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Selective Separation of Cs and Sr from LiCl-Based Salt for Electrochemical Processing of Oxide Spent Nuclear Fuel

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Abstract: Electrochemical processing technology is currently being used for the treatment of metallic spent fuel from the Experimental Breeder Reactor-II at Idaho National Laboratory. The treatment of oxide-based spent nuclear fuel via electrochemical processing is possible provided there is a front-end oxide reduction step. During this reduction process, certain fission products, including Cs and Sr, partition into the salt phase and form chlorides. Both solid state and molten LiCl-zeolite-A ion exchange tests were conducted for selectively removing Cs and Sr from LiCl-based salt. The solid-state tests produced in excess of 99% removal of Cs and Sr. The molten state tests failed due to phase transformation of the zeolite structure when in contact with the molten LiCl salt.

Keywords: Cs and Sr removal, electrochemical processing, pyroprocessing, spent nuclear fuel treatment, zeolite LiCl salt ion exchange

INTRODUCTION

Electrochemical processing is a technology for treating spent nuclear fuel that electrochemically separates fission products and other waste

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material from recyclable actinides (1,2,3). It is entirely a dry process and uses neither organic nor acidic solvents. Rather, it utilizes electrochemical cells with molten salt electrolytes for its major unit operations. One such unit operation is electrolytic reduction, which is used to convert spent oxide fuel to metallic form. Metal fuel is required for feed into the electrorefiner.

In electrolytic reduction, the oxide spent fuel is loaded into a basket and immersed in a pool of molten LiCl containing 1–3 wt% Li_2O (4,5,6). The basket is cathodically polarized, while a platinum anode is lowered into the salt. Actinides and fission products are then electrochemically reduced, while oxygen gas bubbles emerge from the surface of the Pt anode. During this process, Cs, Sr, and Ba are known to be converted to chlorides and accumulate in the LiCl-Li_2O (7). As progressively more spent fuel is processed through the electrolytic reduction vessel, its salt becomes increasingly contaminated with these fission products. Eventually, it is necessary to stabilize and dispose some of the salt as high level waste and replace it with clean LiCl-Li_2O, or to selectively remove the fission products and recycle the purified salt to the electrolytic reduction system.

This problem is similar to that encountered with the molten salt in the electrorefiner. In that case, a eutectic LiCl-KCl pool is progressively contaminated by active metal fission products, which also form chlorides. Once the contamination level becomes too high, waste salt must be removed, disposed of as high level waste, and replaced with clean LiCl-KCl. In the current process for treating waste salt from the electrorefiners at the Idaho National Laboratory (INL) Fuel Conditioning Facility, waste salt is milled, blended with dry zeolite-4A at high temperature, mixed with glass, and thermally consolidated (8,9,10). The final waste form consists of glass and sodalite phases, with the majority of the salt immobilized in the sodalite phase. An advanced version of the ceramic waste process has been designed which would use zeolite-A to selectively remove fission products from the salt, facilitating recycle of most of the LiCl-KCl back to the electrorefiner. This approach is attractive due to the potential to concentrate the fission products in the waste form and thus reduce the volume of high-level waste generated from electrochemical processing. Equilibrium experiments have been performed that verify that ion exchange occurs between the molten salt and zeolite-A (11,12) and models have been developed which closely fit the experimental data (13,14,15).

Thus, one approach to treating the salt from electrolytic reduction is to contact it with zeolite-A and allow ion exchange to occur. Seo et al. from Korea Atomic Energy Research Institute (KAERI) recently published results from experiments that demonstrated zeolite-4A can be used to effectively remove Cs and Sr from molten LiCl via ion exchange (16). KAERI has also investigated the use of a sol-gel process to immobilize waste salt from electrolytic reduction. Kim et al. recently described a process called Gel-Route Stabilization/Solidification in which waste salt is subjected to gelation, drying, mixing with binder glass, and heat-treatment to develop into a waste form (17). This waste form exhibited low leach rates that are comparable to those measured for the sodalite ceramic waste. A waste loading up to 16 wt% can be achieved with this form, much better than the 2 wt% loading achievable in the glass-sodalite ceramic waste form. However, this approach is considered by INL to be less desirable, because it produces a new type of waste form that has not been qualified. The glass-bonded sodalite waste form has been extensively tested using MCC-1, PCT, and vapor hydration leach tests.

In order to leverage the large database for characterization of the glass-bonded sodalite waste form, it was decided to further investigate ion exchange from the LiCl-salts to zeolite-A. Alternative means for achieving this ion exchange are needed. Two such alternatives have been pursued and are reported here. This includes short-duration contacts between molten salt and zeolite-A and an alternative approach of blending LiCl-based salt powder with zeolite-4A granules in a heated V-blender (at temperatures of 550°C or less). This was motivated by the theory that solid-state ion exchange can occur below the melting point of the salt. Some experimental results from salt-zeolite blending tests using LiCl-KCl salt have indicated that solid-state ion exchange can occur under certain conditions. The reported results were meant to be preliminary to scope out the feasibility of these approaches. Further investigations are, thus, planned based on the results reported in this paper.

EXPERIMENTAL METHODS

Materials

For molten salt ion exchange tests, 3-mm diameter zeolite-4A (UOP) pellets were dehydrated and used without any particle size reduction. These pellets contain a proprietary inorganic binder that nominally comprises 10% of the pellet mass. For the solid-state ion exchange tests, dehydrated zeolite-4A was used that had been size-reduced to a diameter range of 45–250 μm using a roller mill. In both cases, zeolite dehydration was achieved by heating to 550°C under vacuum. As measured with Karl-Fischer Titration of the off-gas from samples heated to 600°C, residual moisture concentrations ranged from 0.1 to 0.5 wt% for the particulate zeolite and 0.7 wt% for the zeolite pellets.

The salt mixture (95 wt% LiCl, 1 wt% Li_2O, 2 wt% CsCl, and 2 wt% $SrCl_2$) was prepared by weighing out the individual components into a stainless steel crucible and melting them under a dry argon atmosphere at 650°C for 15 hours. After cooling, the salt was then crushed and milled to an average particle size of 100 μm.

Molten Salt Ion Exchange Tests

Molten LiCl-based salt/zeolite-4A ion exchange experiments were conducted in a small top-loading KERR Auto Electro Melt Maxi Furnace. In a nitrogen-purged glovebox, salt was loaded into the magnesia crucible (1.5″ OD and 2″ H) and placed inside the graphite crucible of the Kerr Lab furnace. Figure 1 shows the schematic of the furnace containing LiCl salt and the zeolite basket.

The zeolite basket was loaded with dry zeolite-4A pellets. It was initially positioned just above the magnesia crucible inside the furnace as shown in Fig. 1a. The furnace was then turned on and gradually heated to 650°C over a three-hour period to melt the salt. Once the temperature reached 650°C, the basket was then lowered into the molten salt (see Fig. 1b) for a duration ranging between one and eight hours. The furnace was then shut off, and the zeolite basket was lifted out of the salt to the top of the furnace. Active cooling of the furnace was achieved via a nitrogen gas purge through the glovebox. The temperature inside the glovebox was monitored by a thermocouple to avoid any excessive heat

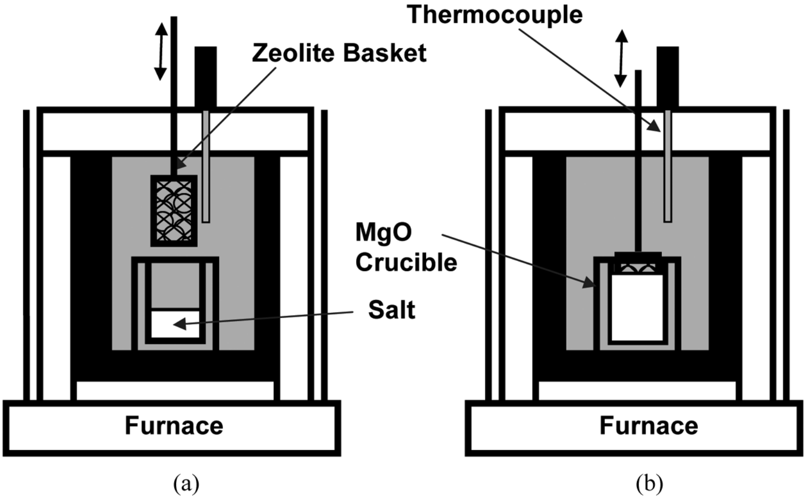

Figure 1. System for molten salt-zeolite ion exchange tests. (a) Zeolite basket outside the crucible, (b) Zeolite basket lowered into the molten salt at 650°C.

Table 1. Test parameters for ion exchange experiment with molten salt. $T_{max} = 650°C$ for all tests

Test #	Time at T_{max} (hr)	Mass salt (g)	Mass zeolite (g)
1	2	21.9	6.7
2	4	28.2	7.0
3	8	24.4	5.4
4	1	13.9	3.8

build up. The inside temperature of the glovebox was less than 40°C throughout the furnace operation. As can be seen in Table 1, the contact time for the ion exchange experiments with molten salt varied from one to eight hours.

The zeolite basket was allowed to cool overnight and removed from the furnace. The salt loaded zeolite pellets were removed from the basket, washed about three to four times using vacuum filtration with nanopure water to clean off the adhering salt and air-dried. The following mixture was then added to a beaker: about 0.1 g of salt loaded zeolite pellets crushed to a fine powder, 3 ml of concentrated nitric acid, 3 ml of concentrated hydrochloric acid, and 2 ml of concentrated hydrofluoric acid. The beaker was gently heated for 10–15 minutes. Following that, a 30 ml mixture of 2.2% boric acid and 0.2% EDTA was also added to the beaker and gently warmed for 15–20 more minutes to avoid any precipitation. Finally, the mixture was diluted with nanopure water to bring the volume to 50 ml and submitted for ICP-MS analysis. For the salt sampling, about 0.1 gm of salt was diluted with 500 ml of nanopure water and submitted for ICP-MS analysis. X-ray diffraction (XRD) on dried and crushed salt loaded zeolite samples was used to detect crystalline damage and/or phase transformations to the zeolite structure.

Solid-State Ion Exchange Tests

Solid state LiCl-based salt/zeolite ion exchange experiments were performed using a 4-liter, stainless steel lab-scale V-blender (Ability Engineering) that is heated externally by a ceramic furnace, as shown in Fig. 2. Rotation of the V-blender was set at 17 rpm for all testing. For each run, the salt and zeolite were pre-mixed in a plastic bottle and poured into the V-blender in such a way as to minimize entrapment of air into the vessel. The vessel itself was air-tight and initially filled with dry argon gas prior to loading with salt and zeolite. After sealing the V-blender, the material was cold mixed for 30 minutes prior to initiating

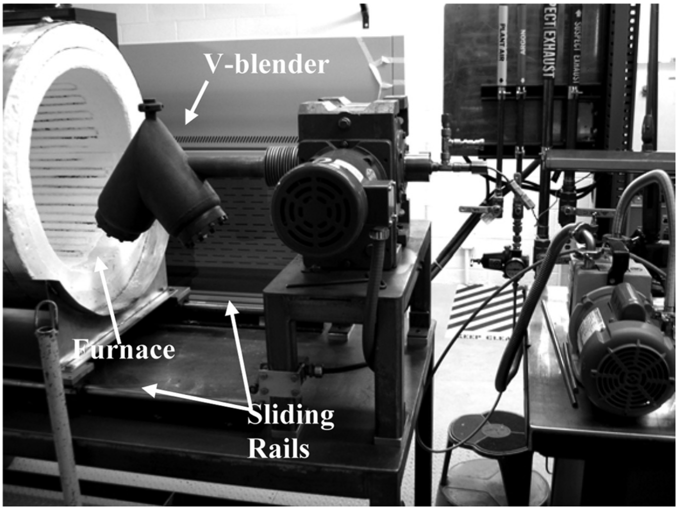

Figure 2. Laboratory scale V-blender.

a 5°C/min heat-up to T_{max}. The set of experiments performed with varying maximum temperatures and times are shown in Table 2.

The amount of salt (100 g) blended with zeolite (300 g) was in excess of how much the zeolite can absorb based on the total Cl^- capacity per unit cell of zeolite. After holding the V-blender at a temperature T_{max} for the specified period of time, the heaters were turned off while the V-blender continued to rotate. Once the V-blender temperature had reached a temperature low enough to allow safe handling (less than 50°C), the furnace was pulled away from the V-blender. The V-blender was opened and its contents transferred into a plastic bottle. One gram of salt-loaded zeolite was then washed with 60 ml of nanopure water for about a minute. About 10 ml of the wash solution was then extracted through a 0.45 μm filter and analyzed for Cl, Cs, and Sr ions using ICP-MS analysis. The analysis was then used to determine the Cl, Cs, and Sr uptake into the zeolite.

Table 2. V-blender parameters for LiCl salt/zeolite ion exchange experiments

Test #	T_{max}(°C)	Time at T_{max}(hr)	Mass salt (g)	Mass zeolite (g)
1	500	20	100	300
2	500	5	100	300
3	550	20	100	300
4	550	5	100	300

X-ray Diffraction Analysis

XRD analysis of un-reacted and reacted zeolite-4A samples first involved grinding the material into a fine powder followed by adhering the powder to a quartz, zero-background sample slide. The analysis was performed using a Scintag X1 diffractometer (Thermal ARL, Franklin, MA) with theta-theta configuration. The incident radiation was Cu K_α X-rays with an X-ray tube voltage of 45 kV, and current of 40 mA. The instrument scan rate was 1°/minute. After analysis, Scintag DMSNT search-match software (version 1.37) was used to identify mineral phases in the XRD pattern.

RESULTS AND DISCUSSION

Molten Salt Ion Exchange Tests

The measured concentrations in the salt samples after each run are shown in Fig. 3. The concentration of Cs and Sr in the salt is reduced after each run. However, the loss of Cs and Sr from the salt cannot be accounted for by the increase in Cs and Sr concentrations in the zeolite as seen in Fig. 4. There is significantly more Cs and Sr lost from the salt than there is gain in the zeolite. The dropping out of Cs and Sr from the salt could be due to volatilization mechanism inside the furnace. Though not shown in the

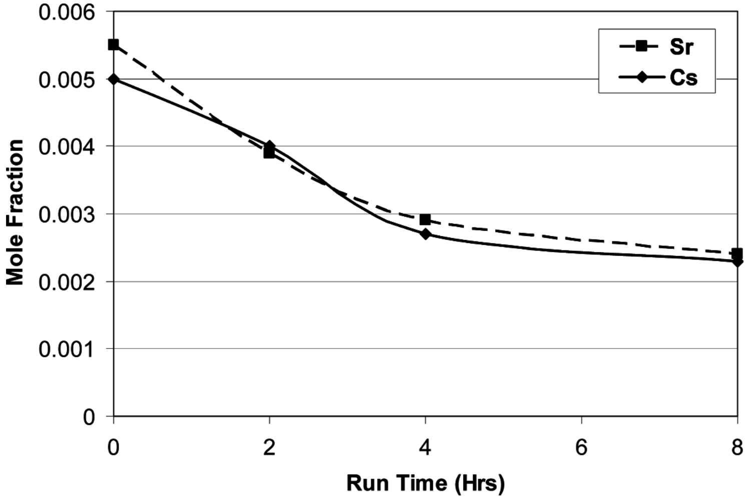

Figure 3. Mole fraction of Cs and Sr in molten LiCl-based salt after contact with zeolite-4A.

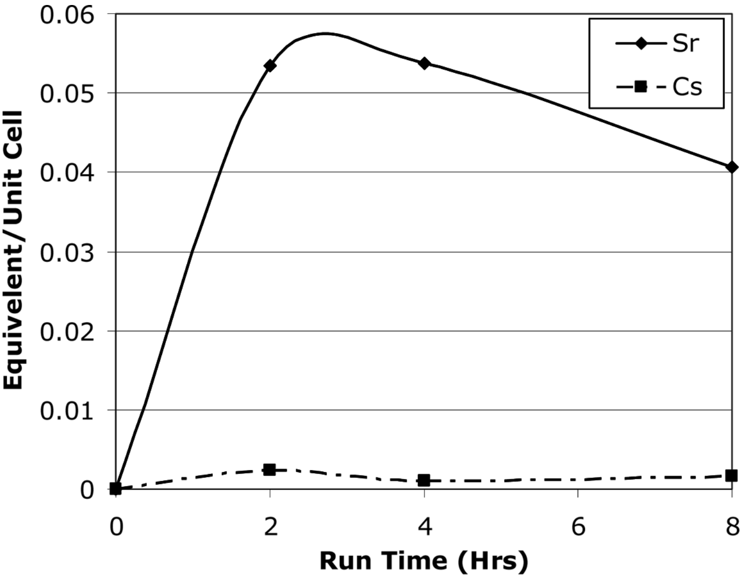

Figure 4. Loading of Cs and Sr ions in zeolite-4A after contact with molten LiCl-based salt.

figures, it was also observed that sodium accumulated in the molten salt. It is apparent that lithium largely replaced the sodium in the zeolite.

ICP-MS analysis results of unreacted zeolite-4A and the samples taken after two, four, and eight hours of contact are shown in Fig. 4. Considering that up to 24 equivalents of cations are in each unit cell of zeolite, an extremely low uptake of Sr into zeolite was observed. The amount of Cs detected in the zeolite was virtually nothing. These results indicate that zeolite has very little affinity for either fission product. ICP-MS was also used to measure the sodium and lithium concentrations in the zeolite. The initial zeolite contains a large amount of sodium, as expected. Within two hours of contact with the molten salt, only 10% of the sodium remained – the rest was replaced by lithium. For longer runs (four and eight hours) almost all of the sodium was replaced by lithium. This shows that zeolite-4A undergoes a thermal transformation in molten LiCl-based salt precluding retention of Cs and Sr in its structure. Based on these observations, it was concluded that zeolite-4A is an inadequate ion exchange material for removing fission products from molten LiCl-based salt.

The XRD analysis of unreacted zeolite-4A in comparison with the product of each run is shown in Fig. 5. The XRD phase identification process reveals that all of the samples, with the exception of the unreacted

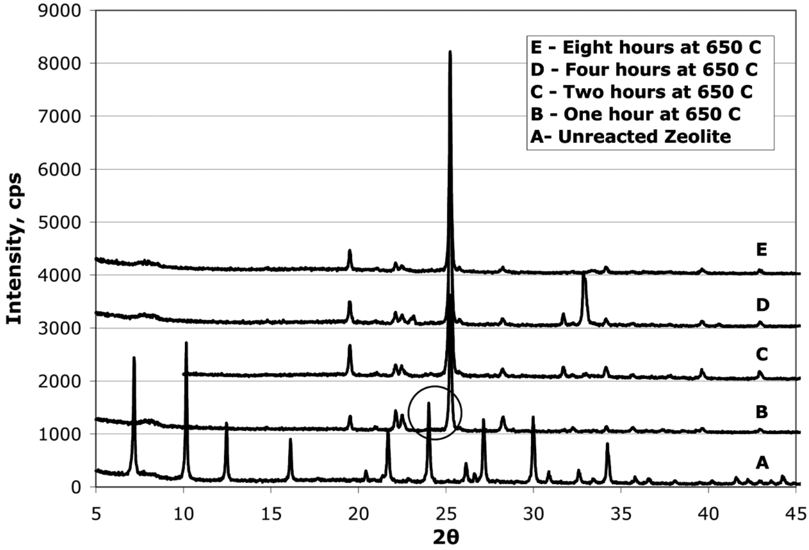

Figure 5. XRD results for molten salt/zeolite ion exchange experiments.

zeolite-4A, appeared to consist of an unknown lithium aluminosilicate structure. The zeolite-4A crystalline structure was transformed in as little as 1 hour of contact with the salt. Thus under these conditions, thermal degradation of zeolite-4A may have resulted in formation of multiple metastable aluminosilicates. This clearly shows the instability of zeolite-4A in molten LiCl-based salt even for a short duration of contact.

Solid-State Ion Exchange Tests

The results of the salt sorption into the zeolite framework are shown in Table 3. Salt occlusion into the zeolite framework occurs via salt sorption or ion exchange with the framework cations. Since Cl^- ions have a negative charge and the framework requires positively charged ions, Cl uptake can only be due to sorption of salt molecules into the zeolite. Therefore, as shown in Table 3, up to 68% of the salt was absorbed into the zeolite, which corresponds to 10 Cl^-/unit cell. It was also observed that the higher temperature (550°C) had the lowest Cl^- uptake.

The results of ion exchange at 500°C for 20 hours are very encouraging with nearly 100% Cs and Sr uptake as seen from Table 3. In contrast, Cs and Sr uptake was lower at 550°C, especially for a 20-hour test. The tests performed at lower temperature demonstrated excellent salt sorption and ion exchange results. But a low Cl^- uptake is desired to

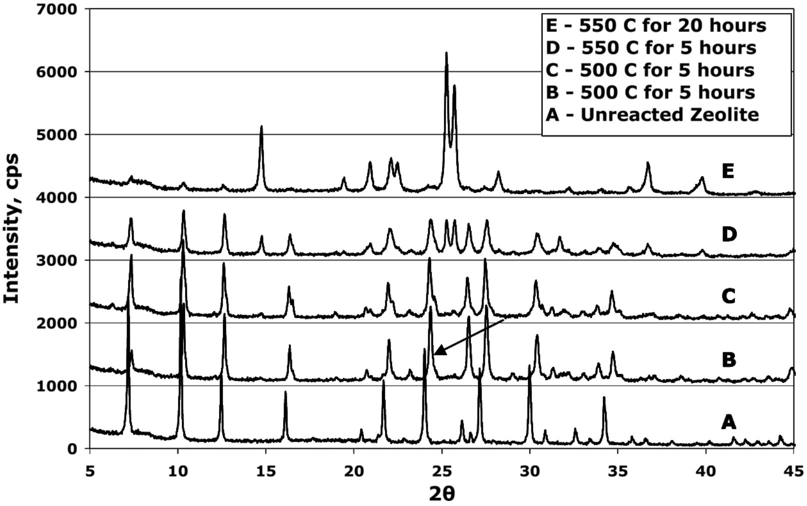

Figure 6. XRD results for solid state salt/zeolite ion exchange experiments.

minimize the amount of salt released into the ceramic waste form. Future experiments should be conducted to investigate the effect of even lower temperatures on salt sorption and ion exchange.

XRD patterns from solid-state ion exchange tests are shown in Fig. 6. These scans, taken for tests at 500°C, reveal that the zeolite-A phase is still present, yet the peaks have shifted slightly to the right. The 2θ value of the characteristic zeolite-A peak has shifted from 24 to 24.4 as pointed out by the arrow sign in Fig. 6. This shift could be due to small changes in the zeolite-A unit cell size – something to be expected as the salt is absorbed and sodium ions in the framework are replaced. However, the XRD pattern for the sample at 550°C (at a five hour hold time) shows a decrease in the intensity of the characteristic zeolite peak. No phase transformation was observed at this stage. But the XRD pattern of the sample run at 550°C (at a 20 hour hold time), indicates that with time

Table 3. Results of LiCl-zeolite-4A solid state ion exchange experiments

Test #	T_{max}(°C)	Time at T_{max}(hr)	Cl^- uptake (%)	Cs uptake (%)	Sr uptake (%)
1	500	20	68.4	99.6	99.5
2	500	5	56.0	99.5	97.4
3	550	20	14.8	71.9	68.8
4	550	5	51.3	96.9	95.8

at temperature, the initial zeolite-A phase transformed to a lithium aluminum silicate phase ($LiAlSiO_4$) matched to Powder Diffraction File (PDF) 12–0709 (18), a minor phase of $Li_2Al_2Si_2O_8$ (PDF 40–0062), and other, unidentified minor phase(s) that are most likely either silicates or aluminum silicates. This transformation of the zeolite-A structure at 550°C could explain the relative lack of affinity for Cs and Sr at that temperature.

CONCLUSIONS

Analyses of solid-state ion exchange between LiCl-based salt and zeolite have shown promising results. At 500°C, solid-state V-blender tests showed a very high selectivity for Cs and Sr to partition into the zeolite phase. However, the problem is that a significant chloride uptake into the zeolite was also noticed at that temperature. Future tests should be conducted at lower temperatures to see if Cl^-uptake can be minimized while still achieving ion exchange. In molten state ion exchange analyses, zeolite-4A crystalline phase transforms into a lithium aluminosilicate phase. The degradation of the zeolite structure was observed in as little as a one hour contact with the molten salt resulting in very low uptake of Cs and Sr into the zeolite-4A structure. Hence zeolite-4A is an inadequate ion exchange material for removing Sr and Cs fission products from molten LiCl-based salt.

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