

Interpretation of ion exchange in soil-bentonite mixtures

Interprétation de l'échange d'ions dans les mélanges sol-bentonite

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ABSTRACT: This study investigated the Ca^{2+} - Na^+ exchange within soil-bentonite (SB) mixtures, commonly employed in the construction of vertical cut-off walls, with a primary focus on the Ca^{2+} sorption and Na^+ desorption processes. Batch tests were conducted using sodium bentonite, decomposed granite soil, and SB (7.5% mass fraction of bentonite), in CaCl_2 solutions with concentrations ranging from 0.5 to 50 mmol/L. The results revealed a significant impact of the water-absorbing swell of bentonite on the volume of the bulk solution, which interfered the calculation of Ca^{2+} sorption. Notably, Na^+ desorption ceased when the bulk Ca^{2+} concentration exceeded 4 mmol/L, simplifying the development of Ca^{2+} - Na^+ exchange into Ca^{2+} sorption process. The sorption isotherms of SB, Soil, and bentonite are proportional to their respective bentonite mass fractions. By incorporating parameters related to volume change and sorption isotherms, an average concentration of montmorillonite interlayer space (C_{in}) was proposed. Correlations were founded between C_{in} and the hydraulic conductivity of SB, offering insights into permeability changes based on batch test results.

RÉSUMÉ: Cette étude explore le comportement d'échange Ca^{2+} - Na^+ dans les mélanges de sol-bentonite (SB) couramment utilisés dans la construction de murs de confinement verticaux. L'accent est mis sur l'adsorption du Ca^{2+} et la désorption du Na^+ dans le mélange SB. Des essais en lots ont été effectués avec de la bentonite sodique, du sol de granite décomposé, et du SB (7,5 % en masse de bentonite), en utilisant des solutions de CaCl_2 de 0,5 à 50 mmol/L. Les résultats montrent un impact significatif du gonflement de la bentonite sur le volume de la solution en vrac, influençant le calcul de l'adsorption de Ca^{2+} . La désorption du Na^+ cesse lorsque la concentration en Ca^{2+} dépasse 4 mmol/L, simplifiant le comportement d'échange d'ions en un processus d'adsorption de Ca^{2+} . Les isothermes d'adsorption du SB, du sol, et de la bentonite sont proportionnelles à leurs fractions massiques respectives de bentonite. En incorporant des paramètres liés au changement de volume et aux isothermes d'adsorption, une concentration moyenne de l'espace interlamellaire de montmorillonite (C_{in}) est proposée. Des corrélations sont établies entre C_{in} et les conductivité hydrauliques du SB, offrant des perspectives sur les changements de perméabilité basés sur les résultats des essais en lots.

Keywords: Soil-bentonite; ion-exchange; batch test; sorption; free swell.

1 INTRODUCTION

Soil-bentonite (SB), a mixture of parent soil and sodium bentonite, is widely utilized in constructing vertical cut-off walls because of its exceptional impermeability and self-healing properties (Evans, 1993; Takai et al., 2013) attributed to the added bentonite (Bradshaw & Benson, 2014; Gleason et al., 1997).

The ion exchange of sodium bentonite involves the replacement of Na^+ within the montmorillonite lattice with other cations from the bulk solution, thereby weakening the barrier performance of bentonite. While previous research has delved into the ion exchange of pure sodium bentonite (Egloffstein, 2001; Whittaker et al., 2019), less attention has been given to the ion exchange behavior of SB, which contains only small

quantities of bentonite. Furthermore, challenges persist in assessing material permeability through ion exchange analysis.

Batch test offers an effective means of evaluating ion exchange by subjecting sodium bentonite to multivalent cation solutions (Kaya & Ören, 2005; Meneguín et al., 2017). Existent sorption theories have been found to align well with the characteristics of bentonite when the bulk cation concentration was below 1 g/L. However, its sorption behavior when bulk cation concentrations resembling those found in real-world contaminated leachate (Naveen et al., 2017) is not comprehensively understood.

The aim of this study is to examine the Ca^{2+} - Na^+ ion exchange behavior of SB and compare it with the behavior in pure bentonite and parent soil. This investigation involves conducting batch tests with pure

Table 1. Physical properties of soil materials.

		Na-bentonite	Decomposed granite soil	SB	Note
Particle density	(g/cm ³)	2.79*	2.65	2.66	JIS A 1202
Montmorillonite content	(%)	48*	-	-	* Komine et al., 2009
CEC Na ⁺	(meq/g)	0.631*	-	-	
CEC Ca ²⁺	(meq/g)	0.464*	-	-	
Plastic limit	(%)	26.55	NP	NP	
Liquid limit	(%)	522.0	NP	25.03	JIS A 1205

bentonite, SB, parent soil and free swell tests with bentonite in CaCl₂ solutions over a concentration range from 0.5 to 50 mmol/L. Additionally, the study seeks to establish a correlation between ion exchange behavior and the permeability of SB.

2 MATERIALS AND METHODS

2.1 Soil materials

The physical properties of soil materials are listed in Table 1. Decomposed granite soil (Soil), which is a sandy soil widely distributed in the subsurface throughout Japan (Ham et al., 2010), was used as the parent soil. Kunigel V1, one of the sodium bentonites collected in Japan (Komine et al., 2009), was used as the bentonite added to the parent soil.

In order to simulate the SB that have been used in Japan (Takai et al., 2016), moisture content of prepared SB is designed as 29%, and mass fraction of sodium bentonite in SB is controlled at $n_{bent.} = 7.5\%$:

$$n_{bent.} = m_{bent.} / (m_{bent.} + m_{soil}) \quad (1)$$

where m_x (g) represents the dry mass of bentonite or decomposed granite soil.

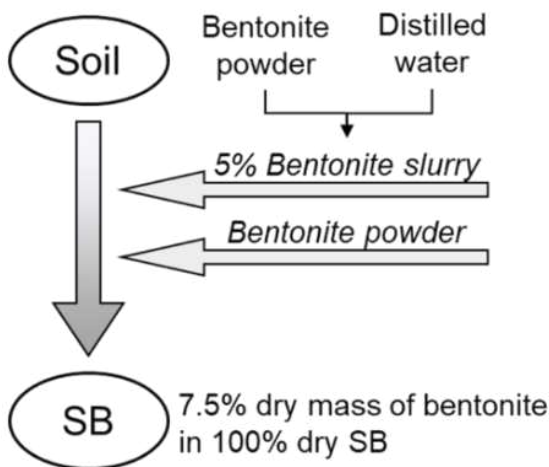


Figure 1. SB mixing procedures.

The procedures of SB preparation is given in Figure 1. The Soil was first passed through 2 mm sieve and

then dried by 110 °C oven, while the bentonite powder was air dried with 7.2% initial moisture content, and the 5% bentonite slurry was prepared by mixing bentonite powder with distilled water at a mass ratio of 1:20 for 20 minutes using an aqueous mixer. The slurry was first added into the dried Soil, where the bentonite mass in the slurry was counted in the total $m_{bent.}$. Then, the input of bentonite powder was divided into several times. After all the bentonite powder and water were inputted, the soil mixer will continue to run for 5 minutes to ensure uniform mixing.

2.2 Batch tests

All batch tests were carried out in 250 mL-PP bottles contain 200 mL CaCl₂ with different initial concentrations, the initial Ca²⁺ concentrations for each test were listed in Table 2. The solid inputs in bentonite and SB batch systems were designed to have 0.75 ± 0.01 g bentonite, hence $\approx 12.9 \pm 0.1$ g SB were placed in SB batch systems, the actual mass of SB input depends on its measured moisture content. And for batch tests of soil, 10 ± 0.1 g were placed in each test.

Table 2. Designed conditions of batch tests.

	Initial Ca ²⁺ (mmol/L)									
	0.5	1	5	10	15	20	25	30	40	50
Bentonite	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Soil	✓	✓	✓	✓		✓	✓			
SB	✓	✓	✓	✓	✓	✓	✓			

After adding the solids, the bottles were secured on an oscillator and agitated at 3.33 Hz for 24 hours. Following agitation, the bottles were left undisturbed for 15 minutes. The solution was then extracted and centrifuged at 3000 rpm for 10 minutes and filtrated through 0.2 μm filter to collect the supernatant for ionic measurement. Each test was triplicated.

The widely known mass conservation for batch system stands as below:

$$q_e = (V_0 C_0 - V_e C_e) / m_s \quad (2)$$

where q_e (mmol/g) is the sorption or desorption amount of specific component at the end of test; V_0 and V_e (L) are the volumes of bulk solution at initial and final states; C_0 and C_e (mmol/L) are the molarities of

specific component in the bulk solution at initial and final states; m_s (g) is the dry mass of solid.

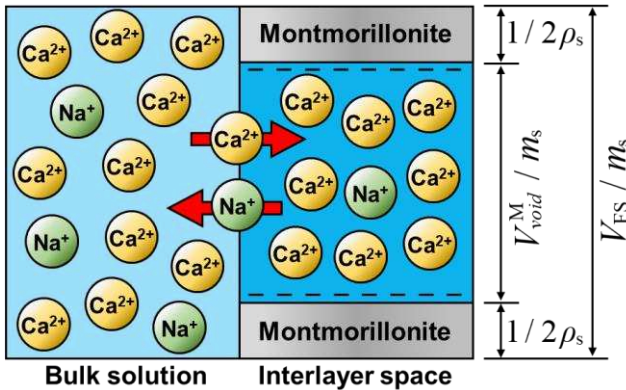


Figure 2. Schematic of montmorillonite unit in bentonite batch system.

Generally, V_0 and V_e are treated as equal. However, in bentonite batch system, the border line between bulk solution and solid particle become ambiguous, the water molecule as well as cations in the solution will be attracted into interlayer space of montmorillonite lattices and be restrained by electrostatic force (Figure 2). In an unfree state, the solution in the interlayer space, strictly speaking, is in a different state than the bulk solution. Therefore, the interlayer space should be eliminated to obtain the volume of bulk solution precisely, the final volume of bulk solution can be calculated by:

$$V_e = V_0 - V_{void}^M + w \cdot m_s / \rho_w = r \cdot V_0 \quad (3)$$

where V_{void}^M (mL) is the volume of the montmorillonite interlayer in batch system; $w \cdot m_s / \rho_w$ (mL) is the volume of water previously present in the soil; w is gravimetric moisture content. Simplifying V_e as V_0 multiplied by a numerical coefficient r , the mass conservation becomes:

$$q_e = V_0 \cdot (C_0 - r \cdot C_e) / m_s \quad (4)$$

It has to be noted that in a batch system of bentonite and CaCl_2 solution, for Ca^{2+} sorption, the value of q_e is positive, it represents the sum of Ca^{2+} amount that directly contact to the solid particles and those trapped in the interlayer of montmorillonite lattice; and for Na^+ desorption, the value of q_e is negative since $C_0 = 0$, it only represents the Na^+ amount in the bulk solution at the end. According to Eq (4), the diversity of q_e between taking volume change into account or not rises when either the r is not approximately equal to one or the value of C_e is very large, the comparison between sorption/desorption isotherms obtained using

coefficient r or not had also been conducted in this study.

2.3 Free swell tests

The free swell tests correspond to ASTM D5890 (2019) were conducted in order to find the volume of interlayer space of montmorillonite under different CaCl_2 concentrations. The designed initial Ca^{2+} molarities were consistent with the batch conditions.

The tests were conducted in 100 mL graduated cylinders. Initially, each cylinder was filled with a solution up to 90 mL. Next, 2 g of dry bentonite powder were carefully added without touching the cylinder's walls. The cylinder was then topped up to 100 mL with a solution and left undisturbed for 24 hours. The results were obtained when the bentonite volume reading in the cylinder remained unchanged for 6 hours, at which point the supernatant was collected and the equilibrium concentrations of Na^+ and Ca^{2+} were measured.

The volume of the montmorillonite interlayer space per unit mass of bentonite was calculated by:

$$V_{void}^M / m_s = V_{FS} / m_s - 1 / \rho_s \quad (5)$$

where V_{FS} / m_s (mL/g) is the free swell volume per gram observed from the test; ρ_s (g/cm^3) is the particle density of bentonite.

2.4 Measurement of ionic compositions

The molarities of Ca^{2+} and Na^+ in the supernatants collected from batch tests and free swell tests, and their initial concentrations in every test were measured by an atomic emission spectrometer (SHIMADZU, ICPE-9800). All fluids were collected in 15 mL centrifuge tubes and stored at 4°C previous to the measurement.

3 RESULTS

3.1 Montmorillonite interlayer space

The change of montmorillonite interlayer space of unit mass V_{void}^M / m_s at different Ca^{2+} concentrations obtained from free swell tests according to the Eq (5) are given in Figure 3, the bulk concentrations in the figure are the concentrations when the free swell volumes were read. It can be seen that the V_{void}^M / m_s decrease significantly as the increase of Ca^{2+} molarity in the solution, and the V_{void}^M / m_s at any Ca^{2+} molarity in bulk solution less than 50 mmol/L can be precisely estimated.

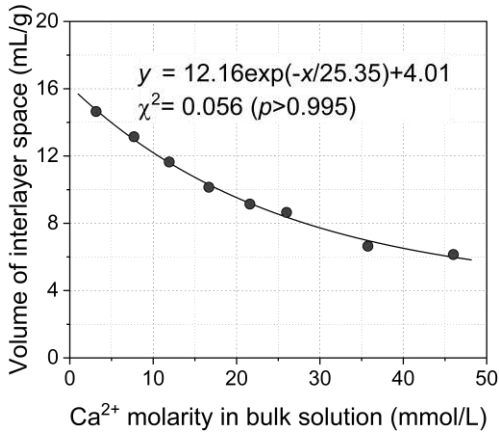


Figure 3. Interlayer space of bentonite in different Ca^{2+} concentrations.

3.2 Sorption and desorption isotherms

All isotherms in this study were plotted with an independent variable of Ca^{2+} molarity in bulk solution, the isotherms obtained without considering the volume change were labelled as Ordinary, while isotherms obtained using Eq (4) were labelled as Modified.

The sorption and desorption isotherms in bentonite and SB batch systems are given in Figure 4, the isotherms in the two systems exhibited same characteristics. For Ca^{2+} sorption, the ordinary isotherms shared a trend of decreasing when the Ca^{2+} concentration in bulk solution exceeded 10 mmol/L while the modified isotherms tended to remain unchanged. The differences between two kinds of isotherms gradually increased with the increase of Ca^{2+} concentration in bulk solution. In Figure 4, when the Ca^{2+} concentration closed to 50 mmol/L, the

modified q_e was almost 3 times of the ordinary q_e , meanwhile the estimated interlayer space for 0.75 g bentonite at 50 mmol/L Ca^{2+} was about 3.75 mL, which was only approximately 1.88% of the V_0 . Such differences between ordinary isotherms and modified isotherms indicate that when the calculation of bentonite sorption based on mass conservation of batch system was proceeded, the volume changes of bulk solution can be eliminated only when the concentration of bulk solution is very low (at least < 4 mmol/L for Ca^{2+}).

On the other hand, the change of bulk volume did not generate huge diversities in Na^+ desorption isotherms. Recalling Eq (4), when $C_0 = 0$, the differences between two kinds of isotherms would only depend on the value of r , hence slightly change in bulk volume only have slightly effect to the calculated Na^+ desorption amount. The Na^+ desorption isotherms indicating that the original Na^+ in bentonite were quickly and completely replaced by Ca^{2+} meanwhile the Ca^{2+} sorption were still developing, the development of so-called Ca^{2+} - Na^+ exchange were dominated by the extent of Ca^{2+} sorption when bulk Ca^{2+} exceeded 4 mmol/L. Thus, the binary process of ion exchange in bentonite and SB batch systems could be simplistically described, to a large extent, by single process of Ca^{2+} sorption.

The isotherms in the Soil batch systems are given in Figure 5. Neither Ca^{2+} nor Na^+ had illustrated obvious sorption or desorption, confirmed that decomposed granite soil did not undergo significant ion exchange process, and the isotherms of SB were mostly contributed by the properties of bentonite.

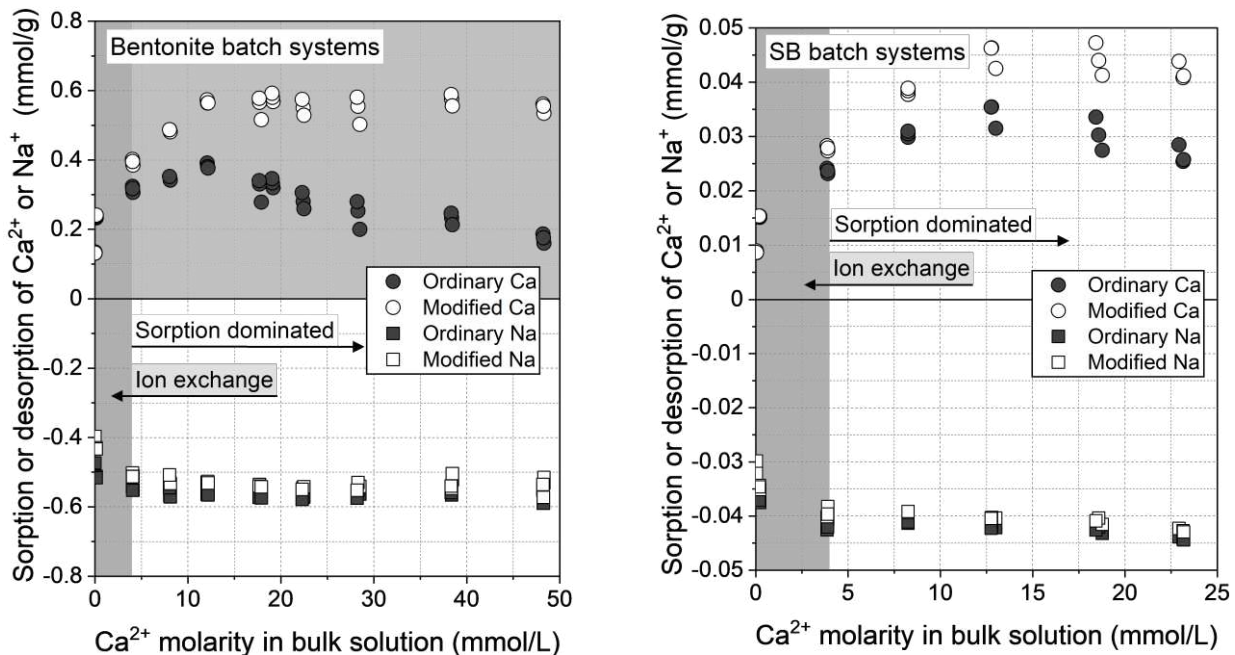


Figure 4. Sorption/desorption isotherms in bentonite (left) and SB (right) batch systems.

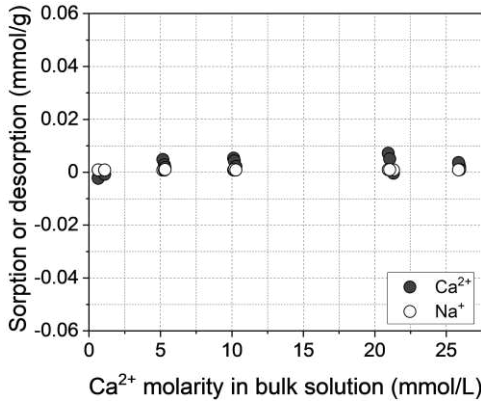


Figure 5. Sorption/desorption isotherms in decomposed granite soil batch systems.

4 DISCUSSION

For the obtained Ca^{2+} sorption isotherms of bentonite, Soil, and SB, quantitative relation based on mass fractions theoretically exist as below:

$$q_{\text{SB}} = n_{\text{bent.}} \cdot q_{\text{bent.}} + (1 - n_{\text{bent.}}) \cdot q_{\text{soil}} \quad (6)$$

where q_{sub} is the numerical function of sorption isotherm of specific substance; $n_{\text{bent.}} = 7.5\%$ in SB mixture, and $q_{\text{soil}} = 0$ is approximated. In Figure 6, $q_{\text{bent.}}$ was well fitted by Exponential model, and the plots of SB were in line with the calculated q_{SB} , indicating that Soil and bentonite did not interact to each other in batch tests, the Ca^{2+} sorption potential of bentonite can be fully exploited in SB with a 7.5% mass fraction.

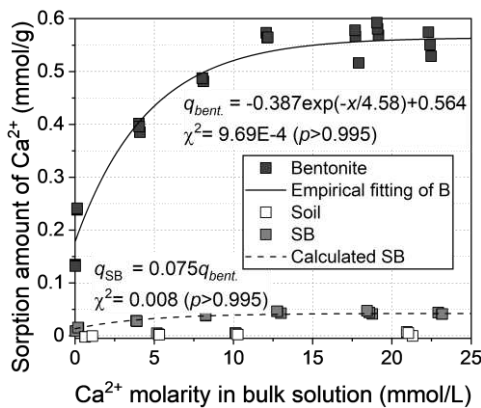


Figure 6. The relation between modified Ca^{2+} sorption isotherms of bentonite, Soil and SB.

Though the ion exchange can be simplified as Ca^{2+} sorption process, the increase of Ca^{2+} sorption amount were observed converged when bulk Ca^{2+} molarity reached 25 mmol/L, while the permeability of bentonite materials will continue to increase in higher cation molarities (Norris et al., 2018), which has revealed the limitation of using sorption isotherms to estimate permeability changes.

In physical sense, it is the particle surface area and volume of interlayer space that mostly determine the sorption capacity of bentonite (Figure 2). But 1 g bentonite could have different volume of interlayer space under different conditions, which brings insufficiencies to the description of q_e (mmol/g) for bentonite and SB. By considering both the mass and volume, a sufficient description of average molarity in bentonite interlayer space C_{in} is proposed as below:

$$C_{\text{in}} = (q_e / n_{\text{bent.}}) / (V_{\text{void}}^{\text{M}} / m_s) \quad (7)$$

where the intensive variable C_{in} (mmol/L) links the results of batch test and the free swell test. Since the scope of C_{in} is only the interlayer space in bentonite, C_{in} is actually independent to the $n_{\text{bent.}}$ (q_e is not). The relation between Ca^{2+} molarity in bulk solution and C_{in} is given in Figure 7. C_{in} of Ca^{2+} keeps increasing as bulk concentration and is linearly related to the Ca^{2+} molarity in bulk solution. It can be inferred that the convergence trend of sorption isotherms is limited by the decrease of volume.

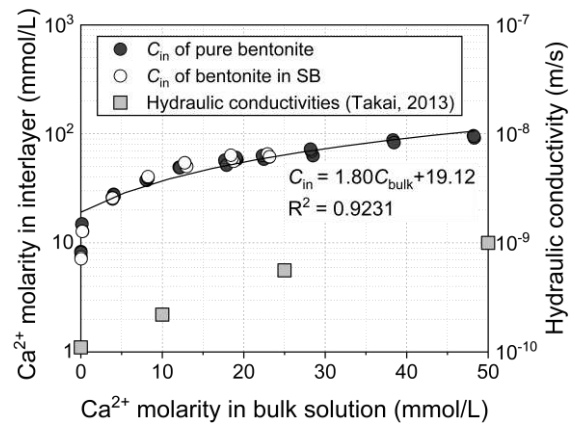


Figure 7. The relations between Ca^{2+} molarity in bulk solution and C_{in} or hydraulic conductivity.

Comparing the C_{in} with hydraulic conductivity of SB prehydrated with CaCl_2 solutions, under same concentration range by flexible-wall permeability test (Takai et al., 2013), the increase in hydraulic conductivity was a macroscopic phenomenon that occurred simultaneously with the increase of C_{in} . In addition, it is possible to estimate the permeability changes of SB based on the value of C_{in} .

5 CONCLUSIONS

By analysing the results of batch test and the free swell test, the following conclusions were obtained.

(1) In bentonite and SB batch systems, the bulk volume changed as the osmotic swell of bentonite, when bulk Ca^{2+} molarity was closed to 50 mmol/L, the

1.88% of the volume change resulted in an error of nearly 300% in the Ca^{2+} sorption amount.

(2) The developments of Ca^{2+} - Na^+ exchange process observed in bentonite and SB batch systems were dominated by the extent of Ca^{2+} sorption, when Ca^{2+} bulk concentrations were >4 mmol/L.

(3) The bentonite with 7.5% mass fraction in SB can fully exploit its Ca^{2+} sorption potential as pure bentonite. The measured Ca^{2+} sorption isotherms of bentonite, Soil, and SB are proportional to their respective bentonite mass fractions.

(4) Average molarity in bentonite interlayer space (C_{in}) was proposed, based on the sorption isotherms and results of free swell test. C_{in} was observed to be linearly related to the bulk Ca^{2+} concentration and can be used to estimate the permeability change of SB.

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