THE PACKAGE TYPE INFLUENCE ON THE PERFORMANCE OF THE CO_2 CAPTURE PROCESS BY CHEMICAL ABSORPTION

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The main objective of this article is to carry out a study of modelling-simulation of CO_2 absorption columns by using 4 types of fillings, among which: Raschig ceramic rings, Raschig metallic rings, Pall plastic rings and Berl rings. The dimension of the absorption column was adjusted according to the L/G ratio, and its influence on the CO_2 capture process efficiency was examined. The increase of the CO_2 capture process efficiency requires the increase of the absorption column height, irrespective of the type of filling analysed, while the diameter of the column is maintained constant.

Keywords: CO_2 capture, post-combustion, amine and blended amines

1. Introduction

In an economy which tends to become global, the mitigation of greenhouse gas emissions (GHG) has become a worldwide priority. An important source of GHG is represented by the energy sector which releases about 41% of the total of emissions in the atmosphere, out of which: 83% CO_2, 8% CH_4; 8%N_2O; 1% freons [1].

According to a report drawn up in 2014 by the World Coal Association [2], approximately 85% of the necessary primary energy used worldwide is produced by fossil fuels (coal, petrol and natural gas).

The threat of climate change as a result of the increase of GHG concentration in the atmosphere over the last decades has led to the need to implement measures for the development of equipment and technologies for greenhouse gas mitigation. At present, the main technologies of CO_2 capture from the flue gases are classified in accordance with the position of the latter's

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integration in power plants: a) post-combustion; b) pre-combustion; and c) oxy-combustion (Fig. 1) [3].

The most developed process for CO_2 capture is by chemical absorption, which has the advantage that it can be integrated both in the existing power plants and in the new ones. In the processes based on chemical absorption, the most frequent solvents are those based on amines (primary, tertiary, and blended amines).

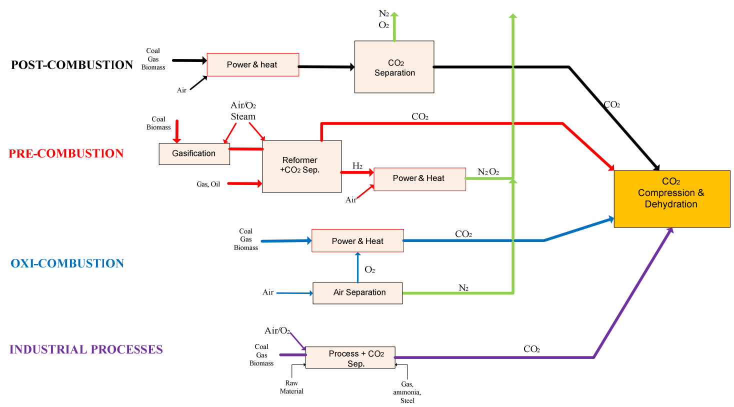


Fig. 1. The CO_2 capture processes [4]

The CO_2 capture by chemical absorption consists in separating CO_2 from flue gases by using a chemical solvent. International research has shown that the chemical solvents to be used had to fulfil the following requirements: reduced regeneration energy consumption, low degradation speed, high CO_2 absorption capacity, low corrosion degree, and low acquisition costs [5].

Monoethanolamine is the chemical solvent which is the most frequently used in the processes of chemical absorption. Apart from MEA, in the family of amines there are also secondary amines (DEA) and tertiary amines (TEA, MDEA). The chemical absorption processes are applicable for gas fluxes which work at high or low pressures, but have a low partial CO_2 pressure (low concentration), because they are based on the reversible nature of chemical reactions which are affected by the temperature and the pressure variation in the absorption-desorption columns [6]. The chemical absorption process has an absorption unit and a desorption one (Fig. 2) [7, 8, 9, 10, 11].

In order to make the mass transfer in the absorption unit as efficient as possible, various fillings are used, such as: Raschig rings, Pall rings, Intalox metallic rings, Berl SEI etc. The fillings are characterized by various specific contact surfaces and various P-T parameters [12].

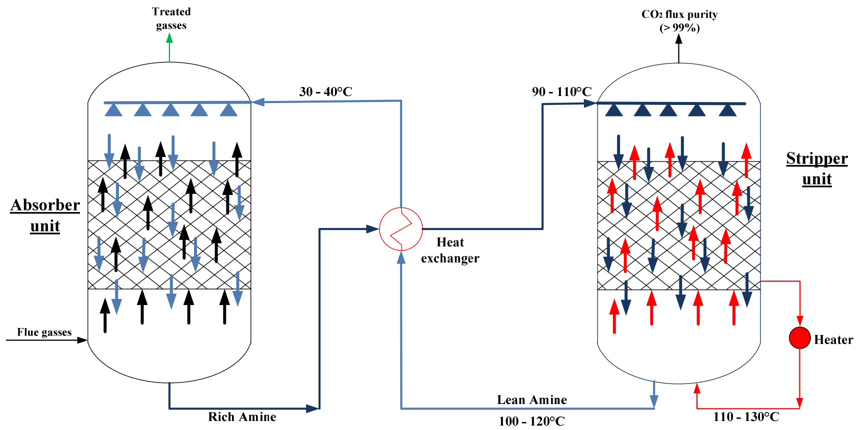


Fig. 2. CO_2 capture by chemical absorption process

The main purpose of the article is to validate the results obtained by means of a mathematical model through the simulation of the process in Aspen Hysys. The results obtained in the mathematical model on different types of fillings (Raschig ceramic and metallic rings, and Pall rings), were compared with the ones obtained by the stimulation of the process in Aspen Hysys. In this study the following amines (cases) were used: MEA, DEA, and TEA.

2. The Mathematical Model for the dimensioning of the absorption unit

The mathematical model was designed in order to establish the dimension of the absorption unit in the CFBC pilot installation (circulating fluidized bed combustion), an installation which is to be found in the Renewable Energy Laboratory of the Faculty of Power Engineering in "Politehnica" University of Bucharest. This installation has the role of separating the CO_2 in the flue gases by using the method of post-combustion by chemical absorption. Fig. 3 shows the process of circulating fluidized bed combustion) [13].

The composition of flue gases was calculated having in mind the elementary composition of the lignite extracted from Valea Jiului (Romania). Table 1 shows the composition of flue gases starting from the elementary composition of lignite used and taking into consideration the air excess in flue gases $\left(\alpha_{vg} = 1.6\right)$.

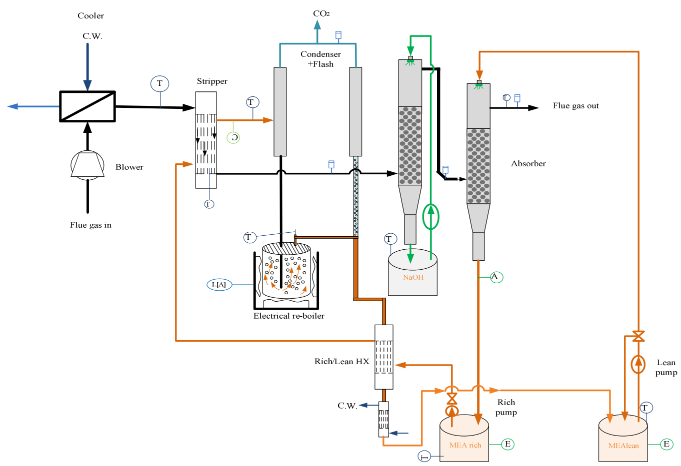


Fig. 3. CFBC pilot instalation for CO_2 capturing

Table 1

Analysis of the lignite used in the combustion process

Elementary composition of lignite							
C^i, [%]	H^i, [%]	S^i, [%]	O^i, [%]	N^i, [%]	W^i, [%]	A^i, [%]	LHV*, [kJ/kg]
24.27	1.4	1.3	1.8	0.86	31	39.37	8935.54

Flue gases composition		
	Dry condition	**Wet condition**
CO_2, [%]	11.461	10.081
SO_2, [%]	0.23	0.202
N_2, [%]	80.304	70.629
O_2, [%]	8.005	7.041
H_2O, [%]	-	12.048

* LHV – low heating value of lignite

In order to determine the molar flux of the flue gases at the absorption unit inlet and outlet the ideal gas law was used:

$$pV = nRT \tag{1}$$

In order to determine the molar balance for the absorption unit the flue gases mol number was calculated by means of the following equation.

$$n_{fg} = p_{fg} \cdot \frac{V_{fg}}{R_{fg} \cdot T_{fg}} \tag{2}$$

Where: V_{fg} – the flue gases volume flow, in l/min

$$V_{fg} = (1 - q_m) \cdot V_{fg_w} \cdot B_c \cdot \frac{T_{fg}}{273{,}15 \cdot K} \tag{3}$$

R_{fg} – the constant of perfect gas, $R_{fg} = 0{,}08205 \cdot \frac{l \cdot atm}{mol \cdot K}$; p_{fg} – the pressure of the flue gases in the absorption column, in atm; T_{fg} – the temperature of flue gases in the absorption column, in K; B_c – the fuel flow, in kg/h.

The number of CO_2 mols in the flue gases was calculated by means of the following equation.

$$n_{CO_2} = C_{CO_{2w}} \cdot n_{fg} \quad (4)$$

Where: $C_{CO_{2w}}$ – the CO_2 concentration in the wet flue gases, in %.

The number of mols in other gases than CO_2, (n_{og}), in the flue gases were calculated as the difference between the number of flue gases and the number of CO_2 mols. The concentration of CO_2 in the flue gases at the absorption column outlet was calculated by using the following equation:

$$C_{CO_2} = C_{CO_{2w}} - \varepsilon_{CO_2} \cdot C_{CO_{2w}} \quad (5)$$

Where: ε_{CO_2} – the CO_2 capture process efficiency.

The number of CO_2 mols retained in the absorption column was calculated by means of the following equation:

$$n_{CO_{2r}} = n_{CO_2} - \left(n_{fg_e} - n_{og}\right) \quad (6)$$

Where: n_{fg_e} – the number of flue gases mols at the bottom of the absorption column.

$$n_{fg_e} = \frac{n_{og}}{1 - C_{CO_2}} \quad (7)$$

In order to decide on the dimension of the absorption unit, several types of fillings are used; their characteristics are shown in Table 2.

Table 2

Package material data used for testing the absorption process (packed tower absorber), [15]

Package type	Size (mm)	Area (m^2/m^3)	Fp (ft^2/ft^3)	Void fraction (%)
Raschig rings ceramic	12.5	374	580	65
	25	185	155	70
	37.5	138	95	72
	50	92	65	75
Raschig rings (steel)	12.5	420	300	84
	25	207	115	92
	50	102	57	92
Pall rings plastic	16	341	97	87
	25	207	52	90
	50	102	25	92
Berl saddle ceramic	6	899	900	63
	12.5	508	240	64
	25	259	110	68
	50	105	45	75

When choosing the dimension of the absorption unit, a degree of flooding of 0.75 is taken in consideration [14].

The operational line of the absorption column was determined for various types of amines. The characteristics of the amines used and of the chemical solvents analysed are shown in table 3. For each of the cases which were analysed, we calculated the CO_2 content in the inert gases at the bottom and the top of the absorption column.

Table 3

Concentration of CO_2 in Amine at the top and the bottom of the absorption unit

Type of Amine	Mass Concentration, (%)	Molar mass of the chemical solvent (kg/kmol)	CO_2 content at the bottom of the absorption column (kmol/kmol)	CO_2 content at the top of the absorption column, (kmol/kmol)
MEA	20	26.6	0.433	0.389
	30	30.9	0.289	0.26
	40	35.2	0.217	0.195
DEA	25	39.8	0.433	0.389
	30	44.14	0.361	0.325
	40	52.86	0.271	0.243
TEA	20	44.24	0.619	0.556
	30	57.36	0.413	0.371
	40	70.48	0.309	0.278

Considering the CO_2 concentration in flue gases to be $y_b = 0.101\ kmol/kmol$, and $y_t = 0.015\ kmol/kmol$, the operational lines of the absorption column were established for every type of amine and concentration analysed in table 3. For the operational lines we took into consideration the hypothesis according to which the CO_2 concentration in the chemical solvent at the absorption column inlet is 0 kmol/kmol.

In the model we designed it was considered that, at the absorption unit, the solvent is always pure, $x_{top} = 0\frac{kmol}{kmol}$.

The CO_2 concentration in the solvent at the absorption unit is determined from the balance equation by knowing the values for the concentration of CO_2 in the flue gases at the absorber inlet and outlet, respectively, γ_{bottom}, y_{top}.

$$\gamma_{bottom} = \frac{n_{CO_2}^{bottom}}{n_{fg}} \tag{8}$$

$$\gamma_{top} = \frac{n_{CO_2}^{bottom} - n_{CO_2}^{abs}}{n_{fg}} \tag{9}$$

The mass balance equation for the absorption unit can be written as follows:

$$L_m \cdot (x_{bottom} - x_{top}) = G_m \cdot (\gamma_{bottom} - \gamma_{top}) \tag{10}$$

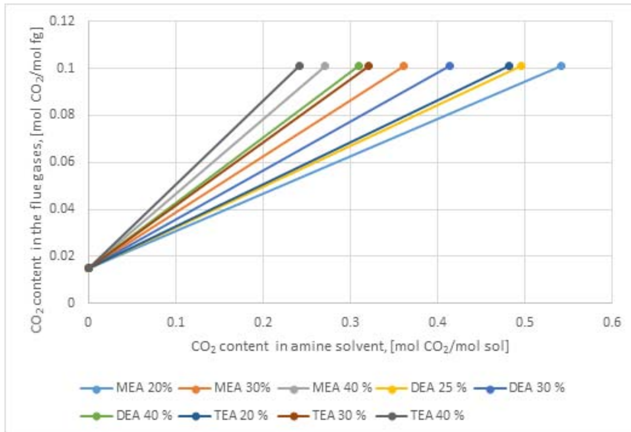


Fig. 4. Operational line for absorber column according to different solvents

For the absorption/desorption units which belong to the CO_2 capture processes, the ratio $\left(\frac{L_m}{G_m}\right)_{min}$ is considered to be 0.7. The ratio $\left(\frac{L_m}{G_m}\right)_{op}$ belongs to the interval (1.1-1.5). In this study we considered that $\left(\frac{L_m}{G_m}\right)_{op} = 1.1 \cdot \left(\frac{L_m}{G_m}\right)_{min}$ [15].

In order to determine the diameter of the absorption unit (D_{abs}) equation (11) was used.

$$D_{abs} = \left(A_{abs} \cdot \frac{4}{\pi}\right)^{0.5} \tag{11}$$

where: A_{abs} – represents the absorber section in m^2.

The absorber section was calculated by using the equation (12); the latter is dependent on the specific flue gases flow in the filling (G_{sp}).

$$A_{abs} = \frac{G_b}{G_{sp}} \tag{12}$$

$$G_{sp} = \left(\frac{F_d \cdot \rho_{fg} \cdot g}{\mu^{0.2} \cdot Fr \cdot \psi}\right)^{0.5} \tag{13}$$

where: F_d –filling factor which is calculated with the help of nomograms [1] according to the loss of pressure in the filling Δp and of the amine-based solution density; ρ_{fg}– represents the density of flue gases in kg/m^3; g – gravity acceleration, in m/s^2; μ –liquid viscosity, in cP; Fr – filling specific factor, in m^2/m^3; ψ – ratio between water and monoethanolamine densities at the process pressure and temperature.

The height of filling H_{abs} was calculated by using the equations (14-16).

$$H_{abs} = H_{tg} \cdot N_{tG} \quad (14)$$

$$H_{tg} = \frac{G_{My}}{FG \cdot a} \quad (15)$$

$$N_{tG} = \int_{y_0}^{y_n} interp(vs, y, fa, \Theta) d\Theta \quad (16)$$

where: G_{My} – represents the specific molar solution flow taking into consideration the surface of the filling, in mol/(m^2s).

For every case analysed we calculated the height and the diameter of the filling, and the results are shown in Table 4.

Table 4

Geometric characteristics of absorber column according to package type

Package type	Diameter ring size [mm]	Absorber diameter [mm]	Absorber height [m]	ΔP_0 [Pa]
Raschig rings ceramic	12.5	129.16	4.9	1 962.94
	25	92.8	3.58	1 421.62
	37.5	82.17	3.19	1 261.33
	50	74.73	2.93	1 154.13
Raschig rings (steel)	12.5	109.5	4.18	1 667.82
	25	86.19	3.34	1 322.97
	50	72.3	2.84	1 117.26
Pall rings plastic	16	82.59	3.21	1 269.23
	25	70.68	2.78	1 092.54
	50	58.85	2.34	913.1
Berl saddle ceramic	6	144.1	5.45	2 188.72
	12.5	103.6	3.97	1 581.65
	25	85.23	3.3	1 306.47
	50	68.17	2.68	1 053.24

Mention must be made of the fact that the results refer only to the usage of MEA in a mass concentration of 30% and for a CO_2 capture efficiency of 85%. The height of the absorption column varied between 2.3 and 5.4 m; the higher the void fraction of the filling, the higher the height. Accordingly, we calculated the diameter of the absorption column starting from the inner diameter of the rings used. The absorption column diameter is inversely proportional with the diameter of filling rings, and they are bigger in the case of Raschig ceramic rings, and Berl rings, respectively. The pressure losses are strongly dependent on the ring diameters; that is why the highest values were frequent in the case of Berl ceramic rings, for 6 mm diameters. Pressure losses represent a factor in the choice of ring types used in the absorption column as a result of the costs induced during functioning.

3. The Simulation of CO_2 Capture processes in ASPEN Hysys

Computer simulation represents a process in the study of real systems, in order to observe the latter's behaviour in a diverse range of conditions. The role of process simulation is to improve the understanding of the process and to make the best decisions.

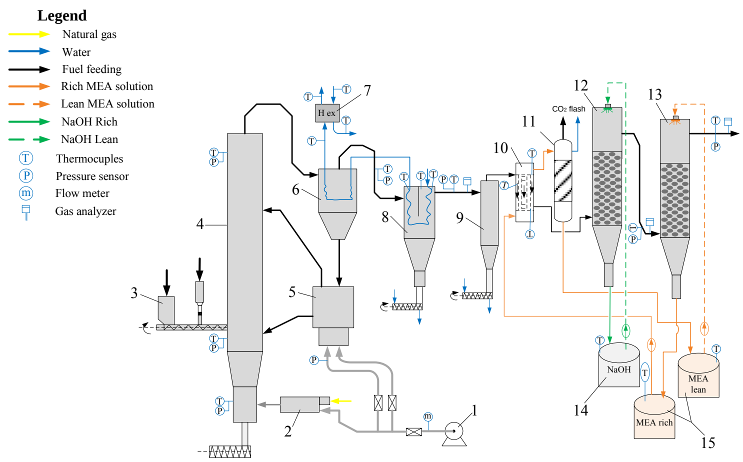


Fig. 5. Circulating fluidized bed combustion with CO_2 post-combustion [16]

Legend

1. Blower, 2. Pre-firing using natural gas, 3. Fuel feeding system, 4. Combustion chamber, 5. Recirculation system, 6. Cyclone, 7. H_2O-H_2O plate heat exchanger, 8. Convective heat exchanger, 9. Cyclone, 10. Economizer, 11. CO_2 desorption column; 12. Desulphurization unit, 13. CO_2 absorption column, 14. NaOH solution reservoir, 15. MEA lean and reach solution reservoirs

The case study was carried out for the CFBC installation (Fig. 5) existing in the Laboratory of Renewable Energy Sources POLITEHNICA of Bucharest. The separation of CO_2 in the flue gases was done by means of chemical absorption, by using the amine as a solvent. In this study various types of amines were analysed (MEA, DEA,TEA), at concentrations which varied between 20-40%, as well as at different L/G ratios.

The simulation and the modelling of CO_2 capture processes in energy conversion systems was carried out with the help of the ASPEN Hysys simulation program. Thus, in this article, for the simulation of the CO_2 capture process by means of post-combustion technology, we used the thermodynamic model Kent Eisenberg [17].

Table 5 shows the most important parameters of the technological flux used in the CO_2 capture process. In the simulations we carried out more types of amines were analysed, as shown in table 3. Fig. 6 shows the results obtained as a result of the simulations carried out for the three types of amines used in accordance with the concentration of 30% wt.

Thus, we can notice the influence of the L/G ratio on the energy consumption and on the CO_2 capture efficiency (Fig. 6). It was found that, when the L/G ratio increased (with a constant flue gases mass flow), the efficiency of the CO_2 capture process increased.

Table 5

Process parameters for CO_2 chemical absorption

Flue gases	Mass Flow [kg/h]		1.5
	Temperature [°C]		40
	Pressure [atm]		1.1
	Gas Composition [% vol]	CO_2	12.03
		N_2	74.45
		O_2	5.5
		H_2O	8.02
Absorption Column	Solvent Inlet Temperature [°C]		50
	Solvent Inlet Pressure [atm]		1.22
	Solvent Inlet Concentration [wt. %]		20–40 %

Nevertheless, for every L/G ratio there is an optimal value which is mainly given by the energy consumption necessary for solvent regeneration. Thus, a higher value of the solvent flow requires a higher consumption of regeneration thermal energy.

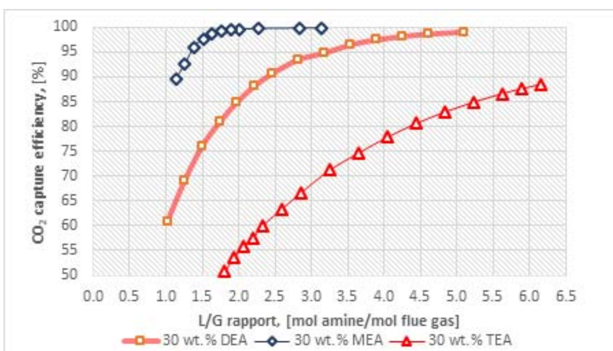
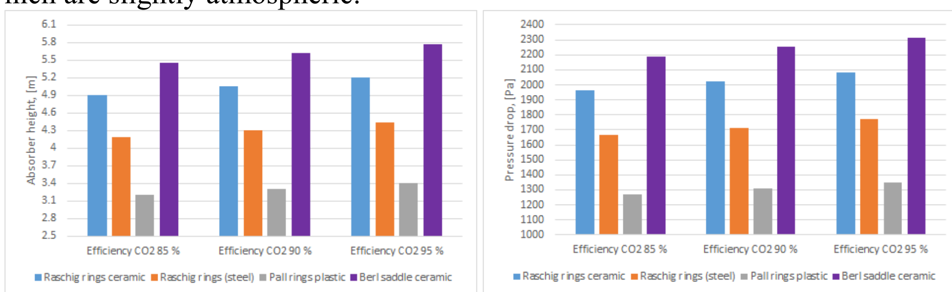


Fig. 6. The influence of L/G ratio on the CO2 capture efficiency

Fig. 7 shows the variation of the height of the CO_2 absorption column (a), and of the pressure losses in the absorption column (b), respectively, according to the efficiency of the CO_2 capture process, and the type of filling analysed, respectively. It was found that the higher the efficiency of the CO_2 capture process, the higher the absorption column, while the absorption column diameter was almost constant (like the one shown in table 4). In addition, it was noticed that the pressure drop raised when the efficiency of the CO_2 capture process was increased; that is the reason why the absorption columns operate at pressures which are slightly atmospheric.



a) b)

Fig. 7 a) the height of the absorption column in accordance with the efficiency of the CO_2 capture process and of the filling type; b) the pressure loss in the absorption column in accordance with the efficiency of the CO_2 capture process and of the filling type

6. Conclusions

In this article four types of fillings (Raschig ceramic rings; Raschig metallic rings, Pall plastic rings and Berl rings) were analysed with a view of finding out what influence they have on constructive data: diameter and height, pressure losses. The dimension of the absorption column was established for the optimal L/G ratio identified (1.5 mol amine/mol fg pentru 30 wt.% MEA; 2.5 mol amine/mol fg pentru 30 wt.% DEA; and 4 mol amine/mol fg pentru 30 wt.% TEA) in the Aspen Hysys simulation processes corresponding to the CO_2 capture efficiencies of 85%, 90% and 95%, respectively.

The height of the absorption column varied between 2.34 m of Pall rings for a CO_2 capture process efficiency and 5.77 m for Berl rings corresponding to a CO_2 capture efficiency of 95%. In addition, it was noticed that the absorption column diameter did not change as a result of the variation of the efficiency of the CO_2 capture process or as a result of the modification of the filling type. Pressure losses increased as a result of the increase of the absorption column height. In practice, pressure losses represent a criterion for the selection of the filling type with a view of optimizing the efficiency of the CO_2 capture process, and of the energy consumption, respectively.

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