Porosity change model for watered super absorbent polymer-treated soil

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Abstract Drought is a great concern in agricultural production, because it restricts normal plant growth, brings about enormous economic loss and deteriorates ecological environment. Proper use of super absorbent polymers (SAP) is helpful in the agricultural and horticultural industry in arid and semi-arid areas, because SAP can ease the burden of water shortage. Because porosity is one of the most important soil physical properties, it is a priority to study SAP to quantitatively express the swelling of watered SAP-treated soil. This study was aimed to evaluate the bulk density curve of watered SAP-treated soil and to construct and test the model for porosity change of watered SAP-treated soil. The results showed that the application of SAP can reduce soil bulk density, improve soil permeability and cause soil swelling. In addition, using three factors, i.e.,

water content, change in swelling ratio and SAP application rate, the paper constructed a model for porosity change of watered SAP-treated soil, which is $\{\ln[(P_m - P)(P_m - P_0)^{-1}]\} \beta P_0 \theta = -\eta_0 c \theta - \eta_0 a$. This is a generic model. Two soil samples, namely, loam and sandy loam, were used to calculate the parameters and test the model. The results of the model were satisfying, thus this model is reliable.

Keywords Super absorbent polymers · Soil porosity · Porosity change model · Soil swelling ratio

Introduction

Since chemicals were applied in agriculture, researches on the technology of chemical-saving water have been drawing extensive attention. Super absorbent polymers (SAP) are one of the maturely developed chemical water-saving agents. In the 1960s, Gugliemelli et al. (1979), a member of the Northern Regional Research Center of the US Department (NRRC), first developed a kind of SAP composed of starch-polyacrylonitrile graft co-polymer and applied it to agricultural production of corn and soybean as well as seedling transplanting. It was found that SAP contributes to water saving and yield enhancement (Fanta et al. 1971). Grain Processing co. industrialized its manufacture as early as 1974 (Nimah et al. 1983; Hemyari and Nofziger 1981). SAP is used in many areas such as pharmaceuticals, food packaging (Matsubara and Toa 1990), paper production (Li et al. 2004), the agricultural and horticultural industry (Wang et al. 2000a, b), oil drilling (Wang et al. 1998), etc.

Drought is a great concern in agricultural production. Compared with other adverse environmental causes, drought, whether permanent or temporary, is much more harmful to plant. It restricts normal plant growth, brings

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about enormous economic loss and deteriorates ecological environment. Proper use of SAP has great significance in the agricultural and horticultural industry in arid and semi-arid areas, because it can ease the burden of water shortage. Current studies on SAP mainly focus on the development of its new material and new product (Liu and Rempel 1997; David and De 1994; Achwal 1997) and its own chemical properties (Janardan 1998; Woodhouse and Johnson 1991; Yang et al. 2003) as well as its field application (Swietlik 1989; Han et al. 2005), while few studies relate to the properties of SAP-treated substance (Liu et al. 2005). This paper studied the change of physical properties of SAP-treated soil. After SAP has absorbed water, its capacity of absorbing and desorbing water closely relates to its volume change. Since porosity is one of the most important soil physical properties, it is a priority to study SAP to quantitatively express the swelling of watered SAP-treated soil. The study is a theoretical basis for determining whether SAP can be used properly and effectively.

The first objective of this study was to evaluate the bulk density curve of watered SAP-treated soil, and the second was to construct and test a model for porosity change of watered SAP-treated soil.

Materials and methods

Materials

The experimental site of Power and Water Supply Center, located in Daxing District of Beijing and the experimental area of China Agricultural University were used for this study. The soil samples were taken from the layer 20–60 cm, with pH of 7.0, classified as sandy loam and loam, respectively.

The particle size of soil samples were analyzed and classified according to soil taxonomy developed by United States (Table 1).

Acrylate sodium co-polymers (ASC) used in this experiment is “Kehan 98” produced by Hebei Kehan Resin Ltd. They are white particles with diameter less than 0.02 mm.

PVC cylinders, 250 mm in outer diameter, 239–240 mm in inner diameter and 80 mm in height were used (see Fig. 1).

Fig. 1 Cylinder

Table 2 Experimental design

Soil sample	SAP application rate (SAP:dry soil weight ratio)	Water content					
		0.10	0.15	0.20	0.25	0.30	0.35
Sandy loam	1:5,000						
	1:2,000						
	1:1,000						
	1:500						
Loam	1:5,000						
	1:2,000						
	1:1,000						
	1:500						

Methods

The experiment was conducted in Soil Physics Laboratory of China Agricultural University in December 2008.

SAP was mixed with air-dried or oven-dried soil samples in SAP:dry soil weight ratios of 1:5,000, 1:2,000, 1:1,000 and 1:500, respectively.

Water content θ began at 0.10 and increased at the interval of 0.05, until it reached 0.35. The detail of the experimental is designed as shown in Table 2.

Experimental steps

The SAP–loam mixture and the SAP–sand mixture at different SAP:soil ratios were filled in separate cylinders, and were compacted until the bulk density of the mixture in each cylinder was equal to that of the corresponding original soil. The height of SAP–soil mixture in cylinders was 40 mm. The amount of water to be added into each

Table 1 Soil physical properties

Soil sample	Particle content (%)			Soil texture	Bulk density
	Clay (<2 μm)	Silt (2–50 μm)	Sand (50–2,000 μm)		
Experimental site of Power and Water Supply Center	7.96	39.47	52.57	Sandy loam	1.49
Experimental area of China Agricultural University	9.95	46.74	43.31	Loam	1.55

cylinder was determined according to different water contents as shown in Table 2. Water was poured into the cylinders evenly until the water content in each cylinder reached the level as required in Table 2. Then the cylinders were covered with cling wrap for preventing the evaporation of water; 24 h later, the bulk density of SAP–soil mixture was measured by cutting ring sampling method. Porosity was calculated according to the measured bulk density; each treatment has three replications.

Results

Bulk density measurement

The height of the SAP–soil mixture in cylinders was too low, so the experiment employed small-sized cutting ring, 52.0 mm in diameter and 10.0 mm in height, to measure the bulk density (refers to dry bulk density in this paper) of the SAP–soil mixture. To ensure the accuracy, the values measured with small cutting ring were compared with those measured with big-sized cutting ring, 50.0 mm in diameter and 50.9 mm in height. The result is shown in Table 3.

Table 3 shows that the values measured with the two different methods, respectively, are highly consistent. The largest deviation between the value measured with big-sized cutting ring and that measured with small-sized cutting ring is 0.013, the smallest 0.002, and the average deviation is 0.0078. Therefore, the values measured with small-sized cutting ring are as reliable as those measured with big-sized cutting ring.

Soil bulk density

Soil bulk density is an important indicator of soil physico-chemical properties, reflecting the tightness of the pore space in soil. Thus, the experiment studied the bulk density of SAP-treated soil in different SAP:soil ratios so as to further study the porosity. The extent of the swelling of SAP varied with water content, so the bulk density of SAP-treated soil also varied with water content (see Fig. 2).

Figure 2 shows that bulk density was reduced after the soil was treated with SAP, and meanwhile, in each figure,

bulk density declined as water content increased. The decline in bulk density indicates the increase in soil porosity. Therefore, the application of SAP can reduce soil bulk density, improve soil permeability and cause soil swelling.

Model for soil porosity change

As mentioned before, after having absorbed water, SAP's capacity of absorbing and desorbing water closely relates to its volume change. Since porosity is one of the most important soil physical properties, it is a priority to study SAP in order to quantitatively express the swelling of watered SAP-treated soil.

Hypotheses for the model

To quantitatively analyze the swelling of watered SAP-treated soil, the following hypotheses were proposed:

1. SAP was mixed with two kinds of dried soil samples thoroughly, respectively. That is to say, the SAP–soil mixture per unit volume (or mass) contained the same amount of SAP; and SAP particles were small enough and were distributed evenly enough to make the volume change of SAP-treated soil homogeneous and isotropic;
2. the impact of applied SAP itself on soil bulk density was ignored. Therefore, in the following analysis, all the volume changes of SAP-treated soil were caused by SAP's performance of absorbing water;
3. after SAP-treated soil had absorbed water, its volume would change instantaneously. That is to say, volume change was just a function of water content, having nothing to do with time; and
4. at room temperature, the effect of temperature on experiment was ignored, so the volume change caused by temperature change was not taken into account.

The diameter of SAP particle is less than 0.02 mm, similar to that of soil particle, so they can be mixed evenly and isotropically by a mixer. In this experiment, the change of soil bulk density caused by the mixing of SAP and soil was only 0.02–0.2%, so this change was ignored; SPA completed absorbing water and expanded to a maximum

Table 3 Bulk density measured with different-sized cutting ring

Given bulk density (g cm ⁻³)	1.45			1.50			1.55		
Big-sized cutting ring	1.446	1.454	1.449	1.505	1.501	1.510	1.545	1.554	1.548
Small-sized cutting ring	1.443	1.441	1.447	1.492	1.509	1.502	1.540	1.552	1.542
Deviation	0.003	0.013	0.002	0.013	0.008	0.008	0.005	0.002	0.006
Average deviation	0.0078								

Fig. 2 Bulk density of SAP-treated soil versus water content (SAP:soil = 1:5,000, 1:2,000, 1:1,000, 1:500)

extent in 3–5 min, this duration being so short that it was negligible for the whole experiment, so the change of soil bulk density during this duration was ignored; the temperature in the laboratory is constant, and the properties of SAP is stable below 100°C (Janardan 1998), so the change of volume caused by the temperature was ignored. Thus, the above hypotheses can be considered reasonable for the purpose of this study.

Construction of the model

Soil is generally considered as a continuous medium, so specific volume P ($\text{cm}^3 \text{g}^{-1}$), i.e., the volume occupied by a unit of mass of soil was used to indicate soil volume in this paper. After having absorbed water, SAP-treated soil's volume changed significantly, that is, specific volume P is a function of soil mass water content θ (g g^{-1}).

Under the above hypotheses, the change in specific volume P was mainly affected by the following three factors:

1. **Water content** It is the basic condition for the volume change of SAP-treated soil. For air-dried or oven-dried soil, the change in P , i.e., ΔP , at a certain water content is a function of $\eta(a + b\theta)$, where η is the swelling ratio, indicating the ratio of ΔP to the filled status of soil pores by water ($a + b\theta$); η , a and b are all dimensionless constants.
2. **Change of swelling ratio** The past studies show that volume change varies with water content, but continually watered SAP-treated soil will not keep swelling, instead, it stops when swelling ratio has reached a

maximum. This process can be expressed as $\eta = \eta_0(P_m - P)$, where η_0 is a dimensionless apparent swelling ratio, and P_m is the specific volume at the maximum swelling ratio.

3. **SAP application rate** According to the above hypotheses, after SAP-treated soil has absorbed water, its volume change is caused only by SAP's performance of absorbing water. Obviously, the volume change at a particular water content depends on SAP application rate. Let W be SAP application rate, i.e., the weight of applied SAP per unit mass of soil, then $W = \beta P_0$, where β is the weight of applied SAP per unit volume of soil (g cm^{-3}); and P_0 is the specific volume of air-dried or oven-dried soil.

By taking above three factors together into account, the numerical model for specific volume change of the soil applied with a certain amount of SAP at a certain water content is constructed as:

$$\frac{dP}{d\theta} = \beta P_0 \eta_0 (P_m - P)(a + b\theta) \quad (1)$$

with the constant differential equations, the explicit general solution of P can be obtained by the following equation:

$$\int \frac{dP}{d\theta} = \beta P_0 \eta_0 \int (P_m - P)(a + b\theta) \quad (2)$$

$$P = P_m - \frac{1}{C e^{\beta P_0 \eta_0 (a\theta + \frac{b}{2}\theta^2)}}$$

where C is an integral constant. Based on the above-mentioned hypotheses, SAP application does not bring

about change of P for air-dried or oven-dried soil, so the initial condition occurs as:

$$P = P_0, \quad \theta = 0. \quad (3)$$

Substitution of Eq. 2 then yields:

$$P_0 = P_m - C^{-1}$$

Let $P_m - P_0 = K$, then

$$K = C^{-1}. \quad (4)$$

With relation Eq. 3, the special solution of differential equation Eq. 1 can be obtained as:

$$P = P_m - Ke^{-\beta P_0 \eta_0 (a\theta + c\theta^2)} \quad (5)$$

where c is $b/2$, and the other symbols are the same to the corresponding formers, respectively. Since the study is on the volume increase after SAP-treated soil has absorbed water, P is an increasing function, that is, it satisfies $a \geq -2c\theta$.

Therefore, Eq. 5 is a numerical model for describing the volume change after SAP-treated soil has absorbed water.

Let $I = \{\theta | 0 \leq \theta \leq \xi\}$, where $\xi \in R_+$, and R_+ is a positive real number, and $f(\theta, P) = \beta P_0 \eta_0 (P_m - P)(a + b\theta)$, then f and $\frac{\partial f}{\partial P}$ are both continuous functions when $\theta \in I$. Thus, Eq. 5 is the only solution to the differential equation derived from Eqs. 1 and 3 in terms of the initial conditions.

However, in mathematics, when $\theta \rightarrow \infty$, then $f \rightarrow \infty$ which shows that the solution to Eq. 1 has singular points P_s .

The differential equation composed of Eq. 1 and initial condition 3 satisfies that f and $\frac{\partial f}{\partial P}$ are both continuous functions, besides, the explicit solution to Eq. 2 has local boundary, so P can be continued to $I_m = \{\theta | 0 \leq \theta < \infty\}$.

In fact, with Eq. 2 and the relation $P_s = P_m$, the following equation can be obtained:

$$\lim_{\theta \rightarrow \infty} \{P(\theta, \theta_0, P_0) - P_s\} = 0.$$

Therefore, the special solution formula is asymptotically stable.

Based on the above-mentioned discussion, Eq. 1 has practical sense when describing the volume change of watered SAP-treated soil, that is, the volume of SAP-treated soil changes after it has absorbed water, and once the volume has reached a maximum value P_m , it will stop changing no matter how much more water is added.

Parameters

To use this model, the parameters η_0 , a and c need to be calculated using the experimental data.

According to Eq. 5, the following equation can be given:

$$P_m - P = (P_m - P_0)e^{-\beta P_0 \eta_0 (a\theta + c\theta^2)}.$$

To solve this equation, take logarithms of both sides, then

$$\ln(P_m - P) = \ln(P_m - P_0) - \beta P_0 \eta_0 (a\theta + c\theta^2)$$

and hence,

$$\ln \frac{(P_m - P)}{(P_m - P_0)} / \beta P_0 \theta = -\eta_0 c \theta - \eta_0 a \quad (6)$$

Equation 6 is a linear equation about water content θ , wherein $\eta_0 c$ is the slope of straight line and $\eta_0 a$ is the intercept of straight line.

The parameters η_0 , a and c in the model can be determined with P , which is measured in SAP-treated soil at different water contents with different SAP application rate. As can be seen from Eq. 6, the model actually has only two parameters, i.e., $\eta_0 c$ and $\eta_0 a$.

Four different SAP application rates were studied. The data, respectively, obtained in SAP: dry soil ratios of 1:5,000, 1:2,000 and 1:500 were used to determine the parameters. After the data were optimized and calculated, the result is as follows.

In terms of loam, $\eta_0 c$ and $\eta_0 a$ are calculated as:

$$\begin{cases} \eta_0 c = 0.25 \times 10^6 \\ \eta_0 a = -0.39 \times 10^5 \end{cases}$$

so the model for loam is:

$$\ln \frac{(P_m - P)}{(P_m - P_0)} / \beta P_0 \theta = -\eta_0 c \theta - \eta_0 a. \quad (7)$$

In this model, the relation between SAP application rate and P_m is shown in Fig. 3.

Thus, P_m can be obtained as:

$$P_m = -1,638 \times W^2 + 25.796 \times W + 0.703. \quad (8)$$

Due to $W = \beta P_0$, substitution of Eq. 7 is:

$$\begin{aligned} \ln \frac{(-1,638 \times W^2 + 25.796 \times W + 0.703 - P)}{(-1,638 \times W^2 + 25.796 \times W + 0.703 - P_0)} / W\theta \\ = -0.25 \times 10^6 \theta + 0.39 \times 10^5 \end{aligned} \quad (9)$$

Fig. 3 Relation between SAP application rate and P_m for loam

where $P_0 = 0.6452$, and the other symbols are the same to the corresponding formers, respectively.

In terms of loam, $\eta_0 c$ and $\eta_0 a$ are calculated as:

$$\begin{cases} \eta_0 c = 0.81 \times 10^5 \\ \eta_0 a = -0.18 \times 10^5 \end{cases}$$

so the model for sandy loam is:

$$\ln \frac{(P_m - P)}{(P_m - P_0)} / \beta P_0 \theta = -\eta_0 c \theta - \eta_0 a \quad (10)$$

In this model, the relation between SAP application rate and P_m is shown in Fig. 4.

Thus, P_m can be obtained as:

$$P_m = -18,680 \times W^2 + 71.877 \times W + 0.679. \quad (11)$$

Due to $W = \beta P_0$, substitution of Eq. 10 gives:

$$\ln \frac{(-18,680 \times W^2 + 71.877 \times W + 0.679 - P)}{(-18,680 \times W^2 + 71.877 \times W + 0.679 - P_0)} / W \theta = -0.81 \times 10^5 \theta + 0.18 \times 10^5 \quad (12)$$

where $P_0 = 0.6711$, and the other symbols are the same to the corresponding formers, respectively.

Test model

The model is tested with the data at SAP:dry soil ratio of 1:1,000. The results are shown in Figs. 5 and 6. They indicate that the average deviation of specific volume P is approximately 0.01. Thus, the model achieved satisfying simulation results.

Besides the above case, we also calculated the parameters of the model using the data of any three of these four ratios, respectively, and tested the model using the data of the rest one ratio, see Table 4. It shows that the average deviation is 0.0099–0.016 for the loam and 0.0094–0.013 for the sandy loam, so simulation results are satisfying, and the model is reliable.

The range of 1:5,000–1:500 of SAP:dry soil ratio has basically covered all the application circumstances for

Fig. 4 Relation between SAP application rate and P_m for sandy loam

Fig. 5 Specific volume P of SAP-treated loam versus water content θ

Fig. 6 Specific volume P of SAP-treated sandy loam versus water content θ

different agricultural crops. The model can be applied to the other ratios and other soil types which are not involved in the experiment. If the soil type and its parameters are, respectively, the same to those used in this paper, the model and its parameters calculated in this paper can be directly used. In other cases, the generic model will be used, but the parameters of the model need to be calculated with the specific experimental data. The following is the application of model (Eqs. 9, 12).

Soil swelling ratio

Based on Eqs. 9 and 12, porosity change of watered SAP-treated soil can be analyzed. By using the models, P – θ curve of each soil sample at different SAP application rates can be obtained, thereby, the model for volume change of watered SAP-treated soil can be constructed, which is the key to study soil swelling.

Soil swelling ratio Assume the specific volume of SAP-treated soil is P_i ($i = 1, 2, \dots$) at each of the different water

Table 4 Average deviation of P at different SAP:dry soil ratios

Test (SAP:dry soil ratio)		Average deviation of P
Loam ($P_0 = 0.6452$)		
1:500	$\ln \frac{(-2,941 \times W^2 + 33,649 \times W + 0.6827 - P)}{(-2,941 \times W^2 + 33,649 \times W + 0.6827 - P_0)} / W\theta = -0.29 \times 10^6 \theta + 0.42 \times 10^5$	0.016
1:2,000	$\ln \frac{(-1,6851 \times W^2 + 84,991 \times W + 0.6849 - P)}{(-1,6851 \times W^2 + 84,991 \times W + 0.6849 - P_0)} / W\theta = -0.36 \times 10^6 \theta + 0.61 \times 10^5$	0.0099
1:5,000	$\ln \frac{(-1,342 \times W^2 + 20,662 \times W + 0.6795 - P)}{(-1,342 \times W^2 + 20,662 \times W + 0.6795 - P_0)} / W\theta = -0.45 \times 10^6 \theta + 0.68 \times 10^5$	0.013
Sandy loam ($P_0 = 0.6711$)		
1:500	$\ln \frac{(-35,984 \times W^2 + 91,568 \times W + 0.6871 - P)}{(-35,984 \times W^2 + 91,568 \times W + 0.6871 - P_0)} / W\theta = -0.75 \times 10^5 \theta + 0.14 \times 10^5$	0.013
1:2,000	$\ln \frac{(-10,546 \times W^2 + 65,278 \times W + 0.6913 - P)}{(-10,546 \times W^2 + 65,278 \times W + 0.6913 - P_0)} / W\theta = -0.88 \times 10^5 \theta + 0.27 \times 10^5$	0.0094
1:5,000	$\ln \frac{(-12,960 \times W^2 + 66,957 \times W + 0.6821 - P)}{(-12,960 \times W^2 + 66,957 \times W + 0.6821 - P_0)} / W\theta = -0.80 \times 10^5 \theta + 0.16 \times 10^5$	0.011

contents, and P_0 is the specific volume of the corresponding air-dried soil or oven-dried soil, then swelling ratio can be measured by the relation:

$$r = \frac{P_i}{P_0} = \frac{V_i/m}{V_0/m} = \frac{V_i}{V_0}$$

where V/m is the formula of P , and V_i/V_0 is the ratio of the volume of SAP-treated soil at different water contents to that of air-dried or oven-dried soil (see Figs. 7, 8).

As can be seen from Figs. 7 and 8, whether it is loam or sandy loam, the swelling ratio r increases with water content θ . As for the same soil sample, the higher SAP application rate, the higher r is, namely, the higher water content, the more SAP absorbs water and the more the soil swells, and thereby the value of r is higher.

According to the above-mentioned simulation process, the value of swelling ratio can be obtained after the

parameters have been calculated. Since volume rate closely relates to volume ratio r , that is, volume rate increases with volume ratio, no more statement about volume rate is made herein.

Soil porosity and saturated water content

$$\phi = 1 - \frac{\rho_b}{\rho_s}$$

The formula of soil porosity is

$$\phi = 1 - \frac{\rho_b}{\rho_s}$$

where ρ_b is the density of SAP-treated soil at different water contents; ρ_s is the density of original soil; and Φ can also be regarded as the volumetric moisture content of SAP-treated soil at a certain water content (see Fig. 9).

Fig. 7 Swelling ratio r of SAP-treated loam versus water content θ (SAP:soil = 1:5,000, 1:2,000, 1:1,000, 1:500)

Fig. 8 Swelling ratio r of SAP-treated sandy loam versus water content θ (SAP:soil = 1:5,000, 1:2,000, 1:1,000, 1:500)

Fig. 9 Porosity Φ of SAP-treated soil versus water content θ (SAP:soil = 1:5,000, 1:2,000, 1:1,000, 1:500)

Figure 9 shows that, for loam, soil porosity Φ increases with water content θ ; for the same soil sample, the higher the SAP application rate, the higher soil porosity Φ is. Quantitative expression of porosity of SAP-treated soil has an important significance for the practical application of SAP and for water movement, solute transport and root water uptake of SAP-treated soil.

With this model, the porosity of SAP-treated soil at any water content can be determined. In addition, by using this model, Φ can be determined and then used to calculate transfer functions so as to provide a basis for determining hydraulic conductivity of SAP-treated soil.

Discussion

After the soil was treated with SAP, the originally stable soil physical properties are changed, so SAP-treated soil is assumed as a kind of soil with super capacity of absorbing and desorbing water. Only by this, can the methods and formulas adaptive to general physical parameters be used in this study.

Soil physical properties change constantly after it is treated with SAP, so the changes occurring in the course of measurement have to be ignored. As we all know, SAP's capacity of absorbing and desorbing water is a physical

process. Although the model has been used to determine the parameters and tested, a lot more need to be further studied on the properties of SAP-treated soil, such as: to conduct an experiment to study its repeated drying–wetting alternation condition as a basis for further quantitative study; to construct a model in the field circumstances where SAP-treated soil coexists with original soil; to study the relation between soil physical properties and SAP's useful time; to study the fate of those changed porosity after SAP is invalidated; to study water movement, solute transport and root water uptake of SAP-treated soil; and to study the effect of SAP on crop transpiration, etc.

Conclusion

The study shows that the application of SAP can reduce soil bulk density, improve soil permeability and cause soil swelling. In addition, the paper constructed a model for porosity change in SAP-treated soil after it had absorbed water, which is $\ln \frac{(P_m - P)}{(P_m - P_0)} / \beta P_0 \theta = -\eta_0 c \theta - \eta_0 a$. This is a generic model. Two soil samples, i.e., loam and sandy loam, were used to calculate parameters and tested the model, and the result showed the model is reliable.

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