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Research Article

VACUUM, REDUCTION, VOLATILIZATION AND RECOVERY GERMANIUM FROM LOW-GRADE GERMANIUM CONCENTRATE

PU Shi-kun[1,2] , LAN Yao-zhong[1,3] , YANG Zai-lei[2], XIE Gao[2], WU Wangchang[2], LI Xuan[2]

[1]Shanghai University School of Materials Science and Engineering, Shanghai 200072, China;
[2]Yunnan Lincang Xin Yuan Germanium Co. Ltd., Lincang, Yunnan 677000, China;
[3]Research Institute of Mineral Development and Recycling Economy, Yunnan University, Kunming 650091, China.
*Corresponding Author: 15198838636@163.com
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Abstract

This paper advocates the process for vacuum ,reduction, volatization, concentration and recovery of Germanium from low-grade Germanium concentrate, and explores the five factors affecting the Germanium volatilization rate through testings: the roast temperature, the dosage of Sodium Hypophosphite, vacuity, volatilization time, and the thickness of the material layer. Optimum process conditions have been identified for volatilization and concentration of reduction of Germanium from low-grade Germanium: the roast temperature, 1000℃; the dosage of sodium hypophosphite, 7.5%; the vacuity, 500 Pa; the flow rate of carrier gas, 200L/h; the volatilization time, 90 min; and the thickness of the material layer, 30 mm. Given such conditions, the volatilization rate can reach 94.76 %~98.35%; the germanium content in volatile products, 12.68%~46.71%; and the concentration ratio, 27~36 times. Compared with the wet-process hydrochloric acid leaching of manganese dioxide by oxidation distillation, the process features higher germanium recovery rate, lower production costs, and less equipment investment. Exempt from discharge and disposal of waste water, gas and residue slag in large quantities, the process can be applied to completely solve the environmental problems caused by the wet process.

Introduction

The application of Germanium (Ge) is increasingly expanding in such fieldsas solar photovoltaic battery [1], optical fiber communication technology[2], infrared optical material[3] and organic health food[4], and PET catalyst. In recent years, the prices of Germanium materials are in the rise.

Germanium is mostly extracted from Ge - containing lignite smoke [5-7] and ash[8-12] by pyrometallurgical concentration, and from the lead and zinc smelting process [13-17]. Besides, Germanium can be recovered from the Germanium material waste produced during the processing and use, or from the residue slag on various lead, zinc, copper and iron smelting [18-21].

At present, more than half of high purity Ge concentrates extracted from the lignite, although in recent years the domestic and foreign research institutions have done a lot of research and have made remarkable technical innovation for some equipment involving the Ge extracting process. The current Ge recovery process, from lignite by pyrometallurgical concentration, is not time-consuming but also with relatively low Ge receevery rate (approximately 60-75 %) and low Ge concentration (merely 35-50 times in general). Therefore, with the decreasing Ge content in lignite, the germanium concentrate also gets degraded. In particular, as the Ge recovery rate is considered as a focus, Ge content in the Ge concentrate will be less.

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This brings a lot of problems for the subsequent recovery of germanium with largely increased lime consumption and application of additional equipment for the purpose of Ge extraction by chlorination distillation from industrial hydrochloric acid, manganese dioxide and neutralization distillation residual liquid.

There is a conventional and commonly applied process known as the Ge leaching concentration wet process, such as hydrochloric acid (oxidized) leaching, sulfuric acid (oxidized) leaching, sulfuric acid (fluoridized) leaching, direct sulfuric or hydrochloric acid leaching, leaching from sodium hydroxide or chloride calcinations, direct leaching from solution of sodium hydroxide, and roasting with soda, chlorination roasting. But, with these processes, first of all it is difficult to exceed the Ge leaching rate of 85 %; second, in case of uneasy Ge recovery from the leaching solution, an inexpensive and effective extracting agent for the alternative solution extracting process would be hardly available; third, both the leaching and extracting processes are long and hard to control with very high cost; and fourth, it is costly to dispose the waste solution from the leaching and extracting processes. Thus, it is difficult to apply the aforesaid processes and solve the problem of Ge recovery from lowgrade Ge-containing lignite concentrate.

# 1. Experiment

1.1 The raw material

The test material comes from the low grade germanium concentrate produced by the pyrometal lurgical smelting factory of Yunnan Lincang Xin Yuan Germanium Co. Ltd. The main chemical compositions (%)include Ge, 1.01; H_2O, 1.62; SiO_2,41.57; Al_2O_3,2.34; Fe_2O_3,6.74; CaO, 3.21; SO_2,2.05；K_2O, 3.54; MgO, 1.26; As_2O_3,1.10 ;ZnO, 3.97;PbO, 1.42; Sb_2O_3 , 1.26.

1.2 Process principle

The moisture, carbon, coal tar, germanium monoxide (710 ℃), arsenic trioxide ((As_2O_3) and other test materials are easily volatile substances at low temperatures. These compositions can be removed for periodical Ge volatilization and concentration at different temperatures. At 600 ℃, by oxidation and volatilization, the coal tar incompletely burnt and

moisture, which are easily volatile at a low temperature, can be removed; and then as the temperature is heated up to 1100 ℃,Ge is volatilized and the volatile substances are collected periodically at different temperatures to minimize other such substances into the Ge volatile substances in periods and increase greatly the Ge content in the volatile substances. As moisture, ferric oxide, coal tar, carbon, a germanium oxide, and the like are strong microwave absorbing materials, the microwave heating approach can be adopted for volatilization. Microwave energy is a clean energy and can also accelerate the heating process for Ge volatilization.

Gein low grade Ge concentrate exists mainly in the form of GeO_2 of Ge(Ⅳ) compounds, followed by Ge(Ⅱ) compounds of GeO, and for the least, in the forms of GeS_2 or GeS. The melting point of GeO_2 is 1125℃, with no volatilization at such a high temperature. But GeO is of prominent volatility at 700 ℃. In a reducing atmosphere GeO_2 appears remarkably volatile at 750℃ or greater because GeO_2 is reduced to GeO. Through isolation from the air, after GeO_2 is reduced to GeO for volatilization by addition of Sodium Hypophosphite to Ge concentrate. Then nitrogen gas is piped as a carrier gas into the process for timely diversion of Germanium Monoxide to a dust collection system in reaction. As a result, the vapor pressure of Germanium Monoxide can be largely reduced in the reaction gas phase for better Ge volatilization from the Ge concentrate. Here is the chemical reaction equation:

$$NaH_2PO_2.H_2O + 2GeO_2 = 2GeO + NaH_2PO_4 + H_2O$$
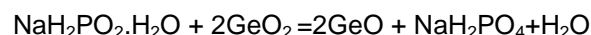
1.3 Test equipment
The microwave heating vacuum purification

system is designed by the researcher and faburicated by Tangshan Nayuan Microwave Thermal Instrument Manufacturing Co., Ltd.. It measures 100*65*75cm, at a voltage of 220V, a power of 4KW+2KW, and a microwave frequency of 2450 MHz. The pure microwave heating mode and the traditional electric heating mode are adjustable, at a temperature control precision of ±1/±2℃. The maximum heating temperature is 1500 ℃and the main heating zone size is Ø160*100mm with water-cooling and air-cooling, structures as shown in Figure 1.
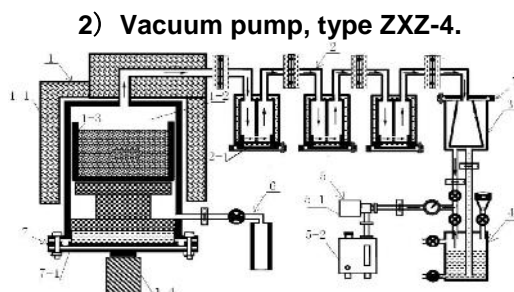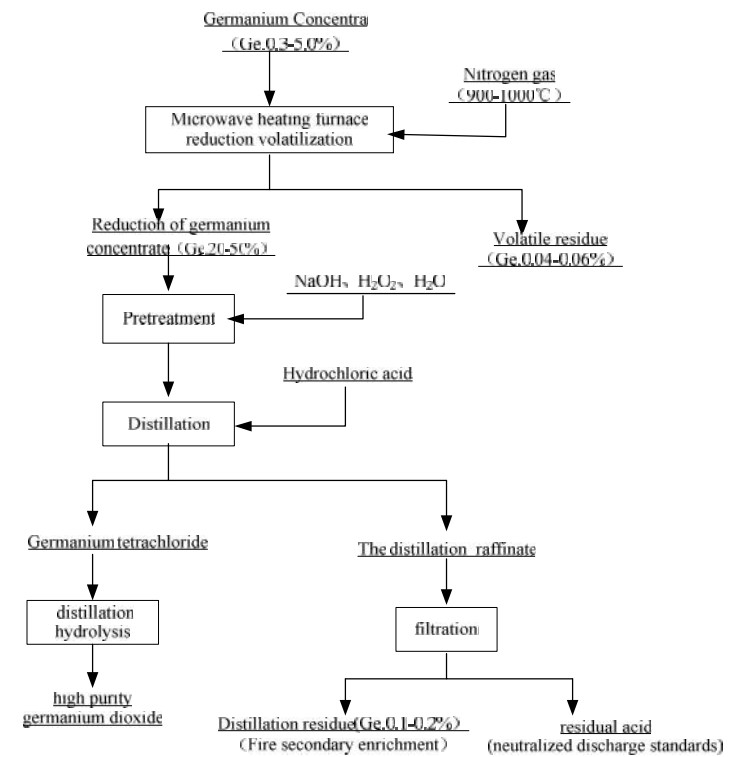
2）**Vacuum pump, type ZXZ-4.**

Figure 1 Testing device for Ge vacuum volatilization and concentration (microwave heating vacuum purification system)

1.4 Process flow diagram and test procedures

The germanium volatilization process flow diagram as shown in figure 2:

Figure 2 The process flow diagram of high purity Germanium Dioxide preparing by microwave heating vacuum eduction, volatilization and concentration

1. Check for tightness of the test equipment and the vacuum degree less than 100 Pa ;
2. Weigh a certain amount of low grade germanium concentrate in the crucible, add - 125 um Sodium Hypophosphite powder in proportion, mix evenly and place the crucible onto the heating section of the microwave heating vacuum volatilization furnace ;
3. Switch on the microwave heating vacuum volatilization furnace, at the rate of 50~60℃ per minute, heat up to the required temperature for the test, and record the test process in detail ;
4. After a certain duration of reaction at constant temperatures, stop the heating process, cool to the ambient temperature, open the settling chamber and bag filter for collection of volatiles, record the weight of the volatiles, and take some volatile samples for laboratory determination of the chemical compositions of the volatiles ;
5. Take out the volatile residue for observation of the residue shapes, weigh the residue from the crucible, and take some samples for laboratory determination of the chemical compositions of Ge and other elements ;
6. Calculate the Ge volatilization rate and concentration ratio based on the Ge content in volatiles and volatile residue.

Results and Discussion

2.1 The effect of roasting temperatures on Ge concentrate roast reduction Ge concentrate and the Ge volatilization rate

The regular consumption of Sodium Hypophosphite is 7.5 %; vacuity, 3000 Pa; carrier gas flow, 400 L/h; material thickness, 30mm; roasting and volatilizing time, 90 minutes. The microwave heating process is adopted, the roasting and volatilization temperatures changed for tests in line with the process steps. The effect of roasting temperatures on for the Ge concentrate and the Ge volatilization rate is shown in figure 3.
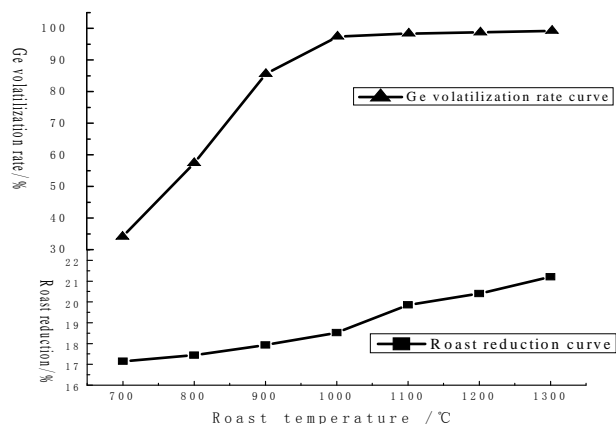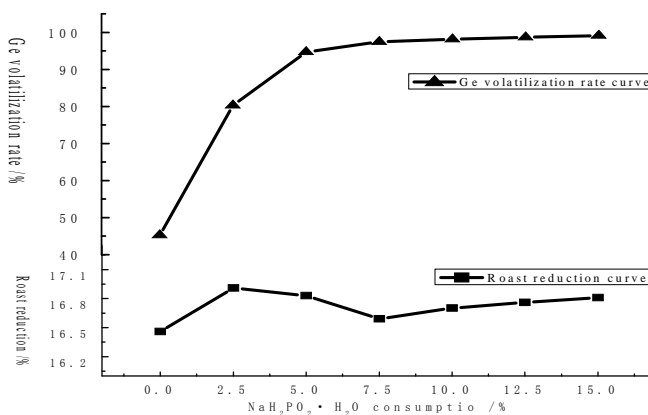
Figure 3 Effect of roast temperature on Ge concentrate roast reduction & volatilization rate

From figure 3, we know that with increase of the volatilization temperatures, the amount of in the Germanium concentrate also increases continuously, from 17.15% to 21.20 % at the temperatures range of 700 – 1300℃.The increase of the roasting temperatures is conducive to the Ge volatilization reaction. At increased roasting temperatures, in addition to vacuum volatilization of the volatile substances, the chemical reaction also reacts more efficiently. At 700–1300 ℃, the germanium vitalization rate increases from 34.13% to 99.26%; after the temperature of 800 ℃,Ge volatilization rate goes up prominently; After 1000℃,the volatile germanium reaches 97.46 %. Then the further temperature

increase exerts little effect on the Ge volatilization rate with excessive costs. Therefore, selection of the volatilization temperature at 1000 ℃ is appropriate.

2.2 Effect of sodium hypophosphite on Ge concentrate roast reduction & volatilization rate

The roasting temperature is set at 1000 ℃; vacuity, 3000 Pa; the carrier gas flow, 400L/h; material thickness, 30 mm; and roasting volatilization time, 90 minutes. Microwave heating is adopted and the consumption of sodium hypophosphiteis changed for the process in steps. The effect of sodium hypophosphite consumption on Ge concentrate roast reduction & volatilization rate is shown in figure 4:

Figure 4 Effect of sodium hypophosphite on Ge concentrate roast reduction & volatilization rate

From figure 4, we know that with increase of sodium hypophosphite, germanium concentrate roast reduction remains basically unchanged at greater Ge volatilization rates. When the consumption of sodium hypophosphite increases to 15 %, the Ge volatilization rate also increases from 45.23 % to 99.12 %; when the consumption of sodium hypophosphite increases

to 7.5 %, the Ge volatilization rate approaches the maximum and then tends to be constant. Greater increase of the consumption of sodium hypophosphite results in less increase of Ge volatilization rate but rather, demand more costs. Therefore, choice of the sodium hypophosphite consumption of 7.5 % is appropriate.

2.3 Effect of the vacuity on Ge concentrate roast reduction & volatilization rate

The roasting temperature is set at 1000 ℃; sodium hypophosphite consumption, 7.5 %; Ge volatilization

time, 90 minutes; material layer thickness, 30 mm; Microwave heating is adopted for the process in steps. The effect of the vacuity (adjustable by the nitrogen flow rate) on the Ge concentrate roast reduction and its volatilization rate is shown in figure 5.
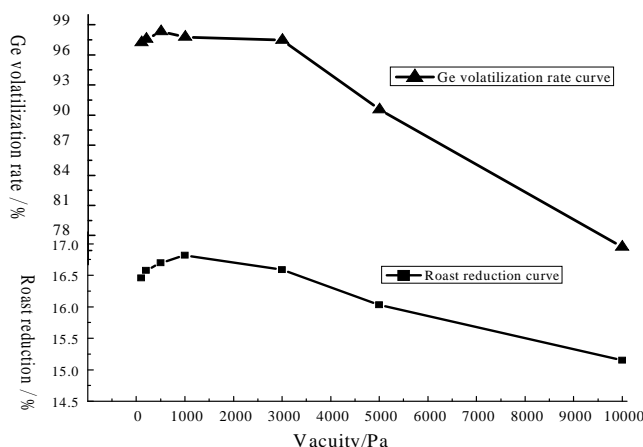

Figure 5 Effect of the vacuity on Ge concentrate roast reduction & volatilization rate

As nitrogen carrier gas flow rate increased such that the degree of vacuum will fall, it can be seen from Figure 5, when the degree of vacuum from 10000 pa to 500 pa, with the increase of the degree of vacuum (reduced nitrogen flow) germanium volatilization rate increased, an increase from 76.85% to 98.32%; germanium concentrate burn reductions while also increased from 15.15% to the 16.82%; After 500 pa with an addition of vacuum degree germanium volatilization rate and burn rate reduction also decreased, So the reduce of nitrogen carrier gas flow have some impact to germanium volatilization and burn rate reduction. When the vacuum degree increased from 3000 pa to 500 pa, germanium volatilization rate reached a higher level, taking into account the amount of nitrogen carrier gas savings,

select a vacuum of 500 Pa is appropriate, at this carrier gas flow rate was 200 L/h.

2.4 Effect of the roast and volatilization time on the Ge concentrate roast reduction and Ge volatilization rate

The roasting temperature is set at 1000 ℃; sodium hypophosphite consumption, 7.5 %; vacuity, 500 Pa; the carrier gas flow rate, 200 L/h; and material thickness, 30 mm. Microwave heating is adopted and the volatilization time is changed for the process in steps. The effect of the roast and volatilization time on the Ge concentrate roast reduction and Ge volatilization rate is shown in figure 6.
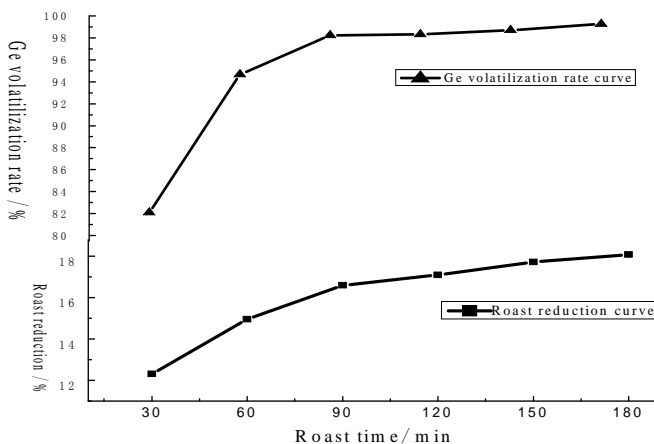
Figure 6 Effect of the roast volatilization time on the Ge concentrate roast reduction and Ge volatilization rate

From figure 6. we know that with the extension of the roasting time, the Ge volatilization rate and concentrate roast reduction also increase. When the roasting time is extended from 30 minutes to 180 minutes, the concentrate roast reduction increases from 12.32% to 18.08% and the Ge volatilization rate increases from 82.10 % to 99.05 %. However, after 90 minutes, the Ge volatilization rate tends to reach the maximum, when extension of the volatilization time may demand additional costs of the energy. So selection of the volatilization time of 90 minutes will be better.

2.5 Effect of material layer thickness on the Ge concentrate roast reduction and its volatilization rate

The roasting temperature is set at 1000 ℃; sodium hypophosphite consumption, 7.5 %; vacuity, 500 Pa; the carrier gas flow rate, 200 L/h; the roasting time, 90 minutes. Microwave heating is adopted and the material layer thickness is changed for the process in steps. The effect of material layer thickness on the Ge concentrate roast reduction and its volatilization rate is shown in figure 7.
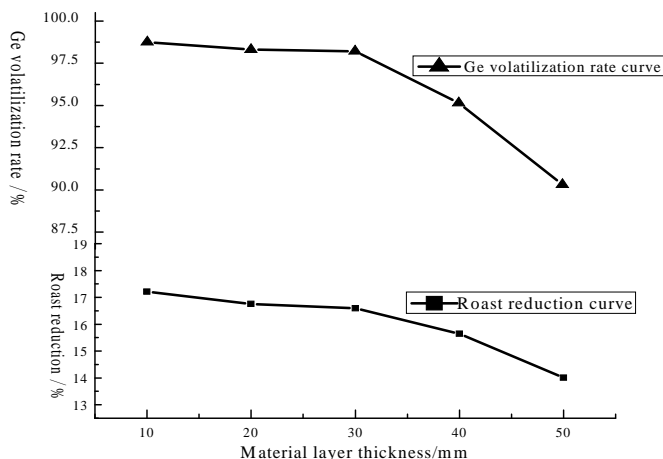

Figure 7 Effect of material layer thickness on the Ge concentrate roast reduction and volatilization rate

From figure7 we know that with increase of the thickness, the Ge concentrate roast reduction and its volatilization rate decreases gradually. When the material layer is thickened from 10 mm to 50 mm, concentrate roast reduction decreases from 17.21 % to 14.01 % and the Ge volatilization rate also falls sharply from 90.32 % down to 98.76 %, which may be attributable to the thickened material layer subsequent prolonged Ge volatilization process from the material bottom to the surface. In order to ensure the germanium volatilization rate and complete the volatilization process in a relatively short period of time, selection of the layer thickness of 30 mm is appropriate.

2.6 The volatilization test result at optimized conditions

To sum up, the optimized test conditions and results above for the microwave heating Ge reduction and volatilization process are as follows: the temperature set for roasting, 1000 ℃; sodium hypophosphite consumption, 7.5 %; vacuity, 500 Pa; the carrier gas flow rate, 200 L/h; volatilization time, 90 minutes; and material layer, 30 mm. For the test, different sources of concentrate samples with various Ge contents are taken: S01, from pyrometallurgicalplant,S02- pyrometallurgical plant II, S03- Xin Xiang Company, and S04- outsourced. At such conditions, the test is optimized with the results shown in table 1.

Table1 The volatilization test result at an optimized condition

Sample No.	Original Ge content, %	Ge, rate/% NO.1	Ge ,rate/% No.2	Ge ,rate/% Arv.
S01	1.00	97.46	98.11	97.79
S02	0.76	96.57	97.36	96.97
S03	0.37	95.08	94.43	94.76
S04	1.68	98.74	97.96	98.35

Table 1 indicates that, use of different raw materials for production of germanium concentrate, by this test process, can help achieve a better effect on volatilization of germanium. The outsourced Ge concentrate with a high Germanium content and the Ge concentrate produced by the pyrometallurgical plant II show a better volatilization efficiency than that produced by Xin Xiang Co many with a smaller Ge content. The analytic result of Ge content in the residual slag is shown in table 2. From the test results we can see that, at the optimized conditions for the test process, the germanium volatilization rate ranges from 94.76 % to 98.35 %.

From table 2 we can see that, the Ge content in the concentrate produced by volatilization ranges from 12.68 % to 46.71 % and the concentration rate reaches (Product Ge concentrate grade / raw Ge concentrate grade) 27~36, with remarkable germanium volatilization efficiency.

Table 2 Results of volatile products and residues of chemical analysis

Sample	Product Germanium concentrate,Ge/Z %	Enrichment ratio	Residue Ge%,Arv.
S01	35.57	36	0.10
S02	20.34	27	0.09
S03	12.68	34	0.06
S04	46.71	27	0.13

Conclusion

Five factors that affect the Ge volatilization rate has been studied through tests: the roast temperature, the consumption of sodium hypophosphite, vacuity (carrier gas flow rate), volatilization time, and material layer thickness. The optimized conditions for the low-Ge-grade concentrate holatilization and concentration process include: the roast temperature at 1000 ℃; sodium hypophosphite consumption of 7.5%; vacuity of 500 Pa; the carrier gas flow rate of 200 L/h; volatilization time of 90 minutes; and material layer thickness of 30 mm. At such conditions, the Ge volatilization rate can reach 94.76 %~98.35 %. The Ge content in the volatile output ranges 12.68 %~46.71 % with the concentration ratios being 27 ~36 times as much as before. From the test results above we can conclude that, it is feasible to apply microwave heating vacuum reduction and volatilization process to Ge extraction from the low-Ge-content lignite concentrate. Compared with the wet process of hydrochloric acid leaching-manganese dioxide oxidation distillation, the process features has high Ge recovery rate, lower production cost, and less equipment investment. Moreover, this process can also avoid discharge and disposal of large quantities of waste water, waste gas and waste residual slag, thus solving completely the environmental problems caused by the wet process, and minimizing significantly any environmental pollution.

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