 wt.% as shown in Fig. 4a. When the addition amount of foam is less than 4 wt.%, the water absorption is low as the results of little interconnected pores. With the increasing volumes of foam, more and more interconnected pores which are benefit for flow of water are appeared. Nevertheless, the
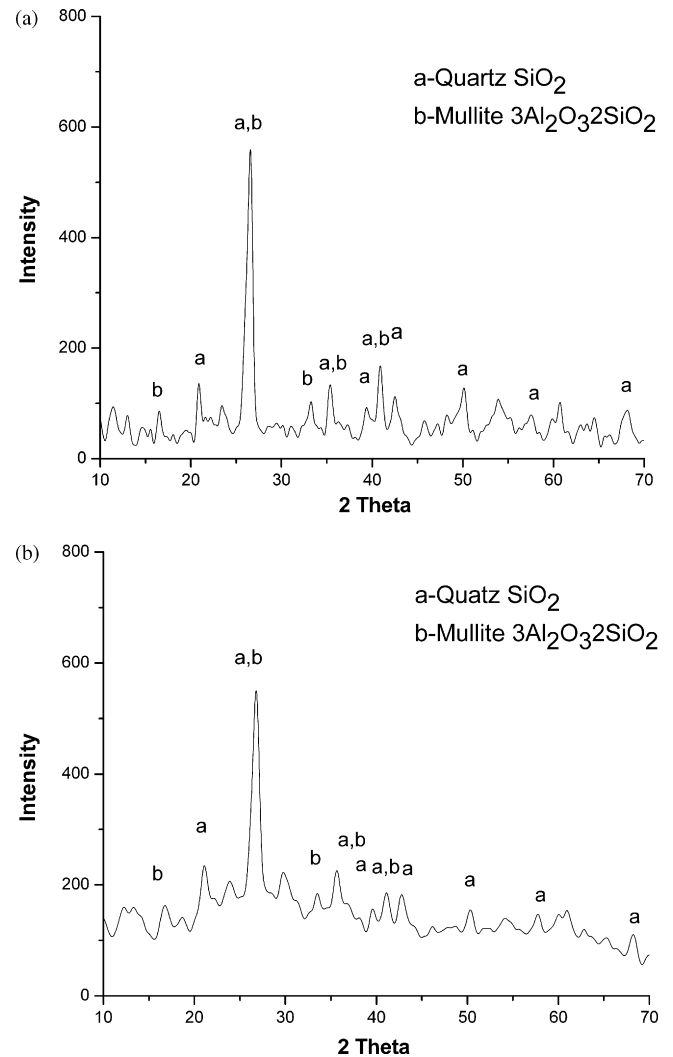
increase of water absorption could decrease compressive strength. Fig. 4b reveals the variation trend of compressive strength with the foam dosage. Obviously, the compressive strength is inversely proportional to the foam dosage. Furthermore, the influence of foam dosage on density was also investigated. Fig. 4c reveals that the density of the sample is reduced because of the increasing of the foam dosage. And the optimal addition of foam is 13 wt.%, leading to foams presenting water absorption, apparent density and compressive strength values of about 126.5%, 0.414 g/cm^3, 6.76 MPa, respectively.

From the experimentation above, we know that water absorption of sample lies on the quantity of interconnected pores. Some scanning electron micrographs were taken in order to prove the existence of interconnected pores. A mass of interconnected pores is discovered as shown in Fig. 5a and the pore wall is not smooth as shown in Fig. 5b. In other words, the sample has high specific surface area so that it can adsorb huge amounts of water. So we can conclude that the process of absorbing water includes two steps: (1) diffusion of water along the interconnected pore; (2) adsorption of water on the surface of the pore by physical adsorption. Because of the type of adsorption, the water adsorbed can be desorbed easily. Thus, this foam material can be applied to permeable or preserve moisture purpose.

3.3. Alkali-activation on CFA

Coal fly ash is appeared as fine particles, mostly of a spherical shape and of about 10 μm in diameter as shown in Fig. 1. The particle of fly ash is compact in configuration and consistent in surface as the CFA is of aluminum-silicate vitreous structure with high degree of polymerization. As a result, its absorptive capacity of water is low, and it is difficult to dissolve in solvents. The structure can be destroyed through adding alkali and polycondensation is taken place [10]. As shown in Fig. 6, the quantity of spherical particles of the CFA which was alkali-activated for 24 h is less than the one for 48 h. Comparing the XRD pattern of alkali-activated ash with original ash (Fig. 7), the amorphous equivalent of the major crystalline framework silico-aluminates are produced due to the protuberant peak in the 2θ range from 15° to 40°. Not only the SEM micrograph but also the XRD pattern can prove the structure of the original CFA is destroyed and the pozzolanic reaction would be taken place easily.

Activation of CFA is successful by adding alkali and polymerization can be schematized as follows. It may be considered as the result of the polycondensation of still hypothetical monomers (silico-aluminates). It has been assumed that the syntheses are carried out through oligomers (dimer, trimer) which provide the actual unit structures of the three dimensional macromolecular edifice. For the reasons above, the primal strength of the abode is obtained, which makes provision for the sintering process.

4. Conclusions

Our studies revealed that coal fly ash from thermal power plant was successfully used to manufacture water-absorbing material by adding about 10 wt.% additives and 13 wt.% foam at 1050 °C for 2 h after alkali-activation. And anorthite crystals, elongated grains, play important roles in the compressive strength of the foam. Furthermore, the principle of alkali-activation and the mechanism of water absorption were discussed. The water-absorbing material has good physical properties including water absorption, density and compressive strength. From the practical point view, such material may be used in the field as an engineering material, a waste water filter, a catalyst carrier, permeable and preserve moisture purpose.

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