Cadena, F. & Peters, R. W. (1988): Evaluation of chemical oxidizers for hydrogen sulfide control. – J. Water Pollut. Con. F., 60(7):1259-1263, 4 Abb., 3 Tab.

Evaluation of chemical oxidizers for hydrogen sulfide control

Fernando Cadena, Robert W. Peters

ABSTRACT: Theoretical hydrogen sulfide oxidation reactions are reviewed. Stoichiometric requirements were determined for typical wastewater samples. To oxidize 1 g of sulfide in laboratory conditions 2.4, 4.2, and 11.8 g of hydrogen peroxide, chlorine, and potassium permanganate, respectively, were required. First-order kinetics with linear sulfide generation describe the hydrogen sulfide oxidation with hydrogen peroxide. The kinetic constants for sulfide oxidation and *in vitro* generation are 0.120 min^{-1} and 0.38 mg/L · h. Chlorine compound and potassium permanganate oxidation reactions are complete in less than 5 minutes contact time. *J. Water Pollut. Control. Fed.*, **60**, 1259 (1988).

KEYWORDS: wastewater, odor control, hydrogen sulfide, corrosion, sewers.

Corrosion and odor problems are common in slow-moving sewers. Corrosion in sanitary sewers is caused by oxidation of hydrogen sulfide (H_2S) to sulfuric acid in the atmosphere above the wastewater.[1,2] Odor problems in sewers are associated with the presence of H_2S, a highly toxic and malodorous gas.[3] Corrosion and odor problems in sanitary sewers are aggravated by high sulfate concentrations, large organic loads, low velocities, and warm temperatures.[1]

Sulfide corrosion in sewers may be controlled by increasing the oxidation-reduction (redox) potential in the wastewater,[3] through addition of oxygen and other chemical oxidizers. Because of the relatively slow oxidation reaction rates of oxygen with sulfide, oxygen addition is practical only under pressurized conditions.[1,2] For example, oxygen may be introduced as pure oxygen or as air into force mains, air lift aerators, and pressure tanks.[2]

Oxygen may also be supplied into a non-pressurized sewer through hydrogen peroxide addition. Hydrogen peroxide provides residual oxidizer protection for up to 1 hour without pressurization. Chlorine gas, hypochlorites, and potassium permanganate are also potent sulfide oxidizers. These chemicals have been used for effective sulfide control in sewers.[1,4–7] However, combination of two or more of these chemicals may be counterproductive for sulfide control. For instance, hydrogen peroxide, which is used as a dechlorinating agent,[8] reduces the efficiency of chlorine to oxidize dissolved sulfides.

Chemical requirements for complete sulfide oxidation depend on solution pH and temperature. Therefore, the oxidizer selection and chemical dose evaluation is a site-specific procedure. Information presented here is applicable to typical wastewater for the city of Albuquerque, N. M. However, procedures used to evaluate oxidizer performance in this investigation may be used to determine stoichiometric oxidizer requirements at disparate sites. Experimental guidelines for determination of stoichiometric requirements for sulfide oxidation with chlorine gas, hypochlorite salts, potassium permanganate, and hydrogen peroxide are presented. Aspects relevant to the economics of sulfide oxidation, oxidizer selection, field implementation, and field-determined stoichiometric requirements are also presented.

Sulfide Oxidation Theory

Sulfide exists in water in three soluble forms: H_2S, HS^- and S^{2-}. Sulfide speciation is a function of solution pH, temperature, and ionic strength. Equilibrium reactions between the three sulfide species are represented by the following reactions:[9]

$$H_2S \leftrightarrow HS^- + H^+ \quad K_1 = (HS^-)(H^+)/(H_2S) \qquad (1)$$

$$HS^- \leftrightarrow S^{2-} + H^+ \quad K_2 = (S^{2-})(H^+)/(HS^-) \qquad (2)$$

The negative logarithms of acidity constants (pK_a) for Reactions 1 and 2 at 25°C are 7.0 and 14.0, respectively.[9] Consequently, H_2S is the main dissolved component at pH values below 7.0, while HS^- predominates at pH values between neutrality and 14.0. The concentration of S^{2-} is negligible in wastewater.[1]

Sulfide-induced odor control in wastewater works may be accomplished by the use of various strong oxidizing agents, which commonly include hypochlorites, chlorine, potassium permanganate, hydrogen peroxide, and oxygen.[1,4–7] End products and oxidizer demands are dependent on solution pH and redox potential (E_h). Influence of these parameters on equilibrium concentrations of various thermodynamically stable sulfur forms is shown in Figure 1.[9] Oxidizers increase the redox potential of the solution. Sulfides, shown in the lower portion of Figure 1, may be converted to more oxidized forms, such as sulfates and elemental sulfur by increasing solution E_h through chemical oxidizer addition.

Unless excessive oxidizer doses are applied, oxidation of sulfides in the acidic range is incomplete, which results in elemental sulfur production. In the basic range, sulfate is the end product of the oxidation reaction. These oxi-

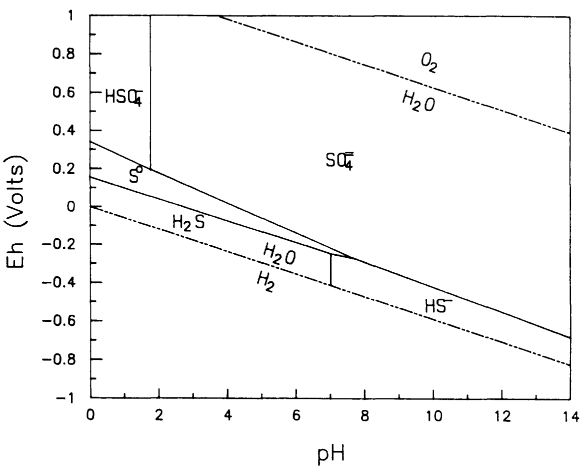

Figure 1—E_h-pH equilibrium diagram for thermodynamically stable sulfur species.

dation phenomena are illustrated in Figure 1 where addition of an oxidizer to a sulfide-containing solution results in an increase of the redox potential, E_h (represented by any vertical line drawn in the direction of the E_h axis in this figure). On the other hand, complete oxidation of sulfide occurs at pH values above 7.5 resulting in the formation of SO_4^{2-}. Lower oxidizer doses are common in the acidic range because elemental sulfur (S^0) possesses a lower oxidation potential than SO_4^{2-}. Therefore, oxidizer dose typically increases with increasing solution pH.

Elemental chlorine, Cl_2, is a strong chemical oxidizer that reacts with water according to Reaction 3.

$$Cl_2 + H_2O \rightarrow 2H^+ + OCl^- + Cl^- \qquad (3)$$

This reaction is acidic in nature because two protons are released in the process. Dissolved sulfides are oxidized by the OCl^- ion formed in the reaction. This same oxidizing ion may be obtained by dissolution of calcium or sodium hypochlorite salts into water as shown in Reactions 4 and 5, respectively.

$$Ca(OCl)_2 \rightarrow Ca^{+2} + 2(OCl^-) \qquad (4)$$

$$NaOCl \rightarrow Na^+ + OCl^- \qquad (5)$$

Therefore, hypochlorite salts and chlorine may be used interchangeably for the oxidation of sulfides in well-buffered waters (where the pH of the solution will not vary significantly because of the introduction of the oxidizer).

Addition of chlorine or hypochlorites to wastewater results in OCl^- production. This radical in turn reacts with H_2S to form sulfur or sulfate as shown in Reactions 6 and 7, respectively. Sulfur formation is favored at pH values below 7.5, while sulfate is typically produced in more alkaline conditions.

$$H_2S + OCl^- \rightarrow S^0 + H_2O + Cl^- \quad \text{if pH} < 7.5 \qquad (6)$$

$$H_2S + 4OCl^- \rightarrow SO_4^{2-} + 2H^+ + 4Cl^- \quad \text{if pH} > 7.5 \qquad (7)$$

Based on the stoichiometry of Reactions 3, 6, and 7, between 2.1 and 8.4 g of elemental chlorine are required to oxidize 1.0 g of sulfide as H_2S. The lower value for the chlorine demand is required in the acidic range. The larger demand value is required at pH values higher than 7.5, when sulfate is produced.

Hypochlorous ion requirements to fully complete Reactions 6 and 7 are 1.5 and 6.1 g per gram of sulfide oxidized, respectively. Corresponding chemical requirements for pure calcium hypochlorite vary from 2.1 and 8.4 g, while those for pure sodium hypochlorite are between 2.2 and 8.8 g per gram of sulfide oxidized.

Reactions 8 and 9 depict the oxidation of sulfide by potassium permanganate ($KMnO_4$) in the acidic and basic ranges, respectively. In acidic solutions, where elemental sulfur is formed, 3.3 g of $KMnO_4$ are needed to oxidize 1.0 g of H_2S, as shown in Reaction 8. According to Reaction 9, the oxidizer demand in alkaline environments equals 13.2 g of $KMnO_4$ per gram of H_2S.

$$3H_2S + 2KMnO_4 \rightarrow 3S^0 + 2H_2O + 2MnO_2 + 2KOH \quad \text{if pH} < 7.5 \qquad (8)$$

$$3H_2S + 8KMnO_4 \rightarrow 8MnO_2 + 3K_2SO_4 + 2H_2O + 2KOH \quad \text{if pH} > 7.5 \qquad (9)$$

The oxidation rate of sulfide with hydrogen peroxide is relatively slow. Twenty to 30-minute contact times are normally required for a completed reaction.[1,6] In the absence of bacterial mass, hydrogen sulfide reacts directly with hydrogen peroxide as shown by Reactions 10 and 11. Reaction 10 occurs in the neutral and acidic range (pH < 7.5) while Reaction 11 predominates under alkaline conditions (pH > 7.5). According to the stoichiometry of these reactions, between 1.0 to 4.0 g of pure hydrogen peroxide (H_2O_2) are required to oxidize 1.0 g of H_2S.

$$H_2S + H_2O_2 \rightarrow 2H_2O + S^0 \quad \text{if pH} < 7.5 \qquad (10)$$

$$H_2S + 4H_2O_2 \rightarrow SO_4^{2-} + 4H_2O + 2H^+ \quad \text{if pH} > 7.5 \qquad (11)$$

The mechanism of oxidation of hydrogen sulfide by hydrogen peroxide in wastewater is not well understood. Others[6] suggest that direct oxidation of sulfide by H_2O_2 (Reactions 10 and 11) is unlikely in the presence of large concentrations of bacterial catalase in wastewater. Hydrogen peroxide first reacts with the bacterial catalase producing oxygen and water.[6] It is more likely that sulfides in wastewater are oxidized by the dissolved oxygen (DO) generated during gradual decomposition of H_2O_2. Nevertheless, the stoichiometric requirements should be identical regardless of the oxidation reaction pathway. Therefore, Reactions 10 and 11 are also commonly accepted for sulfide oxidation in wastewater, where the bacterial catalase is abundant.[1,6,11]

Hydrogen peroxide is manufactured as a fluid in concentrations as high as 50%. Fifty-percent pure hydrogen peroxide has a specific gravity of 1.2 cm^3/g at 20°C. The stoichiometric requirements to satisfy Reactions 10 and 11 are 1.7 and 6.7 mL of 50% H_2O_2, per 1.0 g of H_2S, respectively.

Experimental

Oxidation of hydrogen sulfide with chlorine, potassium permanganate, and hydrogen peroxide was conducted under controlled laboratory conditions. Wastewater samples used in the experimental studies were collected at Wastewater Treatment Plant Number 2 in Albuquerque. The pH of the wastewater samples used in this study varied between 7.2 and 7.5. Oxidation reactions were maintained at approximately 25°C (±1°C). Free sulfides were analyzed using the methylene blue method as described in Standard Methods.[11]

During preliminary experimental investigations, chlorine compounds and potassium permanganate reacted rapidly with the dissolved sulfides in solution. Oxidation of sulfides with these strong oxidizers occurred within 5 minutes after chemical addition (the minimum time required to collect and analyze a sample). On the other hand, the kinetics of sulfide oxidation with hydrogen peroxide were significantly slower. Two different experimental procedures were designed to evaluate kinetic rate differences.

In the first type of experimental procedure, sodium hypochlorite (commercial hypochlorite in liquid form containing 7.5% elemental chlorine, Cl_2) and free-flowing potassium permanganate (industrial grade, 97% pure) were used to prepare dilute stock solutions for the oxidation tests. Different volumes of stock oxidizer solutions were dispensed into replicate 300-mL BOD bottles previously filled to capacity with typical wastewater samples. The bottles were carefully stoppered to evacuate the gas phase. Concentration of free sulfides was measured before each test and 5 minutes after each oxidizer was added. Because of the celerity of oxidation in these tests, kinetic rates of the reactions were not evaluated.

A 2-L reactor similar to one used by others[12] was used in the second phase of the experimental studies to determine oxidation kinetics of H_2S by H_2O_2 in typical wastewater samples. Oxygen-free conditions are created inside the reactor after the introduction of the sample by flushing the headspace with approximately five equivalent volumes of nitrogen gas. An exploded view of the 2-L reactor used during the hydrogen peroxide tests is shown in Figure 2. The DO and pH of the solution were measured using a combination pH and DO electrode. These galvanometric devices were connected to a digital specific ion analyzer. Precision of pH and DO measurements was 0.01 pH units and 0.1 mg/L, respectively. Solution temperature was monitored with an immersion thermometer sensitive to 0.1°C.

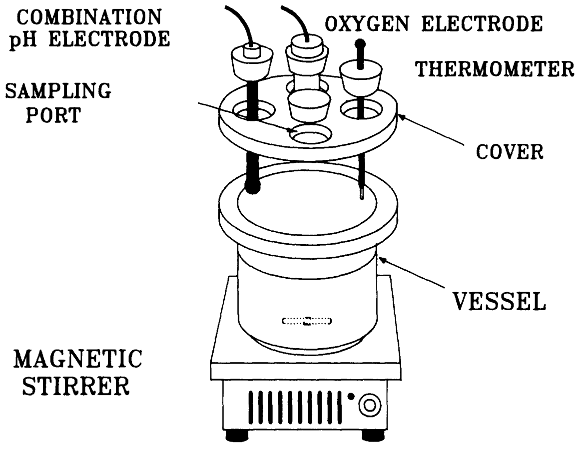

Figure 2—Reactor used in hydrogen peroxide oxidation studies.

Table 1—Effect of oxidizer dose on hydrogen sulfide removal.

Oxidizer	Oxidizer, S_0^{2-} in g/g	Removal, percent
Cl_2	0.0	0
	1.4	29
	2.9	57
	4.3	93
	5.7	100
	7.1	100
$KMnO_4$	0.0	0
	2.5	25
	5.0	38
	7.5	63
	10.0	88
	12.5	100
H_2O_2	0.0	0
	0.6	22
	1.2	45
	1.8	78
	2.4	97
	3.0	98

Results

The experimental results for chlorine oxidation of free sulfide with chlorine compounds, $KMnO_4$, and H_2O_2 are summarized in Table 1. Values presented in this table represent the sulfide removal efficiencies after equilibrium was attained for various oxidizer to free sulfide ratios (S_0^{2-}). For the tests with strong oxidizers (chlorine compounds and $KMnO_4$), equilibrium conditions occurred 5 minutes after chemical addition. Oxidation of sulfides by hydrogen peroxide is a slower process, requiring approximately 30 minutes to reach equilibrium. Results presented in this table correspond to values obtained at 5 minutes for strong oxidizers and at 30-minutes contact time for the H_2O_2 tests.

The raw wastewater used during the chlorine oxidation studies contained 1.4 mg/L of free sulfides before chemical addition. The sulfide removal efficiency by chlorine compounds is shown as a function of chlorine:free sulfide ratio in Figure 3. This figure shows that the minimum dose (as elemental chlorine) required for complete sulfide removal in a typical Albuquerque wastewater sample is approximately 4.2 g per gram of sulfide in solution. This experimentally determined demand is well within the theoretical limits predicted by Reactions 6 and 7.

Figure 3 also depicts results of the sulfide oxidation test with potassium permanganate. The wastewater sample used for these tests contained a natural concentration of

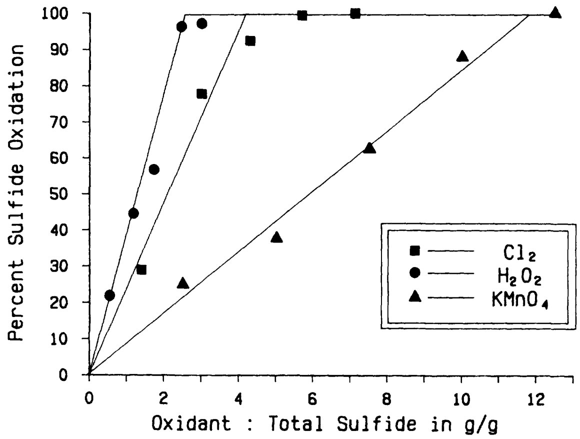

Figure 3—Effect of oxidant dose on sulfide removal efficiency.

0.8 mg/L of free sulfides. The minimum potassium permanganate dose required for free sulfide removal was approximately 11.8 g per gram of sulfide oxidized. This optimum dose ratio also falls within the theoretical limits predicted by Reactions 8 and 9.

Measured sulfide concentrations in the H_2O_2 tests depended on both the H_2O_2:H_2S ratio and the contact time. A more elaborate experimental setup described previously was required to evaluate the effect of contact time on sulfide removal by H_2O_2.

Free sulfide concentrations for five different tests where H_2O_2 was used as oxidizing agent are reported as functions of H_2O_2:H_2S ratio and contact time in Table 2 (a slight pH increase of up to 0.15 units was observed in all runs). No DO was detected by the DO electrode, even at the highest H_2O_2:S_0^{2-} rates.

Free sulfide concentrations in the absence of oxidizers were also measured as a function of time in four kinetic tests. Because of anaerobic degradation, sulfide concentration in the reactor increased throughout the test duration. The average *in vitro* increase of free sulfide concentration for these four tests was 0.38 mg/L • h. Results for a typical *in vitro* sulfide production test are shown in Table 2 (H_2O_2:free sulfide = 0.0 g/g). This table also includes the results of five H_2O_2 oxidation tests at increasing oxidizer:free sulfide ratios.

Table 2—Oxidation kinetics of hydrogen sulfide with hydrogen peroxide, sulfide concentrations in mg/L.

Time, minutes	H_2O_2: S_0^{2-}, g/g					
	0.00[a]	0.6	1.2	1.8	2.4	3.0
0	0.00	0.8	0.4	1.0	0.8	1.3
5	0.03	0.5	0.2	0.5	0.4	0.7
10	0.06	0.6	0.2	0.3	0.3	0.4
15	0.10	0.7	0.3	0.3	0.2	0.3
20	0.13	0.7	0.3	0.3	0.2	0.2
25	0.16	0.8	0.4	0.4	0.2	0.2
30	0.19	0.8	0.4	0.4	0.2	0.2

[a] Average of four runs.

Table 3—Calculated sulfide concentration ratios, (S^{2-}:S^{2-}).

Time, minutes	H_2O_2:S_0^{-2}, g/g				
	0.6	1.2	1.8	2.4	3.0
0	1.00	1.00	1.00	1.00	1.00
5	0.59	0.43	0.47	0.46	0.52
10	0.67	0.35	0.24	0.30	0.26
15	0.75	0.50	0.20	0.13	0.15
20	0.71	0.42	0.17	0.09	0.05
25	0.80	0.60	0.24	0.05	0.03
30	0.76	0.53	0.21	0.01	0.01

Most of the sulfide generation in sewers occurs in the biological slime layer on the pipe wall or in sludge and silt deposits accumulated on the pipe invert.[1,6] Therefore, sulfide generation is expected to be significantly greater in slow-moving sewers than in ideal laboratory conditions. On the other hand, sulfide generation may not be a problem in properly aerated sewers.

The *in vitro* generation of sulfide is important in the consideration of sulfide oxidation rates by H_2O_2, which are of approximately the same order of magnitude. Therefore, to evaluate the net effectiveness and rate of oxidation of H_2O_2 it became necessary to subtract sulfide generation from the actual sulfide measurements. This difference provides the actual concentration of free sulfide removed by H_2O_2. The ratios of sulfide oxidized (that is, measured values minus *in vitro* generation) to initial sulfide concentration are presented in Table 3. A graphical representation of the information in this table is presented in a semi-logarithmic form in Figure 4.

Two distinct zones are characterized in Figure 4. Figure 4 shows that regardless of the H_2O_2:free sulfide ratio, sulfide decays in the first zone according to first-order kinetics (a straight line in the semi-logarithmic plot). This trend occurs as long as H_2O_2 actively oxidizes H_2S. This pattern continues until the chemical is totally consumed.

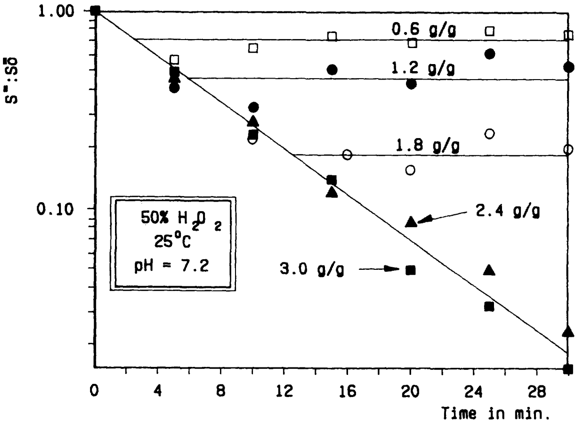

Figure 4—Rate of sulfide decay at various hydrogen peroxide ratios.

The second zone occurs after the oxidizer is consumed by sulfides from the solution. No additional sulfide removal is observed after this time. The residual effect of H_2O_2 is more marked at $H_2O_2{:}S_0{}^{2-}$ ratios greater or equal to 2.4 g/g, where oxidation continues after 30 minutes. On the other hand, at ratios lower than 1.2 g/g the oxidation reaction stops in less than 5 minutes. Termination of the reaction is possibly because of the total consumption of the oxidizer at under-stoichiometric conditions.

The first zone in Figure 4 is described by a first-order kinetic expression of the form

$$S^{2-} = S_0{}^{2-} \exp(-k_1 t) \qquad (12)$$

Where S^{2-}, $S_0{}^{2-}$, k_1, and t represent the concentration of free sulfide remaining, the initial sulfide concentration, the first-order kinetic constant for sulfide oxidation and the contact time, respectively. A best-fit line in the oxidation zone yields a value of 0.120/min for k_1 (slope of the line) for the typical wastewater studied.

Therefore, the applicability of hydrogen peroxide is limited to field situations where the oxidation kinetics exceeds the generation ratio. Sewers that generate sulfides faster than the rate at which they can be removed by hydrogen peroxide oxidation may be protected by using other strong oxidizers at field stations located relatively close to each other.

It is interesting to observe from Figure 4 that hydrogen peroxide is completely depleted at $H_2O_2{:}S_0{}^{2-}$ ratios lower than 2.4 g per gram of sulfide in less than 30 minutes. Thus, the minimum H_2O_2 requirement for complete oxidation is approximately 2.4 g of pure H_2O_2 (4.0 mL of 50% H_2O_2) per gram of free sulfide. Such dose falls within the theoretical range of 1.0 to 4.0 g of pure chemical per gram of free sulfide predicted by Reactions 9 and 10.

Conclusion

Kinetics of oxidation of sulfides with chlorine compounds and potassium permanganate is very rapid. Chemical equilibrium is attained in 5 minutes after oxidizer addition. Oxidation of sulfides with hydrogen peroxide is a relatively slow process that may be described by first-order kinetics. For the particular wastewaters used here, the first-order kinetic constant for the sulfide oxidation reaction is 0.120/min. This oxidation reaction proceeds as long as residual peroxide remains in solution. Minimum doses of oxidizer required to remove 1.0 g of free sulfides are equal to 2.4, 4.2, and 11.8 g of hydrogen peroxide, chlorine, and potassium permanganate respectively. Because of the relatively slow reaction rate, hydrogen peroxide provides extended sulfide protection, while chlorine compounds and potassium permanganate remove sulfides rapidly, without providing residual protection. Effective sulfide control in sewers using hydrogen peroxide is limited to conditions where sulfide generation is relatively slower than the removal rate (0.120/min). Stronger oxidizers may be used in more adverse conditions.

Acknowledgments

Credits. The City of Albuquerque funded this research project. T. A. Glasco implemented field investigations, and A. N. Gaume supervised this project.

Authors. Fernando Cadena is associate professor, Civil Engineering Department, New Mexico State University, Las Cruces. Robert W. Peters is an environmental systems engineer, Energy and Environmental Systems Division, Argonne National Laboratory, Argonne, Ill. All correspondence should be directed to Fernando Cadena, Associate Professor, Civil Engineering Dept., Box 3CE, New Mexico State University, Las Cruces, NM 88003.

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