

# VARIOUS CHEMICALS IN SUPPRESSING EXPANSION DUE TO ALKALI-SILICA REACTION

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## ABSTRACT

More than 10 kinds of chemical admixtures have been studied to suppress the deleterious expansion of mortars. The results show that their suppressive effectivenesses depend on the ionic surface charge densities ( $\sigma$ ). The larger the value of  $\sigma$  of a cation and the smaller the value of an anion of an admixture the stronger the suppressive effectiveness.

Among the nitrite salts of different metals, those of calcium and lithium exhibit good results, of which the cations possess large surface charge densities; whereas for different lithium salts, those such as chloride, bromide, sulphate and nitrite as well as nitrate show their significance in the suppression of expansion, of which the anions are characterized by small surface charge densities. Generally, the values of  $\sigma$  for those chemicals are less than  $0.13 \text{ e}/\text{\AA}^2$ . But those e.g. lithium hydroxide, fluoride and carbonate, which are usually used in the current researches, just give certain suppressions at some limited alkali levels.

On the other hand, the results also suggest that calcium chloride can almost inhibit ASR when its addition is determined by the ratio of  $\text{CaCl}_2/\text{Na}_2\text{O}=0.8$  at various alkali levels, and the addition less than those amounts will also show an obvious suppressive effectiveness.

*Keywords: ASR, suppression of expansion, chemical admixtures, surface charge density, calcium, lithium*

## INTRODUCTION

For a very long time the study of Alkali - Silica Reaction (ASR) has called a great deal of attention. ASR is considered as a "cancer" occurred in mortars or concretes due to the presence of alkali reactive aggregates and high available alkali contents, and therefore, it has been regarded as irremediable. However, the continuous effort for the exploration of possible remediable methods has not been ceased since the early 1950s. McCoy et al (1951) showed that some kinds of lithium compounds and other admixtures such as AE agents and protein additives offer promise as expansion inhibitors. After that other studies mainly dealing with the effect of lithium compounds on expansion have been sequentially

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published.

The recent results (Sakaguchi et al, 1989) verified that the addition of lithium compounds with certain Li/Na molar ratios into mortars can decrease the expansion to a lower level when a range of alkali content of 0.8 ~ 1.2% is present. Moreover our previous work (Bian et al, 1995) allows the conclusion that when Na<sub>2</sub>O content is greater than 2.0% a molar ratio of Li/Na of 0.8 is recommended and when Na<sub>2</sub>O content less than that value a Li/Na ratio smaller than 0.8 is also effective for LiNO<sub>2</sub> used as an expansion-suppressing agent.

The other results (Lawrence et al, 1961) show that different hydroxides behave differently. Lawrence et al elaborated that lithium hydroxide reacts slowly with opal to a negligible extent compared with sodium and potassium hydroxides, revealing its obvious inhibiting action on ASR. Currently, most attention has been put to the functions of lithium hydroxide and carbonate as well as fluoride, however, the other chemicals, especially those containing lithium, might be also of practically prospective in suppressing excessive expansion because their special properties. Based on this point of view a variety of lithium compounds and nitrite salts of different metals as well as calcium chloride were studied with varied additions into mortars in the present paper.

## EXPERIMENTAL

### Materials

Cement and aggregate were same as those used in another work (Bian et al, 1996), and we recall their chemical compositions here (Table 1).

Table 1 Chemical compositions of starting materials (%)

	LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO
OPC	2.1	20.9	5.1	3.1	64.2	1.5	1.9	0.20	0.42	0.26	0.10	0.11
Andesite	1.9	66.2	16.1	3.4	3.3	2.0	0.0	3.50	2.60	0.23	0.10	0.06

A variety of chemical reagents of LiF, LiCl, LiBr, LiNO<sub>3</sub>, Li<sub>2</sub>SO<sub>4</sub>, LiH<sub>2</sub>PO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, LiOH, NaNO<sub>2</sub>, KNO<sub>2</sub>, Ca(NO<sub>2</sub>)<sub>2</sub> and CaCl<sub>2</sub> as well as a commercial LiNO<sub>2</sub> solution of 40% mass concentration were used as chemical admixtures; A solid NaOH was used to give desired levels of Na<sub>2</sub>O in mortars.

The reason for Ca(NO<sub>2</sub>)<sub>2</sub> was selected here is because the fact that it can react with NaOH to form reactive Ca(OH)<sub>2</sub> in solutions, and the latter can react further with N(K)-S-H to form CSH and thus to stabilize the expansive gels, and that it contains NO<sub>2</sub><sup>-</sup> anion, which appears to benefit the suppressive effect; while that for LiH<sub>2</sub>PO<sub>4</sub> is based on its containing of Li<sup>+</sup> and H<sup>+</sup> ions, and Li<sup>+</sup> ions have been previously verified to show their suppressive effect and H<sup>+</sup> ions will contribute to lower the PH value of solutions, and so it releases PO<sub>4</sub><sup>3-</sup> in alkaline solutions.

The amounts of addition of these admixtures were determined by their cation amounts

that are equivalent to that of lithium when using  $\text{LiNO}_2$  as an inhibitor so as to give an equivalent molar ratio of  $M/\text{Na}$  of 0.8 ( $M=\text{Li Na, K, Ca}$ ) for only one exception of  $\text{CaCl}_2$ , which amounts were determined by  $\text{Ca}/\text{Na}=0.8$  (CC1) and by the amounts of  $\text{Cl}^-$  equivalent to that of  $\text{NO}_2^-$  when  $\text{Li}/\text{Na}=0.8$  (CC2), separately, at varied  $\text{Na}_2\text{O}$  levels.

The incorporation of these chemicals are shown in Table 2.

TABLE 2 Proportions of chemical admixtures in mortars (% relative to cement mass)

$\text{Na}_2\text{O}$ %	0.50	1.00	1.50	2.00	2.50	3.00	3.50
M/Na molar ratio= 0.80							
$\text{LiNO}_2$	0.68	1.37	2.05	2.73	3.42	4.10	4.78
$\text{NaNO}_2$	0.89	1.78	2.67	3.56	4.45	5.34	6.23
$\text{KNO}_2$	1.10	2.20	3.30	4.39	5.49	6.59	7.69
$\text{Ca}(\text{NO}_2)_2$	1.71	3.41	5.12	6.82	8.53	10.23	11.94
$\text{LiOH}\cdot\text{H}_2\text{O}$	0.54	1.08	1.63	2.17	2.71	3.25	3.79
$\text{Li}_2\text{CO}_3$	0.47	0.95	1.43	1.91	2.38	2.86	3.33
$\text{LiCl}$	0.55	1.10	1.64	2.19	2.74	3.28	3.83
$\text{LiF}$	0.33	0.67	1.01	1.34	1.67	2.01	2.34
$\text{LiNO}_3$	0.89	1.78	2.67	3.56	4.45	5.34	6.23
$\text{Li}_2\text{SO}_4$	1.42	2.84	4.26	5.68	7.09	8.51	9.93
$\text{LiBr}\cdot 2\text{H}_2\text{O}$	1.38	3.17	4.76	6.34	7.93	9.52	11.10
$\text{LiH}_2\text{PO}_4$	1.34	2.68	4.03	5.37	6.71	8.05	9.39
$\text{CaCl}_2$ <sup>1</sup>	1.43	2.87	4.30	5.73	7.16	8.60	10.03
$\text{CaCl}_2$ <sup>2</sup>	0.72	1.43	2.15	2.87	3.58	4.30	5.01

\*  $\text{Ca}(\text{NO}_2)_2$  is a hydrated substance,  $\text{Ca}(\text{NO}_2)_2\cdot\text{H}_2\text{O}$

<sup>1</sup>  $\text{CaCl}_2$  were calculated according to the molar ratio of  $\text{Ca}/\text{Na}=0.8$ ;

<sup>2</sup>  $\text{CaCl}_2$  were determined by  $\text{Cl}^-$  amounts equivalent to that of  $\text{NO}_2^-$  when added  $\text{LiNO}_2$  under  $\text{Li}/\text{Na}=0.8$  at varied  $\text{Na}_2\text{O}$  levels.

## Procedures

The same procedures as described in another paper (Bian et al. 1996) were followed and the results after an autoclave treatment are analyzed as follows.

## RESULTS AND DISCUSSIONS

### Effect of nitrite salts of different metals

Results on the effects of different nitrites are shown in Fig.1. It can be seen that the additions of  $\text{NaNO}_2$  and  $\text{KNO}_2$  always increased the expansions and the expansions were increased generally by a factor of 1-16 by  $\text{NaNO}_2$ , 0.6-11 by  $\text{KNO}_2$  from 0.5 through 3.5%  $\text{Na}_2\text{O}$ , as are listed below:

$\text{Na}_2\text{O}\%$	0.5	1.0	1.5	2.0	2.5	3.0	3.5
increased by $\text{NaNO}_2$	3.0	16.1	5.4	7.7	3.3	3.9	3.3
increased by $\text{KNO}_2$	0.6	11.3	1.0	4.0	1.2	1.9	1.5

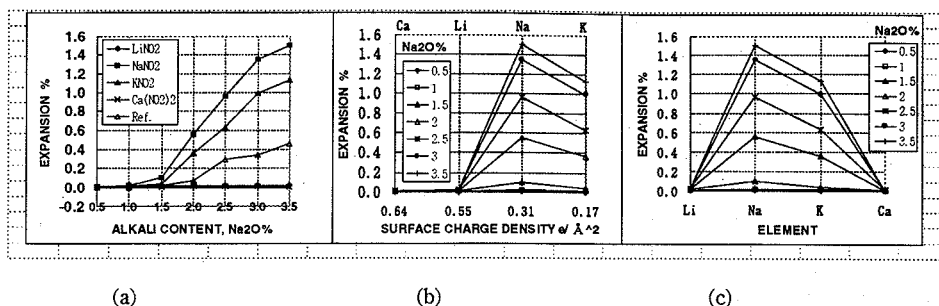


FIG. 1 The effect of different metal nitrites on expansion of mortars: (a) relation between expansion and alkali contents; (b) relation between expansion and surface charge density of cation; (c) relation between expansion and element

This is because NaNO<sub>2</sub> and KNO<sub>2</sub> enhanced the total concentrations of alkalis in pore solutions of mortars, and hence accelerated the corrosion of reactive component in aggregates. On the other hand, 6-coordination hydrated ions of Na and K in gels will occupy more space than the 4-coordination ones of Li. However, adding LiNO<sub>2</sub> and Ca(NO<sub>2</sub>)<sub>2</sub> most greatly suppressed the expansion except the lowest Na<sub>2</sub>O levels of 0.5 and 1.0%, where the corresponding values of expansion were approximately equal to that of control samples (cf. the following data):

Na <sub>2</sub> O	Ref.	LiNO <sub>2</sub>	Ca(NO <sub>2</sub> ) <sub>2</sub>
0.5	-0.0026	0.0025	0.0079
1.0	0.0011	0.0113	0.0083

From the above we can deduce that the effect of Ca(NO<sub>2</sub>)<sub>2</sub> in suppressing expansion is similar to or even greater than that of LiNO<sub>2</sub>, so by taking into account the availability and price, the use of Ca(NO<sub>2</sub>)<sub>2</sub> is thus more economical and of more prospects than that of LiNO<sub>2</sub>.

We have previously attributed the effect of LiNO<sub>2</sub> in suppressing expansion to the substitutions of Li ions for some Na and K ions in the final products of N(K)-S-H gels, and thus this make the gel structure densified and further enveloping aggregates with these gels will also alleviate the aggregates from subsequent corrosion (Bian et al. 1995). But for Ca(NO<sub>2</sub>)<sub>2</sub>, first it react with OH<sup>-</sup> to form Ca(OH)<sub>2</sub> and then the latter, newly formed Ca(OH)<sub>2</sub> of high reactivity, will combine with N(K)-S-H, converting it to commonly stable CSH gels because Ca<sup>2+</sup> is a structure-forming ion and Na<sup>+</sup> and K<sup>+</sup> are structure-breaking ones.

On the other hand, just as shown in Fig.1b the expansion of mortars relates satisfactorily to the surface charge densities ( $\sigma$ ) of cations. Generally, with the decrease in the value of  $\sigma$  the expansion increases, and this implies that the bigger the value of  $\sigma$  of a cation, the bigger its electron affinity and thus the stronger the bonding between the cation and anions in the gels. Therefore, it contracts the gel structures strongly and make the structures densified (structure-forming effect). Conversely, the small  $\sigma$  value signifies that the cation has a small electron affinity and thus a weak bonding with the around anions (such as Na and K), and this also implies the cation has a bigger freedom in the

gel structures, thus it could bond freely more water molecules to form bigger hydrated ions with a greater coordination number even in the gels, as a result it expands the gels (structure-breaking effect) and the mortars. Based on this, therefore, it is not difficult to understand why  $\text{Ca}^{2+}$  has a stronger effectiveness than  $\text{Li}^+$  in suppressing expansion. However, we also attribute the relative smaller expansion in the case of  $\text{KNO}_2$  than in the case of  $\text{NaNO}_2$  to the difference in the radii of  $\text{Na}^+$  and  $\text{K}^+$ .  $\text{Na}^+$  ions have smaller radii and occupy more sites than do  $\text{K}^+$  ions, that is, most part of  $\text{K}^+$  ions are excluded by  $\text{Na}^+$  ions from gels. This could be confirmed by the contribution of  $\text{Na}$  to expansion by comparing the data on  $\text{Na}_2\text{O}+\text{NaNO}_2$  and  $\text{Na}_2\text{O}+\text{KNO}_2$  where in most cases  $\text{Na}^+$  ions contribute more than 80% to the expansion. Consequently, as a summary the effectiveness of cations in suppressing ASR expansion should follow the order:  $\text{Ca} > \text{Li} > \text{K} > \text{Na}$ .

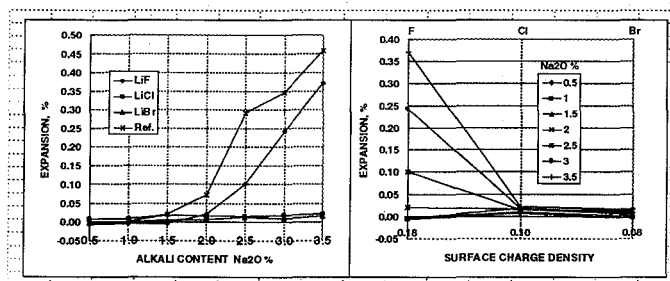
Furthermore, there appears to be also some evidence to verify the effectiveness of anions in such a process because lithium salts containing different anions behaved differently, and this will be dealt with immediately in the following sections.

### Effect of lithium halides

Lithium fluoride, chloride and bromide were used in this study to show their effects of anions and the results are schematically shown in Fig.2. Obviously, lithium chloride and bromide limited the expansion to a very low value, while lithium fluoride exhibited a slightly increased expansion when  $\text{Na}_2\text{O}$  being 1.5% ~ 2.0% though when  $\text{Na}_2\text{O}$  less than 2.0% it could keep the expansion within the same range as did the others. When  $\text{Na}_2\text{O}$  greater than 2.0% it led to a much greater expansion than the former two, but still demonstrated, though very less evident, the suppressive effect even in this event (cf. Fig.2a).

Fig.2b allows the relation between expansion and the surface charge density of an anion. Generally, expansion decreases with the decrease in the value of surface charge density despite the extraordinary behavior of fluoride when  $\text{Na}_2\text{O}$  less than 1.5%. A possible explanation for such an unexpected behaviour of fluoride appears to associate with its special properties based on its almost same size of ionic radius as that of  $\text{OH}^-$  and  $\text{O}^{2-}$  ions (ca. 1.40 Å).

On the other hand fluoride ion is a structure-forming ion and can be a ligand to form complex ions (Bailar et al. 1973). Therefore, in gels (and certainly in other hydrated products) fluoride will substitute for  $\text{OH}^-$  or  $\text{O}^{2-}$  ions. As alkali increases the amount of fluoride increases proportionally and the substitution in gels increases



(a)

(b)

FIG.2 Effects of lithium halides on expansion: (a) Expansion vs. alkali contents (b) Expansion vs surface charge density

too. Meanwhile due to the equally stereoelectric static, which is different than  $\text{OH}^-$ ,  $\text{F}^-$  will form bigger ionic groups with a large number of water molecules even in gels through the formations of hydrogen bonds and coordinating bonds, as also leads to more expansion.

In contrast with  $\text{F}^-$  ion,  $\text{Cl}^-$  and  $\text{Br}^-$ , belonging to "structure-breaking" category, behave differently and tend to keep the expansion steadily low through all the alkali levels. In consequence, the effectiveness of halides in suppressing expansion is in the following order:  $\text{F} > \text{Cl} < \text{Br}$  when  $\text{Na}_2\text{O} < 1.5\%$ , and  $\text{F} < \text{Cl} < \text{Br}$  when  $\text{Na}_2\text{O} > 2.0\%$  which is in consistent with the order of  $\sigma$  at this moment.

### Effect of other lithium compounds

The effects of the other lithium compounds rather than lithium halides were also studied and the results are schematically shown in Fig.3.

Obviously,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  as well as  $\text{PO}_4^{3-}$  effectively suppress the expansion while  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  can only exhibit evidently their effect at limiting  $\text{Na}_2\text{O}$  levels.

Similarly, Fig.3b also allows the obvious relation between expansion and surface charge densities of anions. Evidently, the  $\sigma$  values less than 0.13 will keep the mortars from excessive expansion, and the expansion could be controlled less than 0.05 only for the exception of  $\text{PO}_4^{3-}$ , which slightly increased the expansion when  $\text{Na}_2\text{O}$  greater than 2.5% despite showing a similar effect to the others (eg.  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$ ) at relative low  $\text{Na}_2\text{O}$  levels and the reason for such a character of  $\text{PO}_4^{3-}$  is not clear by now.

For comparison the overall results on the suppression of expansion are generalized in Fig.4. From that we can draw the following remark points: the usually used chemical admixtures of  $\text{LiF}$ ,  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$  can give evidently their effectiveness in suppressing ASR expansion only when relatively low  $\text{Na}_2\text{O}$  levels are available, otherwise, their effectiveness are so limited that an excessive expansion can still occur;

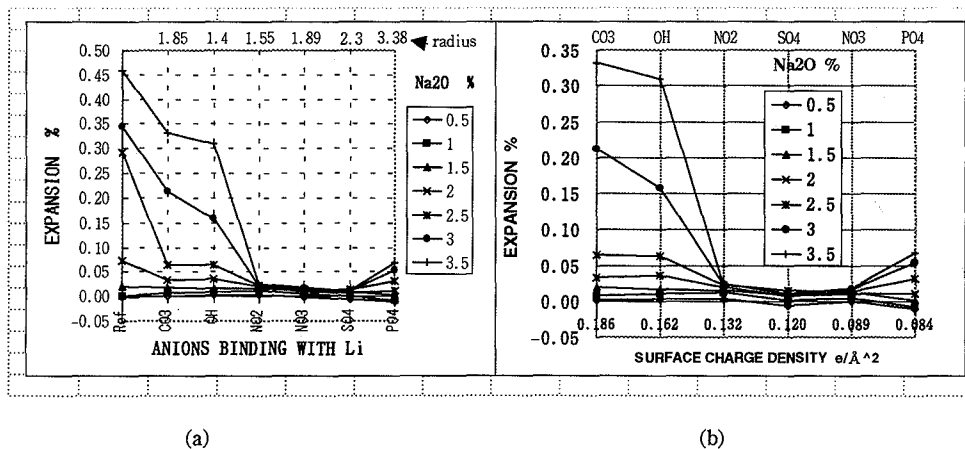


FIG.3 Effects of lithium compounds (rather than halides) on expansion: (a) expansion vs anions; (b) Expansion vs surface charge density of anion (values of radii from I. Sato, 1979)

LiNO<sub>2</sub>, LiNO<sub>3</sub>, Li<sub>2</sub>SO<sub>4</sub> and LiCl as well as LiBr can suppress expectantly the expansion, of which the values of surface charge densities of anions are relatively small (smaller than 0.13 e/Å<sup>2</sup>). LiH<sub>2</sub>PO<sub>4</sub> gives rise to a similar result to those ones mentioned above only when Na<sub>2</sub>O less than 2.0%.

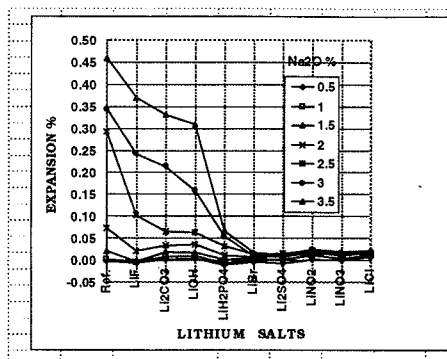


FIG.4 Overall results of the effects of lithium compounds on expansion of mortars after autoclave

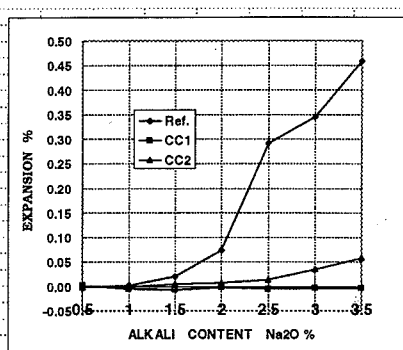


FIG.5 Effect of calcium chloride on expansion of mortars after autoclave

### The effect of calcium chloride

Since calcium and chloride ions, with their appropriate  $\sigma$  values, exhibit good behaviors in controlling excessive expansion, separately, just as mentioned above, therefore, we think the use of CaCl<sub>2</sub> might be also plausible though it was already concluded to be ineffective (McCoy et al. 1951). However, the present results really suggest that CaCl<sub>2</sub> shows its significance in controlling ASR expansion, and its effectiveness depends strongly on the incorporation amount (Fig.5), and it must be noted that in both the present cases the CaCl<sub>2</sub> amounts are much greater than that used by McCoy et al. Based on the results it can be concluded that ASR was practically inhibited in the case of CC1, giving rise to the most ideal result, and in fact the mortars shrunk to some extent in this event. Whereas the reaction was only prevented by a relative big factor in the case of CC2. Thus we invoke CaCl<sub>2</sub> is not so enough that to completely inhibit the reaction in the latter case, however, increasing CaCl<sub>2</sub> amount will also be accompanied by the risk of corrosion of steel reinforcements and the formation of calcium aluminochloride hydrate despite the effectiveness in suppressing ASR expansion such as in the case of CC1, this is another problem which should be further extensively studied.

### CONCLUSIONS

1. The effectiveness of an admixture in suppressing ASR expansion depends on the values of ionic surface charge densities ( $\sigma$ ) of its cation and anion, the bigger the value of  $\sigma$  of cation and the smaller this value of anion, the more effective the admixture is.
2. The effectiveness is in the order: Ca<sup>2+</sup> > Li<sup>+</sup> > K<sup>+</sup> > Na<sup>+</sup> for cations, therefore, Ca(NO<sub>2</sub>)<sub>2</sub> and CaCl<sub>2</sub> as well as LiNO<sub>2</sub> obtain ideally suppressing results.

3. The effective values for surface charge densities for anions should be less than  $0.13 \text{ e}/\text{\AA}^2$  and the chemicals of which the values within this range will greatly suppress the ASR expansion.

4.  $\text{Li}_2\text{SO}_4$ ,  $\text{LiNO}_3$ ,  $\text{LiNO}_2$  and  $\text{LiCl}$  as well as  $\text{LiBr}$  can practically produce similar suppressive effect on ASR expansion, while  $\text{LiOH}$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{LiF}$  can only exhibit certain effect under limiting  $\text{Na}_2\text{O}$  levels.

5. The effect of  $\text{CaCl}_2$  depends on its addition amount. Less enough addition will not produce ideally inhibiting effect, and the sufficient addition will practically inhibit ASR.

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