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TECHNICAL NOTE

Sr^{2+} Sorption and Leach Rate Studies on Synthetic Calcium Silicate Hydroxy Hydrate

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Synthetic calcium silicate hydroxy hydrate, which is identical to unsubstituted and substituted 1.1-nm tobermorite mineral, has the capacity to pickup selectively Sr^{2+} cation from mixed cationic solutions in the presence of 1,000 times concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, and Ba^{2+}. The selective uptake of Sr^{2+} from mixed cationic solutions and simulated intermediate level waste (ILW) solutions has been quantified as distribution coefficient (K_d) and decontamination factors (Df). The sorption studies have been performed by analysis of Sr^{2+} in solution both by atomic absorption spectrophotometry and radiometric measurements. The proportional depletion of β activity from strontium solutions labeled with isotope Sr^{90} has been utilized to study the concentration and mass dependence of the Sr^{2+} uptake by the exchanger. Kielland coefficients at 25°C have been determined from the isotherms plotted for the $Sr^{2+} \rightleftharpoons Ca^{2+}$ system. Leach rate studies on the blocks made from ordinary portland cement (OPC) + tobermorite admixtures show that the release rate of Sr^{2+} from cement matrix is drastically lowered when the additive is increased. By using 40 wt% Al-substituted tobermorite as an additive to OPC, we found that it was possible to fix about 77% of Sr in cement matrix against 17% fixation in the OPC. ADVANCED CEMENT BASED MATERIALS 1995, 2, 119–124

KEY WORDS: Al-substituted tobermorite, Intermediate level waste, $Strontium^{90}$, Sorption, Leaching

Various inorganic cation exchangers, such as framework alumino-silicates, layered zirconium phosphates [1–4], and clay minerals [5], have potential applications due to their low cost of synthesis and ion selective properties toward a large number of alkali metal, alkaline earth, and transition metal cations. These applications vary from use in water softening, catalysis, and fertilizers to use in fixing of hazardous radioisotopes of nuclear effluents in cement and concrete matrices. Recently, synthetic crystalline aluminium substituted calcium silicate hydroxy hydrate close to natural tobermorite has been shown to possess ion selectivity for cesium [6–9]. The mechanism of cation uptake in these minerals has been determined, for example, the selectivity for radiocesium of aluminium-substituted tobermorite [10]. The aim of this study is to examine the reactivity of 11 Å tobermorite toward Sr^{2+} using radiometric and conventional analytical methods. The title study has been undertaken to explore the possibility of the use of this material as an additive to ordinary portland cement (OPC) for radioactive waste management. It is well known that the OPC and allied materials are often used to handle the nuclear effluents that contain small amounts of Sr^{90}. It was, therefore, thought appropriate to study the sorption behavior of synthetic 11 Å tobermorite and to perform leach rate studies on compact blocks prepared from OPC-tobermorite mixtures after 40 days of curing.

Experimental

Various formulations of phase pure tobermorites have been synthesized by the procedure described by Kalousek [11]. The hydrothermal preparations of tobermorite samples matched well in intensities and positions with JCPDS file no. 19-1364 [12]. The commercially available OPC sample was thoroughly powdered to 200 mesh, and its phases were identified by X-ray diffraction before samples were prepared for the cation sorption experiments on admixtures. The Sr^{2+} uptake experiments were carried out on various formulations of Al-substituted tobermorite using the following general procedure: 0.025 g of the sample was equilibrated with a mixed cationic solution containing 0.0001 N Sr^{2+} + 0.1 N M^{n+} where $M^{n+} = Na^+/K^+/Ca^{2+}/Mg^{2+}/Ba^{2+}$. After 7 days of equilibration in sealed polyethylene bottles, the supernatent solution was analyzed for Sr^{2+} by GBC 902 atomic absorption spectro-

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TABLE 1. Selective uptake of Sr^{2+} onto various tobermorites from mixed cationic solutions

	Unsubstituted Tobermorite		5% Al-Substituted Tobermorite		6% Al-Substituted Tobermorite		10% Al-Substituted Tobermorite	
Ion Pair	% Sr Removal	K_d*	% Sr Removal	K_d	% Sr Removal	K_d	% Sr Removal	K_d
Sr + Na	20.0	500.0	32.0	941.2	36.0	1125.6	38.4	1246.8
Sr + K	26.4	716.1	36.4	1280.0	40.9	1384.6	40.9	1384.6
Sr + Ca	18.6	457.6	24.1	636.4	27.6	761.9	28.3	788.5
Sr + Mg	26.7	727.3	33.3	945.5	39.7	1319.2	42.3	1466.7
Sr + Ba	2.5	51.3	3.1	64.5	3.1	64.5	4.1	84.7

Normality of solution = 0.0001 N Sr^{2+} + 0.1 N M^{n+} where M^{n+} = $Na^+/K^+/Ca^{2+}/Mg^{2+}/Ba^{2+}$

$$^*K_d = \frac{Sr^{2+}\text{ sorbed/g of exchanger}}{Sr^{2+}\text{ left/ml of solution}}$$

photometer. The amounts of Sr^{2+} uptake were determined from the difference in concentration between the reference and the sample. The selective sorption of Sr^{2+} from simulated intermediate level waste (ILW) solution onto different samples of tobermorites has also been determined following the batch method.

The Sr^{90} uptake on tobermorite samples and OPC was determined by using the ECIL Geiger-Müller counter following the standard procedure of tracer technique. We equilibrated 1.0 g of the material with 50 ml of $1 \times 10^{-2} - 4 \times 10^{-2}$ N $SrCl_2$ solution spiked with Sr^{90} tracer. After 7 days of equilibration, the contents were centrifuged, and the supernatent liquid was separated. We collected 1.0 ml of this liquid on aluminium planchettes and its β activity was measured on the G-M counter. The Sr^{2+} uptake was calculated in terms of the difference of β counts before and after equilibration.

Preparation of the Test Specimen (Blocks) for Leaching

The cylindrical blocks of OPC-tobermorite admixtures were prepared. In the first step, the tobermorite powder in bulk was saturated with Sr^{2+} by equilibrating it 2–3 times in 1,000 mg/dm^3 strontium chloride solution for 48 hours. This was repeated until Sr^{2+} content in the solid became constant. The strontium-loaded powder then was separated by centrifugation and was dried in an oven at 110°C. This material has been used to prepare the 20, 30, and 40 wt% tobermorite containing cylindrical blocks keeping water:solid (w:s) ratio = 0.6.

Sr^{2+} Leach Rate Studies

Leaching behavior of Sr^{2+} from tobermorite was studied at room temperature using the standard method described by Hespe [13] under the following test conditions:

1. The whole specimen was exposed and leachant (water) covered all surfaces of the block.
2. Cylindrical blocks were prepared from the OPC-tobermorite admixtures after 40 days of curing in 100% humidity.

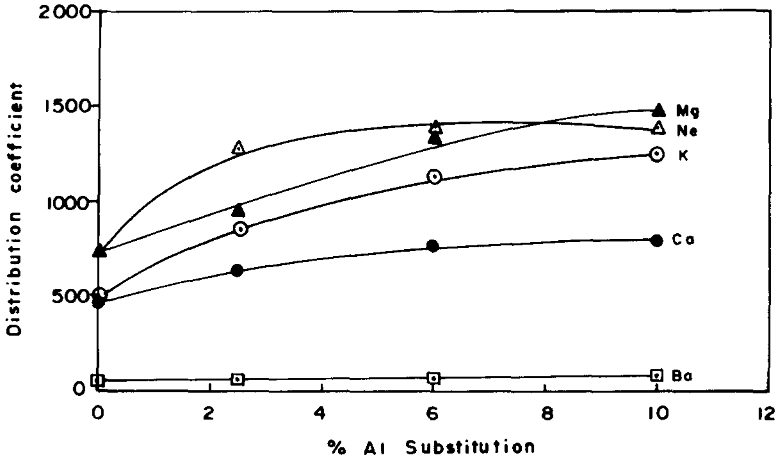

FIGURE 1. Plot of distribution coefficient (K_d) against mol% aluminum-substituted tobermorites.

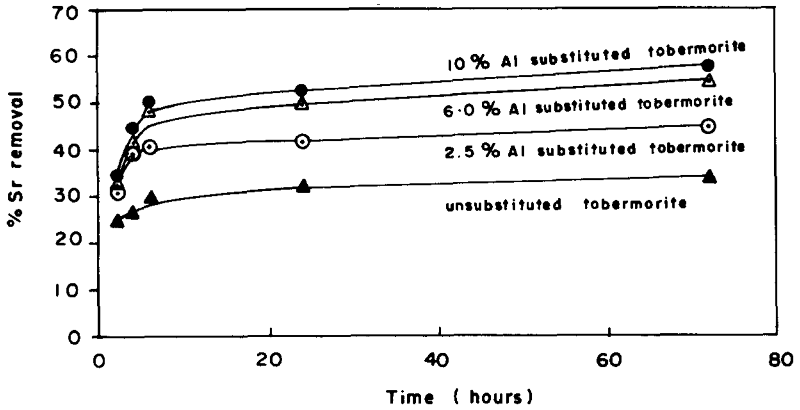

FIGURE 2. Time dependence of strontium uptake onto 0, 2.5, 6, and 10 mol% aluminum-substituted tobermorite. Normality of solution = 0.0001 N Sr; weight of sample = 0.025 g; volume of strontium solution = 50 ml.

3. Sealed polyethylene bottles were used as leachant containers.
4. The leachant was 50 ml of distilled water at 25°C renewed at each sampling. The sampling was done daily for the first week, weekly for 3 weeks, and fortnightly until the 112th day of leaching.

Results and Discussion

Table 1 demonstrates the selective uptake of Sr^{2+} from mixed cationic solutions. The selective sorption of Sr^{2+} is quantified in terms of distribution coefficient and percent strontium removal by various aluminium-substituted tobermorites. The data indicate that Sr^{2+} selectivity increases with increasing level of Al^{3+} substitution for silicon, as also reported elsewhere [14]. This effect can be noticed in Figure 1. The alkali metal exchange in tobermorite is said to be a reversible process [15]. But in the case of Sr^{2+}, the distribution coefficients are greater than those for Cs^+, although they are lower than the values reported for the uptake of several transition metal cations [16,17]. Figure 2 demonstrates the time dependence of Sr^{2+} sorption onto unsubstituted and Al-substituted tobermorites.

It is well known that Sr^{90} is a hazardous isotope (half life = 27.7 years) present in the ILW of nuclear power plants [5]. To study the direct application of this material for Sr^{90} decontamination, the authors have carried out the sorption experiments with simulated ILW. The Sr^{2+} uptake data have been summarized in Table 2. The distribution coefficient (K_d) for 10 mol% Al-substituted tobermorite has been found to be around 971, which corresponds to 32 wt% removal of Sr^{2+}.

To study the radiation stability of the material, we subjected the unsubstituted tobermorite sample to equilibration with Sr^{90} solution for 24 hours. The Sr^{2+} uptake was determined in terms of depletion of β activity. Tables 3 and 4 summarize the concentration and mass dependence of Sr^{90} uptake onto unsubstituted tobermorite, respectively. In case of 0.01 N strontium chloride solution, approximately 56% Sr^{90} removal was observed. Figure 3 compares the concentration dependence of Sr^{90} on tobermorite vis-à-vis OPC. Likewise,

TABLE 2. Selective uptake of Sr^{2+} onto various tobermories from simulated intermediate level waste* solution

	Unsubstituted Tobermorite		5% Al-Substituted Tobermorite		6% Al-Substituted Tobermorite		10% Al-Substituted Tobermorite	
Time of contact (days)	% Sr Removal	K_d	% Sr Removal	K_d	% Sr Removal	K_d	% Sr Removal	K_d
1	14.7	345.9	23.1	600.0	26.9	736.8	29.5	836.4
3	15.4	363.6	25.0	666.7	28.8	810.8	32.1	943.4
7	16.0	381.7	26.3	713.0	29.5	836.4	32.7	971.4
21	15.4	363.6	24.4	644.1	28.2	785.7	31.4	915.9

*Composition of ILW (g/dm^3): Na^+ = 114.170; Al^{3+} = 9.980; Fe^{3+} = 0.025; NO_2^- = 4.800; OH = 21.220; NO_3^- = 160.200; CO_3^- = 6.240; Cs^+ = 0.010; Sr^{2+} = 0.010; Specific gravity = 1.19.

TABLE 3. Radiochemical data on concentration dependent uptake of Sr^{90} onto unsubstituted tobermorite

Normality of Solution	meq/100 g	Df*	K_d	% Sr Removal
4×10^{-2}	79.21	1.66	83.0	39.61
3×10^{-2}	69.47	1.86	93.0	46.31
2×10^{-2}	48.21	1.93	96.5	48.21
1×10^{-2}	28.21	2.29	114.5	56.43

*Decontamination factor (Df) $= \frac{\text{initial concentration}}{\text{final concentration}}$

TABLE 4. Radiochemical data on mass dependent uptake of Sr^{90} onto unsubstituted tobermorite

Amount of Exchanged (g)	Δ Counts*	% Sr Removal	Df	K_d
1.0	3,657	32.84	1.49	74.50
2.0	4,808	43.27	1.76	44.20
3.0	8,014	72.13	3.57	59.50
4.0	9,969	80.72	9.54	119.50
5.0	10,577	95.19	19.89	198.90

Initial counts = 11,137 + 80 counts/min.
*Δ = initial counts − final counts.

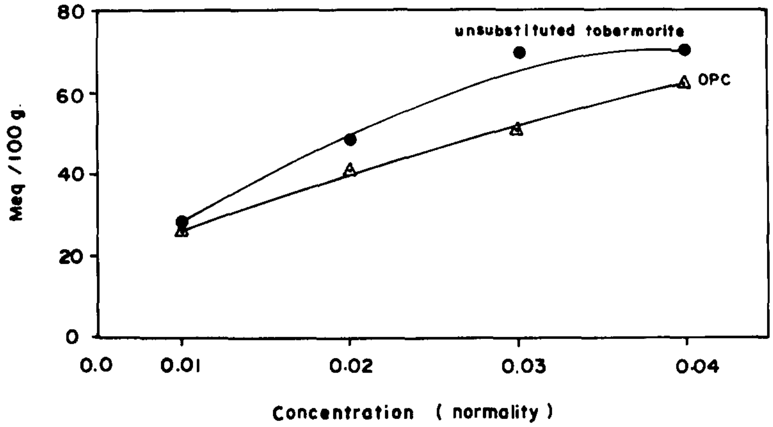

FIGURE 3. Comparison of Sr^{90} uptake onto unsubstituted tobermorite and ordinary portland cement. Time of contact = 24 hours; amount of exchanger = 1.0 g; volume of solution = 50 ml.

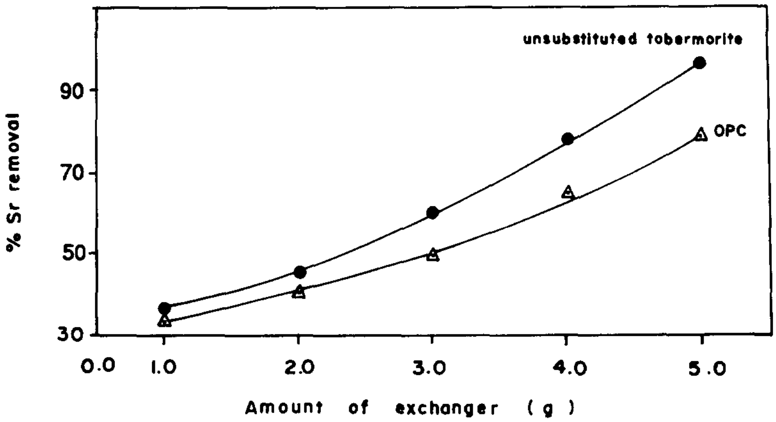

FIGURE 4. Mass dependence of Sr^{90} uptake recorded as percent strontium removal. Time of contact = 24 hours; normality of solution = 0.05 N; volume of solution = 50 ml.

TABLE 5. Mass balance data on $Ca^{2+} \leftrightarrows Sr^{2+}$ system in unsubstituted tobermorite

Initial Concentration ($mmol/dm^3$)	Sr2+ Uptake ($mmol/dm^3$)	Ca^{2+} Release ($mmol/dm^3$)	ΔCa/ΔSr	wt% Sr	K_c^*	meq/100 g Sr^{2+}
1.000	0.652	0.769	1.179	0.232	0.072	2.61
2.135	1.506	1.565	1.039	0.536	0.187	6.02
3.483	2.674	2.972	1.111	0.952	0.491	10.69
4.551	3.292	3.698	1.123	1.172	0.484	13.17
6.854	5.483	6.212	1.133	1.952	1.240	21.93
7.101	5.573	6.869	1.233	1.984	1.253	22.29
8.045	5.910	7.423	1.430	2.104	1.027	23.64
8.674	6.472	7.874	1.217	2.304	1.123	25.89
9.933	6.089	7.756	1.274	2.468	0.615	24.36
11.191	6.652	7.802	1.173	2.368	0.573	26.61
13.573	6.742	7.163	1.062	2.400	0.353	26.97
17.843	6.966	8.212	1.179	2.480	0.272	27.87

*Kielland coefficient (K_c) = (AcBs)/(AsBc) where Ac and As are equivalent fractions of Sr^{2+} in crystal and solution, and Bc and Bs are equivalent fractions of Ca^{2+} in crystal and solution, respectively.

Figure 4 indicates that this material picks up more of Sr^{90} as compared with OPC when the amount of exchanger varies in the range of 1–5 g. In the case of Sr^{90} spiked 0.05 N strontium chloride solution, 5 g of exchanger could decontaminate 50 ml of solution to the extent of 95%. To study the mechanism of selective uptake of Sr^{2+}, we generated the mass balance data (Table 5) from the solution analysis for the $Sr^{2+} \rightleftharpoons Ca^{2+}$ system before and after equilibration. These data show that a little more of Ca^{2+} than the equivalent amount of Sr^{2+} is released leading to a ΔCa:ΔSr ratio of approximately 1.1. This additional release of Ca^{2+} could be due to an unreacted portion of calcium that might be present as traces of $Ca(OH)_2$. To study the retention of strontium, we carried out the Sr^{2+} leach rate determination for each admixture on the cylindrical blocks prepared from OPC + tobermorite admixtures following the International Atomic Energy Agency (IAEA) method [13,18]. When the leach rate of tobermorite containing blocks is compared with that of 100% OPC blocks, we found that Sr^{2+} leach rates are drastically lowered (up to a maximum of 1,000 times) due to addition of 10–40% of tobermorite in OPC (Table 6 and Figure 5). Thus, the following conclusions may be drawn:

1. The Sr^{2+} uptake is accompanied by an equivalent release of Ca^{2+} ions in solution.
2. The tobermorite selectively takes up Sr^{2+} from mixed cationic solutions containing 1,000 times concentrated competing cations, namely Na^+, K^+, Ca^{2+}, Mg^{2+}, and Ba^{2+}. The exchanger shows good stability in aqueous solutions of alkali and alkaline earth cations, however, in the presence of 0.1 N Mg^{2+} solutions (pH ~ 6.5) the precipitation of Mg^{2+} as $Mg(OH)_2$ could also have taken place along with the $Sr^{2+} \rightleftharpoons Ca^{2+}$ exchange reaction. The phase characterization of the after-exchange products is under investigation.
3. The tobermorite has a capacity to effect Sr^{2+} removal from simulated ILW, although to a lesser extent as compared with pure Sr^{2+} solution.
4. The leach rate measurements on tobermorite-containing blocks indicate that addition of tobermorite lowers the leaching of Sr^{2+}.
5. Further, the final analysis of the three post-leached blocks have shown that the strontium content appears to be permanently fixed in cement matrix as follows:

wt% Tobermorite in Block	%Sr Retention after 120 Days of Leaching
00	17.8
20	51.0
30	64.8
40	77.8

TABLE 6. Leach rate data for blocks of OPC + tobermorite admixtures containing 0–40% of 2.5 mol% Al-substituted tobermorite

Leach Time (days)	Leach Rate* (g/m^2 day) × 10^{-3}			
	0% Block†	20% Block	30% Block	40% Block
1	1117.86	250.90	180.34	65.56
2	888.39	178.10	124.28	61.94
3	390.75	110.30	58.38	35.94
4	198.33	78.00	50.37	27.79
5	127.52	57.50	32.68	18.57
6	104.33	50.10	20.00	13.14
7	75.29	37.97	22.55	10.32
14	27.33	13.01	7.16	4.24
21	12.91	7.11	4.43	3.16
28	10.33	3.83	1.59	1.99
43	3.48	1.94	0.87	0.69
58	2.67	0.82	0.35	0.41
73	1.08	0.59	0.21	0.18
97	1.08	0.50	0.24	0.15
112	1.08	0.50	0.24	0.13

Curing time = 40 days. 0% block: wt of block (g) = 4.895; Surface area (sq m) = 0.00113; initial Sr^{2+} (wt%) = 0.06; S/V (cm^{-1}) = 4.498; 20% block: wt of block (g) = 4.962; surface area (sq m) = 0.00126; initial Sr^{2+} (wt%) = 1.44; S/V (cm^{-1}) = 4.013; 30% block: wt of block (g) = 4.927; surface area (sq m) = 0.00138; initial Sr^{2+} (wt%) = 2.16; S/V (cm^{-1}) = 3.662; 40% block: wt of block (g) = 4.983; surface area (sq m) = 0.00150; initial Sr^{2+} (wt%) = 2.88; S/V (cm^{-1}) = 3.412.

*Leach rate $(l)/(c) \cdot (w)/(t \times s)$ (g/m^2day) where l = quantity of ion in leach solution, c = quantity of ion left in solid block, w = initial weight of solid test specimen, t = time of leach, s = surface area of test specimen.

†0% block has been prepared from 1000 mg/dm^3 solution keeping w:s ratio 0.6.

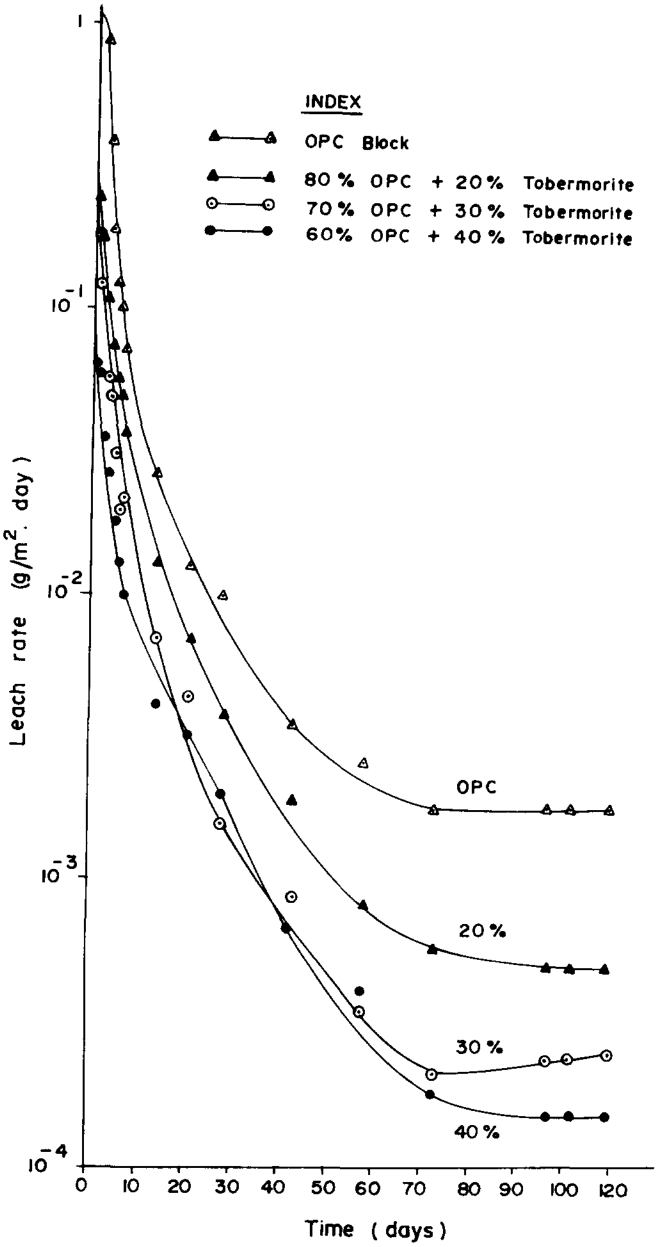

FIGURE 5. Plot of Sr^{2+} leach rate against leach time.

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