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Deterioration Patterns on Engineering Properties of Hipparion Red Clay under Acid Rain Conditions

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Abstract: *Acid rain significantly affects the properties of cohesive soils, and it is a major factor contributing to subgrade diseases in cohesive soil areas. Studying the deterioration patterns on engineering properties of cohesive soils under acid rain conditions is of great engineering significance for subgrade design in such regions. By configuring solutions with different pH values to simulate acid rain erosion on Hipparion red clay, expansion tests, shear tests, and permeability tests were conducted to analyze influencing factors and their extent. The results show that the macroscopic properties of Hipparion red clay deteriorate in acidic environments, including increased expansibility, reduced shear strength, and enhanced permeability. The extent of these deteriorations is related to the dry density of the soil sample and the pH value of the solution. Under the same dry density conditions, the deterioration of macroscopic properties increases as the pH value decreases. Under the same pH conditions, the deterioration of macroscopic properties decreases as the dry density increases. Compaction control of Hipparion red clay in acidic environments has a significant impact on the soil samples. Analysis shows that when the compaction degree reaches about 94%, the impact of acid rain on Hipparion red clay is minimized.*

Keywords: Hipparion red clay, Acid rain, Deterioration patterns, Compaction.

1. Introduction

In nature, cohesive soils are widely distributed, primarily composed of clay minerals such as kaolinite and illite. Cohesive soils exhibit characteristics like swelling and shrinkage, and the development of cracks. Due to these properties, cohesive soils often cause slope instability and uneven settlement of subgrades in engineering projects [1]. Cohesive soils are water-sensitive and exhibit significant changes in physicochemical properties under acidic conditions. With the worsening of acid rain problems [2], the swelling, permeability, and strength of cohesive soils used as foundations in engineering projects are altered, leading to engineering issues. To improve the safety of cohesive soil foundations in acidic environments, it is urgent to address the effects of acidic conditions on the swelling, permeability, and shear strength of cohesive soils, thereby optimizing and proposing more suitable design and construction parameters for cohesive soil foundations in acidic environments.

Since cohesive soils contain expansive clay minerals and acid-soluble calcite minerals, acidic solutions have a significant impact on cohesive soils, mainly manifested as property deterioration. Domestic and international studies have shown that under the influence of water, rock and soil masses undergo erosion, leading to changes in mineral composition and microstructure, which in turn alter the physicochemical properties of the soil mass [3]. Sharma et al. studied the changes in the liquid and plastic limits of cohesive soils under acidic conditions, using immersion time and pH as variables. The study found that the liquid and plastic limits of cohesive soils are positively correlated with immersion time [4]. Bakhshipour et al. investigated the effect of acid solutions on the permeability coefficient of residual soils, and the results indicated that the permeability coefficient of contaminated soil exhibited varying degrees of increase [5]. Hamdi et al. found that under long-term exposure to acidic waste liquids, the permeability coefficient of attapulgite and montmorillonite soils decreased, while that of illite-kaolinite soil increased [6]. Sunil discovered that the strength of lateritic soil significantly decreased when soaked in solutions with different levels of acidity [7]. Sun Chongchu, while studying the property changes of cohesive soils in different solutions, found that after immersion in acidic solutions, the moisture content, liquidity index, and soluble salt content in the solution increased, while the shear strength, plasticity, and compression modulus decreased [8].

Existing research indicates that the physical and mechanical properties of cohesive soils are significantly affected by the pH value of acidic solutions and immersion time. Acidic solutions weaken the engineering properties of cohesive soils by dissolving cementing materials and mineral components. Current research on the changes of cohesive soils in acidic environments mainly focuses on liquid and plastic limits and shear strength, with less attention given to the effects of acidic environments on the expansibility of cohesive soils and compaction control measures.

2. Experimental Setup

The soil samples used in this experiment are Hipparion red clay, taken from the cohesive soil strata in Yima Town and Baimapu Township, Qingcheng County, Qingyang City, Gansu Province. Hipparion red clay is rich in montmorillonite, illite, and kaolinite clay minerals, exhibiting swelling properties. The soil samples are light red in color, with high clay content, compact structure, hard plasticity, and contain a small amount of grayish-green debris particles (0.5-1 cm in diameter) without obvious joints. The basic physical property indicators are shown in Table 1.

Table 1: Physical and Mechanical Property Indicators of Qingyang Hipparion Red Clay

Moisture Content	Liquid Limit	Plastic Limit	Plasticity Index	Cohesion (c)	Internal Friction Angle (φ)	Free Swelling Rate	No-load Swelling Rate
16.7%	37.6%	18.6%	19	39.6kPa	22.2°	49	0.93

To simulate the composition of natural acid rain, this experiment used concentrated nitric acid and sulfuric acid to prepare acidic solutions with a molar ratio of $NO_3^-:SO_4^{2-}$ of 3:1, based on the characteristics of acid rain composition in China [9]. To simulate soil sample changes under different acidity levels, the prepared solutions were diluted to pH values of 2, 3, 4, and 5.

Through compaction tests, the maximum dry density of Hipparion red clay was determined to be 1.65 g/cm^3, with an optimal moisture content of 20%. According to the experimental requirements, five groups of remolded soil samples with dry densities of 1.25 g/cm^3, 1.35 g/cm^3, 1.45 g/cm^3, 1.55 g/cm^3, and 1.65 g/cm^3, all with a moisture content of 20%, were prepared for testing.

To simulate the changes in soil under acid rain in engineering environments, the prepared soil samples were immersed in sufficient acidic solution until the ion conductivity of the solution no longer changed. Five groups of soil samples with different dry densities (1.25 g/cm^3 to 1.65 g/cm^3) were taken, with one sample from each dry density group forming a set, totaling five sets. Four sets of soil samples were immersed in acidic solutions with pH values of 2, 3, 4, and 5, while the fifth set was immersed in pure water with a pH of 7 as a control. The five sets of samples were placed in a cool, dark place, and the conductivity of the solution was measured daily to determine if the immersion was complete. Once the ion conductivity stabilized, the immersed samples were removed, air-dried until no natural dripping occurred, and then sealed and stored in the dark.

3. Deterioration Patterns and Analysis of Engineering Properties of Hipparion Red Clay

3.1 Effects of Acidic Environment on the Swelling of Hipparion Red Clay

To analyze the changes in engineering properties of Hipparion red clay under acidic conditions, no-load swelling tests were conducted on each set of immersed samples to obtain the final swelling amounts under different pH values and dry densities. The results are shown in Figures 1 and 2.

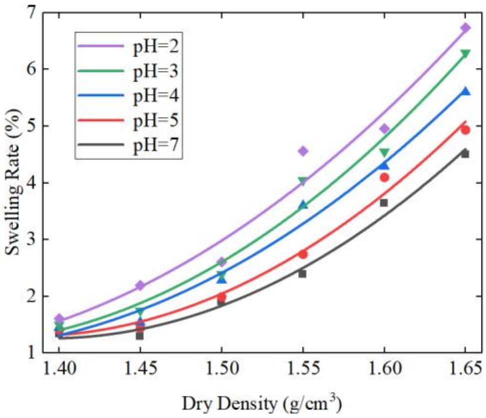

Figure 1: Final Swelling Amount vs. Dry Density Curve

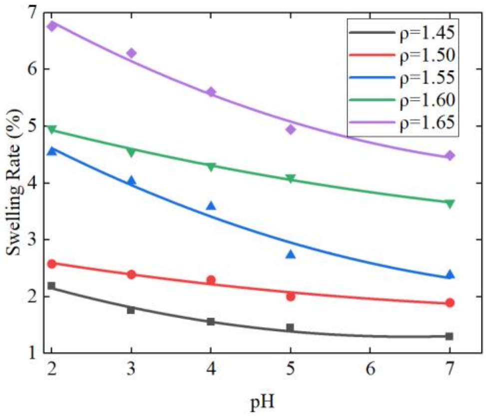

Figure 2: Final Swelling Amount vs. pH Curve

As shown in Figure 1, the swelling time curves of immersed soil samples under different pH values do not vary significantly, but the final swelling amount increases with increasing acidity (i.e., decreasing pH). This may be related to the reaction between the soil samples and the acidic solution, generating other minerals and dissolving components.

As shown in Figure 2, the final swelling amount increases with increasing dry density, and dry density has a significant impact on the final swelling amount. Whether in the high or low dry density range, the rate of change in the final swelling amount under different pH values is similar, but the influence of pH is far less than that of dry density. Dry density is the dominant factor affecting the final swelling amount of soil samples, but the influence of pH on soil swelling cannot be ignored in engineering. Dry density is positively correlated with swelling rate, consistent with Yao Huayan's research [10] on the no-load swelling rate of expansive soils, indicating that soil samples with higher dry density have greater swelling potential, while those with lower compaction have smaller swelling potential, leading to different final swelling rates.

3.2 Shear Strength of Hipparion Red Clay in Acidic Environments

To observe the changes in shear strength of soil samples under different pH values and dry densities in acidic environments, direct shear tests were conducted on the immersed samples.

To study the influence of dry density on soil samples, the shear strength indicators of soil samples with the same pH but different dry densities were compared. The experimental results are shown in Figures 3 and 4.

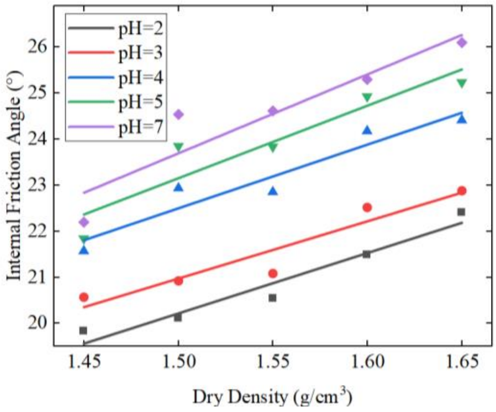

Figure 3: Internal Friction Angle vs. Dry Density Curve

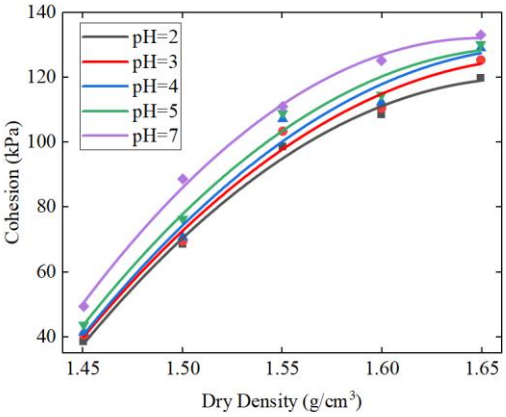

Figure 4: Cohesion vs. Dry Density Curve

From the above data, it can be seen that as dry density increases, both cohesion and internal friction angle increase, indicating that shear strength increases with increasing dry density. This may be related to the dissolution and loss of cementing materials in the soil samples in acidic solutions, leading to reduced shear strength.

To study the influence of pH on soil samples, the shear strength indicators of soil samples with the same dry density but different pH values were compared. The experimental results are shown in Figures 5 and 6.

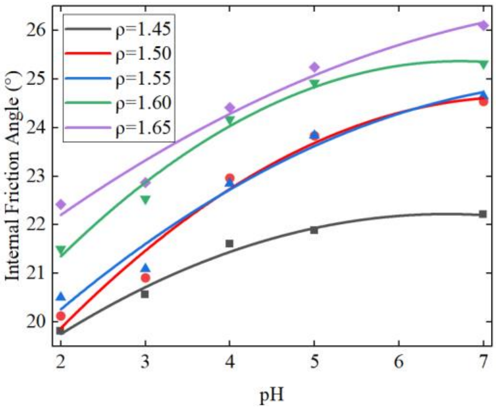

Figure 5: Internal Friction Angle vs. pH Curve

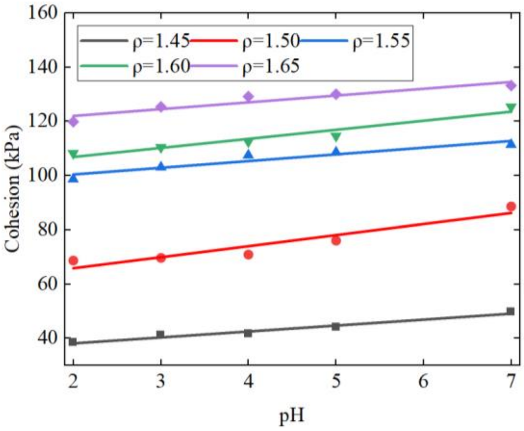

Figure 6: Cohesion vs. pH Curve

From the above data, it can be seen that under the same dry density, as pH increases, both cohesion and internal friction angle increase, indicating that shear strength increases. Soil samples immersed in solutions with lower pH values (higher acidity) experience greater loss of shear strength. Under higher dry density conditions, the shear strength remains relatively high before and after immersion. Analysis suggests that acidic solutions react with mineral components in the soil samples, causing mineral loss and thereby reducing shear strength.

3.3 Effects of Acidic Environment on the Permeability of Hipparion Red Clay

The permeability coefficient reflects the permeability characteristics of soil. Since the soil samples are fine-grained, the permeability coefficient was measured using a falling head permeability test, following the standard SL237-014-1999 *Permeability Test*.

Based on the permeability test results, the relationship between permeability and dry density under different pH values is plotted, as shown in Figure 7. The figure shows that the permeability coefficient of soil samples decreases exponentially with increasing dry density. Therefore, during cohesive soil subgrade construction, increasing soil density through compaction can effectively reduce the adverse effects of acid rain infiltration on subgrade engineering.

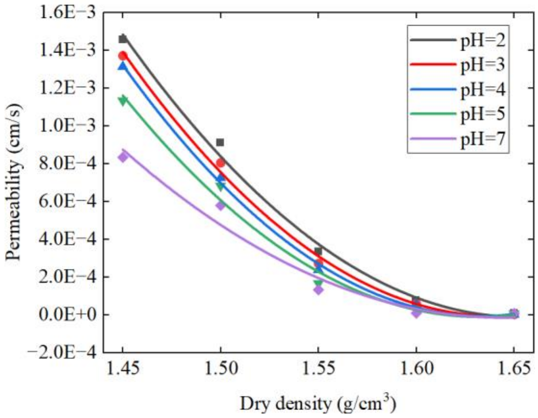

Figure 7: Permeability Coefficient vs. Dry Density Curve

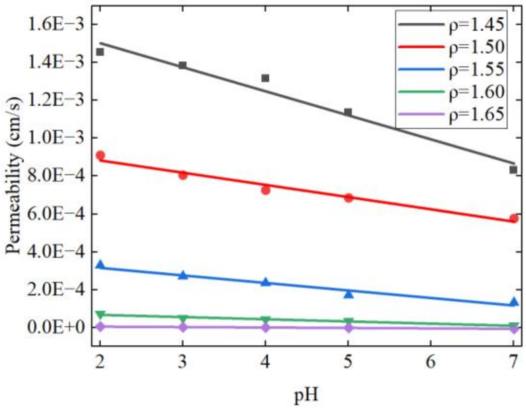

Figure 8: Permeability Coefficient vs. pH Curve

The permeability coefficient can reflect the porosity ratio of soil samples to some extent. Figure 7 shows that as dry density increases, the permeability coefficient of soil samples decreases sharply. When the dry density reaches 1.65 g/cm³, the permeability coefficient of the soil samples approaches zero, indicating that the interconnected pores in the soil samples have almost disappeared. It can be seen that the higher the dry density, the smaller the influence of pH on permeability, which may be related to the difficulty of acidic solutions reacting with soil samples due to small pores.

Figure 8 shows that when dry density remains constant, the permeability of Hipparion red clay is linearly negatively correlated with pH, and the smaller the dry density, the more significant the change in permeability with pH. This also indicates that increasing soil density can effectively reduce the adverse effects of acid rain infiltration on subgrade engineering.

4. Sensitivity Analysis of Influencing Factors

Through the above experimental analysis, it was found that the engineering properties of Hipparion red clay are significantly affected by soil dry density and acid rain pH. To further study the extent of the influence of acid rain pH and soil dry density on the swelling, cohesion, internal friction angle, and permeability of Hipparion red clay, orthogonal experimental methods were used for sensitivity analysis.

Orthogonal experimental design is implemented through orthogonal tables, where each column represents different influencing factors, and each row represents different levels of influencing factors. This design ensures comprehensive and representative data. The orthogonal table is denoted as, where L is the orthogonal table symbol; C is the number of rows in the orthogonal table, representing the number of level combinations; a is the number of levels of influencing factors; and b is the number of influencing factors.

In this experiment, swelling rate, cohesion, internal friction angle, and permeability are the test indicators, while solution pH and soil dry density are the influencing factors. According to the experimental design, solution pH values of 2, 3, 4, 5, and 7 were used as one set of level values, and cohesive soil dry densities of 1.25 g/cm³, 1.35 g/cm³, 1.45 g/cm³, 1.55 g/cm³, and 1.65 g/cm³ were used as another set of level values. The two influencing factors with five levels each were used to create an experimental factor level table, as shown in Table 2. The five levels of acidity and dry density were designed into an orthogonal table, resulting in 25 experimental conditions (5×5) for the test indicators of Hipparion red clay, as shown in Table 3.

Table 2: Factor Level Table

Influencing Factors	Dry Density (g/cm^3)	Acidity(pH)
Range	1.45~1.65	2~7
Level 1	1.45	2
Level 2	1.50	3
Level 3	1.55	4
Level 4	1.60	5
Level 5	1.65	7

Table 3: Orthogonal Experimental Scheme

Scheme	Influencing Factors		Evaluation Indicators			
	Dry Density (g/cm^3)	Acidity(pH)	Swelling Rate (%)	Cohesion (kPa)	Internal Friction Angle (°)	Permeability(cm/s)
1	1.45	2	2.2	38.42	19.83	1.45E-3
2	1.50	2	2.6	68.89	20.12	9.13E-4
3	1.55	2	4.55	98.72	20.52	3.33982E-4
4	1.60	2	4.96	108.47	21.51	7.42E-5
5	1.65	2	6.75	119.83	22.42	7.17898E-6
6	1.45	3	1.75	41.20	20.57	1.38 E-3
7	1.50	3	2.4	69.91	20.93	8.024E-4
8	1.55	3	4.05	103.35	21.10	2.70088E-4
9	1.60	3	4.56	110.79	22.53	5.18E-5
10	1.65	3	6.3	125.48	22.88	5.47016E-6
11	1.45	4	1.55	41.864	21.59	1.31E-3
12	1.50	4	2.3	71.12	22.95	7.261E-4
13	1.55	4	3.6	107.52	22.86	2.42784E-4
14	1.60	4	4.3	112.58	24.18	4.63E-5
15	1.65	4	5.6	129.34	24.42	3.97235E-6
16	1.45	5	1.45	43.70	21.86	1.13E-3
17	1.50	5	2	76.35	23.84	6.84E-4
18	1.55	5	2.75	108.98	23.84	1.68837E-4
19	1.60	5	4.1	114.74	24.91	3.84E-5
20	1.65	5	4.95	130.25	25.24	2.5441E-6
21	1.45	7	1.3	49.85	22.20	8.34344E-4
22	1.50	7	1.9	88.82	24.54	5.81E-4
23	1.55	7	2.4	111.44	24.62	1.36354E-4
24	1.60	7	3.65	125.53	25.30	1.17E-5
25	1.65	7	4.5	133.29	26.10	1.67757E-6

Table 4: Range Analysis Results of Influencing Factors

Indicators	No-load Swelling Rate (%)		Cohesion (kPa)		Internal Friction Angle (°)		Permeability (cm/s)	
Influencing Factors	Dry Density (g/cm^3)	Acidity (pH)	Dry Density (g/cm^3)	Acidity(pH)	Dry Density (g/cm^3)	Acidity (pH)	Dry Density (g/cm^3)	Acidity(pH)
Level 1	1.65	4.21	43.01	86.87	21.21	20.88	1.22E-03	5.56E-04
Level 2	2.24	3.81	75.02	90.15	22.47	21.60	7.41E-04	5.02E-04
Level 3	3.47	3.47	106.00	92.48	22.59	23.20	2.30E-04	4.66E-04
Level 4	4.31	3.05	114.42	94.80	23.69	23.94	4.45E-05	4.05E-04
Level 5	5.62	2.75	127.64	101.78	24.21	24.55	4.17E-06	3.13E-04
Range	3.97	1.46	84.63	14.92	3.00	3.67	1.22E-03	2.43E-04
Sensitivity Ranking	Dry Density ＞Acidity		Dry Density ＞Acidity		Acidity＞ Dry Density		Dry Density＞ Acidity	

Range analysis is a common method for analyzing orthogonal experimental results. By calculating the range, the extent of influence of each factor on the test indicators can be determined. The range value represents the extent of influence of the corresponding factor. By performing range analysis on Table 3, the sensitivity ranking of each factor on the test indicators is obtained, as shown in Table 4. From the range analysis results in Table 4, it can be concluded that the primary and secondary relationships influencing the no-load swelling rate, cohesion, and permeability are: dry density > acidity. That is, dry density has a greater impact on the no-load swelling rate, cohesion, and permeability of Hipparion red clay. Only in the case of the internal friction angle of the soil samples does acidity have a greater influence. Through the above analysis, it is concluded that dry density is the main factor affecting the engineering properties of Hipparion red clay in the region, with acid rain being secondary.

5. Compaction Control of Hipparion Red Clay in Acidic Environments

Through sensitivity analysis, it is known that the dry density of soil samples has a more significant impact on engineering properties than acidity. Therefore, the adverse effects of acid rain on Hipparion red clay subgrades can be reduced by controlling the compaction degree of subgrade soil during construction.

The experiments show that the free swelling rate of Hipparion red clay increases with decreasing pH and increases with increasing dry density. In a pH=7 environment, when the dry density is 1.45 g/cm³, the free swelling rate is 1.3%, and when the dry density reaches 1.65 g/cm³, the free swelling rate is 4.5%. In a pH=2 environment, when the dry density is 1.45 g/cm³, the free swelling rate is 2.2%, and when the dry density reaches 1.65 g/cm³, the free swelling rate is 6.75%. Since Hipparion red clay has swelling properties, to reduce the adverse effects of soil swelling on subgrade engineering, it is necessary to appropriately reduce the compaction degree.

The experimental results show that the cohesion and internal friction angle of Hipparion red clay decrease with decreasing pH and increase with increasing dry density. Under the same dry density conditions, acidity and cohesion follow a function relationship of ($C = apH + b$), and the internal friction angle follows a function relationship of ($\varphi = dpH^2 + epH + f$). Analyzing the coefficients of the cohesion function, when the dry density is 1.50 g/cm³, 1.55 g/cm³, and 1.60 g/cm³, the slope values a are 4.06, 2.47, and 3.32, respectively. Differentiating the internal friction angle function, when the dry density is 1.50 g/cm³, 1.55 g/cm³, and 1.60 g/cm³, the slope values are -0.32, -0.24, and -0.36, respectively. It can be seen that when the dry density is 1.55 g/cm³, the trend of strength change with acidity is smaller.

In the permeability test results, the permeability coefficient decreases exponentially with increasing dry density. Based on the rate of change in permeability, the dry density is divided into intervals. When the dry density is below 1.55 g/cm³, permeability is significantly affected by dry density. When the dry density is above 1.55 g/cm³, the influence of dry density on permeability decreases significantly. Therefore, a dry density of 1.55 g/cm³ is considered the node for permeability changes in Hipparion red clay. That is, when the dry density is below 1.55 g/cm³, the permeability is smaller, and when the dry density is above 1.55 g/cm³, the permeability is larger.

Comprehensively analyzing the influence of dry density on different test indicators, it is concluded that when the dry density of remolded Hipparion red clay is 1.55 g/cm³, corresponding to a compaction degree of 94%, the impact of acid rain on Hipparion red clay is minimized.

6. Conclusions

(1) In acidic environments, the macroscopic properties of Hipparion red clay deteriorate, including increased expansibility, reduced shear strength, and enhanced permeability. The extent of these deteriorations is related to the dry density of the soil sample and the pH value of the solution. Under the same dry density conditions, the deterioration of macroscopic properties increases as the pH value decreases. Under the same pH conditions, the deterioration of macroscopic properties decreases as the dry density increases.

(2) Through orthogonal experimental analysis, it is found that the macroscopic properties of the soil are mainly controlled by the dry density. In different dry density ranges, the influence of pH varies. When the dry density is small, the influence of pH on the deterioration of macroscopic properties is more significant. When the dry density is large, the influence of pH on the soil is smaller.

(3) Compaction control of Hipparion red clay in acidic environments has a significant impact on soil samples. Through analysis, when the compaction degree of Hipparion red clay reaches about 94%, the impact of acid rain on the soil is minimized.

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