

# THE EFFECT OF Li AS A DOPANT IN Na<sub>2</sub>ZrO<sub>3</sub> HIGH TEMPERATURE CO<sub>2</sub> ACCEPTOR

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## INTRODUCTION

World economy in the present relies on burning fossil fuels to produce affordable energy. A consequence of the use of these fuels is the emission of important amounts of carbon dioxide (CO<sub>2</sub>) to the atmosphere creating environmental problems such as global climate warming. In the near future, if CO<sub>2</sub> removal is mandatory by stringent regulations, industry will certainly require improved and novel technologies for the efficient removal of CO<sub>2</sub>. Therefore, there is a need to develop alternate processes that may improve energy savings and conversion efficiencies. In the energy field those improvements are essentially related with a reduction of CO<sub>2</sub> emissions to the atmosphere. Among such technologies is the use of the CO<sub>2</sub> sequestration that in many cases has proven to be an alternative (Draper and Becker, 2000). Examples of such processes are the high temperature CO<sub>2</sub> capture during coal gasification (Masahiro et al., 2001), the sorption enhanced reaction (SER) for the production of hydrogen (Lopez-Ortiz and Harrison, 2001) and the use of inorganic membranes for CO<sub>2</sub> separation in molten carbonate fuel cells (MCFC) (Jun-ichi Ida et al., 2004).

The use of solid acceptors for CO<sub>2</sub> sequestration have been widely used in the past and started several years ago for the CO<sub>2</sub> separation in the coal gasification process (Ichi Ida and Lin, 2003). Several investigators examined the effects of temperature, pressure, and reactive gas composition of calcium oxide (CaO) based materials using thermo-gravimetric (TGA) reactor techniques (Silaban and Harrison, 1996, Han and Harrison, 1997). However, degradation (sintering) of these materials was observed during multicycle tests. Calcined mineral dolomite (MgCO<sub>3</sub>\*CaCO<sub>3</sub>) proved to be superior in multicycle performance to previous CaO based past materials (Silaban and Harrison, 1996,). However, high regeneration temperatures were needed (950°C) using this acceptor of mineral nature. Bandi et al (2002) also proposed the use of mineral Huntite (Mg<sub>3</sub>Ca(CO<sub>3</sub>)<sub>4</sub>) presenting good regeneration properties. However high regeneration temperatures again were the drawback. Also of mineral nature hidrotalcites (Mg<sub>6</sub>Al<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>16</sub>·4H<sub>2</sub>O) were used by Hufton et al (1999) and Ding and

Alpay, (2001) at relatively high temperatures 400-550°C. However the sorption capacity of these hidrotalcites were low.

Within the past four years a new generation of synthetic acceptors evolved from the work from Ohashi et al (1999), which developed a novel CO<sub>2</sub> separation technique by using regenerable lithium zirconate (Li<sub>2</sub>ZrO<sub>3</sub>) as a solid CO<sub>2</sub> acceptor in the temperature range of 450-700°C. Main advantages of this material was its lower regeneration temperature (750°C) compared to current mineral origin based sorbents, which tend to sinter at high temperatures, and its stability that allowed an important number of cycles without losing its sorption capacity. However, the sorption rate of Li<sub>2</sub>ZrO<sub>3</sub> was very slow. Kato et al. (2004) proposed other acceptors based on lithium such as: lithium ferrite (LiFeO<sub>2</sub>), lithium nickel (LiNiO<sub>2</sub>), lithium titanate (Li<sub>2</sub>TiO<sub>3</sub>), lithium methasilicate (Li<sub>2</sub>SiO<sub>3</sub>) and lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) used at various temperatures. Certainly, among all these Li<sub>4</sub>SiO<sub>4</sub> was found to present the highest capacity (28% higher than Li<sub>2</sub>ZrO<sub>3</sub>) and sorption rate with CO<sub>2</sub>. Kato (2004) exposed Li<sub>4</sub>SiO<sub>4</sub> to 50 sorption-regeneration cycles without losing its sorption capacity. However the weight increase during carbonation was only about 70% of its theoretical maximum capacity.

This new generation of synthetic high temperature CO<sub>2</sub> acceptors (Li<sub>4</sub>SiO<sub>4</sub>) (Masahiro, et al.,2001) and Li<sub>2</sub>ZrO<sub>3</sub> (Jun-ichi Ida et al., 2004), which posses good sorbent regeneration and exceptional stability features are based on mixtures of oxides with Li as their main sorbent component. However, the abundance of lithium element is very low and expensive as compared with other cheaper alkali metal elements such as sodium and potassium. In previous studies, carried out in our laboratory, we synthesized CO<sub>2</sub> acceptor mixtures based on Na oxides (López Ortiz et at, 2004) and we observed that specifically, sodium zirconate (Na<sub>2</sub>ZrO<sub>3</sub>) presented similar or even superior CO<sub>2</sub> sorption performance properties as reported in Li based oxides (Masahiro et al., 2001 and Jun-ichi Ida et al., 2004). The sorption mechanism was based upon the following reaction (1):



where sodium zirconate reacts reversibly with CO<sub>2</sub> forming sodium carbonate and zirconium oxide with a regeneration temperature of 780°C. In that study it was found that Na<sub>2</sub>ZrO<sub>3</sub> showed superior sorption kinetics compared to lithium based sorbents Li<sub>2</sub>ZrO<sub>3</sub> and Li<sub>4</sub>SiO<sub>4</sub>. However, the success of any CO<sub>2</sub> acceptor depends much on its life cycle, which the material under consideration, Na<sub>2</sub>ZrO<sub>3</sub>, is lacking. Na<sub>2</sub>ZrO<sub>3</sub> regeneration problems were encountered specially towards the final portion of the TGA regeneration step, which was associated to a diffusion resistance within the particle not allowing CO<sub>2</sub> to be easily removed during regeneration. This regeneration problem was even more accentuated as the number of cycles increased.

### **The Use of Alkali Metals as Promoters in Solid CO<sub>2</sub> Acceptors**

Nakagawa and Ohashi (1998) reported the use of potassium carbonate (20% wt K<sub>2</sub>CO<sub>3</sub>) as a promoter dispersed on Li<sub>2</sub>ZrO<sub>3</sub>. This promoter was added in order to increase the sorption rate compared to Li<sub>2</sub>ZrO<sub>3</sub> alone. Ichi Ida and Lin (2003) and Ohashi et al (1999) explained with the use of a reaction model and TGA-DSC data how

$\text{Li}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  formed an eutectic mixture at around  $500^\circ\text{C}$ . The K doped  $\text{Li}_2\text{ZrO}_3$  showed improved  $\text{CO}_2$  sorption kinetics of about 40 times faster than pure  $\text{Li}_2\text{ZrO}_3$ . However, sorption kinetics is restricted to the formation of mixture eutectic  $\text{Li}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$  at  $500^\circ\text{C}$ .

Kato et al (Patent 2004) also used other alkali carbonates as promoters (from 5 to 30% mol) for  $\text{Li}_4\text{SiO}_4$  sorption kinetics. Examples of such promoters used by Ohashi et al. were sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), magnesium carbonate ( $\text{MgCO}_3$ ) and calcium carbonate ( $\text{CaCO}_3$ ). The use of these promoters increased the sorption kinetics of  $\text{Li}_4\text{SiO}_4$  in about 30 times compared to non-doped acceptors. However sorption temperatures were restricted to only  $500^\circ\text{C}$  and greater temperatures (in the case of K) where the eutectic region between  $\text{Li}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$  is readily available. Other options for improvement consist in the addition of dopants such as Yttrium as discussed by J.-i. Ida et al (2004).

All of the previous examples where alkali dopants were used towards improving the  $\text{CO}_2$  sorption-regeneration generally resulted in an increase of sorption kinetics and multicycle stability. Therefore, the objective of this work is to study the effect of Li as a dopant of the  $\text{Na}_2\text{ZrO}_3$  in order to solve the previously reported problems encountered (Lopez et al., 2004) with the regeneration performance of this material.

## EXPERIMENTAL

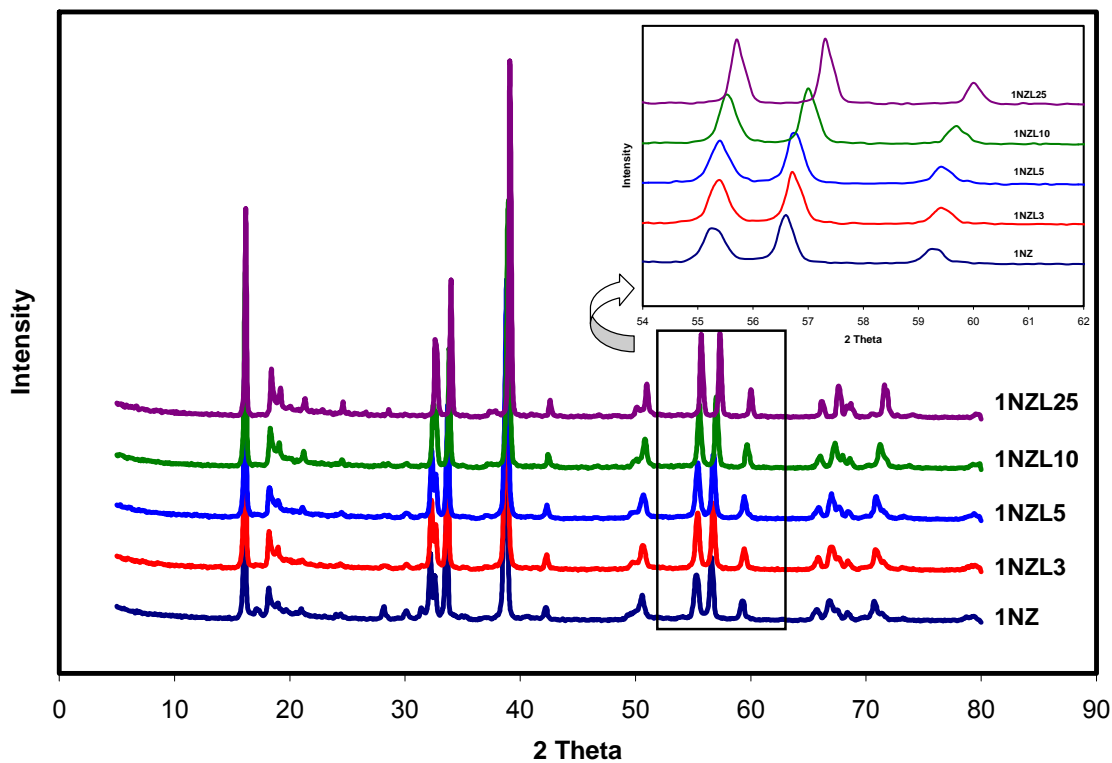
$\text{Na}_2\text{ZrO}_3$  was synthesized by the solid state method according to the procedure described by Lopez-Ortiz et al (2004) and using Na/Zr molar ratio of 1. A large mixture of  $\text{Na}_2\text{CO}_3$  (J.T. Baker) and  $\text{ZrO}_2$  (Spectrum Co.) was mixed and calcined at  $900^\circ\text{C}$  for 4 hours and later divided in five equal portions of 2 grams each. These portions were separated to later be doped with a 1 M aqueous solution of  $\text{LiNO}_3$  (Sigma Aldrich) by the incipient wetness method using Li/Na molar ratios of 0, 0.03, 0.05, 0.1 and 0.25: Details of the samples are shown in Table 1. After impregnation, the samples were re-calcined at  $900^\circ\text{C}$  for 1 hour in an air-heated box furnace. Characterization of the samples consisted in X ray diffraction (XRD, Phillips XPERTMPD with  $\text{CuK}\alpha$ .) and Scanning electron microscopy (SEM, JEOL JSM-5800LV). The  $\text{CO}_2$  sorption/regeneration performance was evaluated through thermogravimetric analysis (TGA, System-Pyris-1 Perkin Elmer). TGA test conditions for the experimental evaluation were:  $600^\circ\text{C}$ , 80% mol  $\text{CO}_2/\text{Ar}$  and 150 sccm, while regeneration used  $800^\circ\text{C}$ , air and 100 sccm.

**Table 1.** TGA Sorption/Regeneration Conditions Used During Experimental Evaluation

Sample	% Mol Li	Sorption Temperature	Regeneration Temperature	Sorption Gas Conc., % Vol	Gas Flowrate sccm	Regeneration Gas
2NZ	0	$600^\circ\text{C}$	$800^\circ\text{C}$	80% $\text{CO}_2/\text{Ar}$	100	Air
2NZL3	3	$600^\circ\text{C}$	$800^\circ\text{C}$	80% $\text{CO}_2/\text{Ar}$	100	Air
2NZL5	5	$600^\circ\text{C}$	$800^\circ\text{C}$	80% $\text{CO}_2/\text{Ar}$	100	Air
2ZL10	10	$600^\circ\text{C}$	$800^\circ\text{C}$	80% $\text{CO}_2/\text{Ar}$	100	Air
2ZL25	25	$600^\circ\text{C}$	$800^\circ\text{C}$	80% $\text{CO}_2/\text{Ar}$	100	Air

## RESULTS AND DISCUSSION

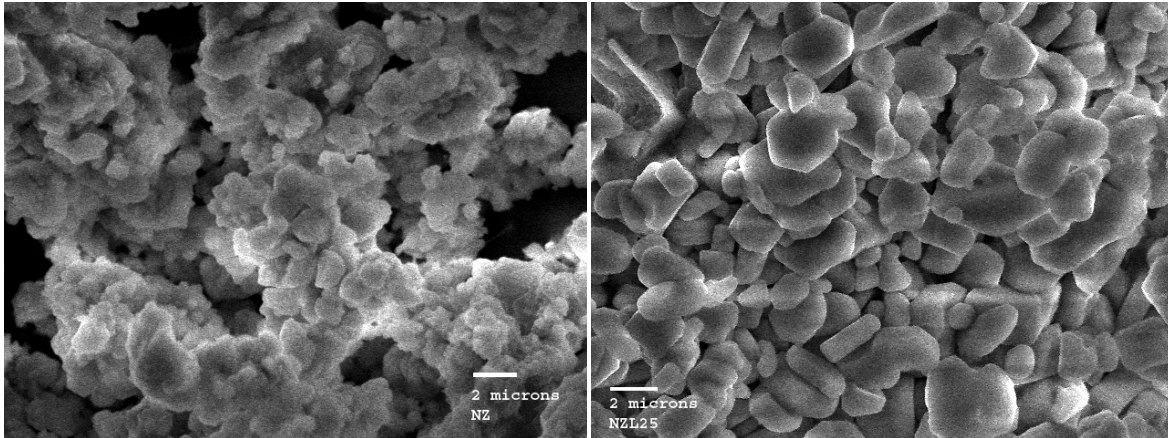
XRD analysis resulted in similar  $\text{Na}_2\text{ZrO}_3$  crystalline structures as shown in Figure 1 for  $\text{Na}_2\text{ZrO}_3$  as well as Li-doped  $\text{Na}_2\text{ZrO}_3$  with no other phases being observed. However, the structure of all the Li-doped  $\text{Na}_2\text{ZrO}_3$  samples, presented a slight shift to greater 2-theta values of the characteristic peaks in the diffraction patterns as the Li content increased with respect to the non-doped  $\text{Na}_2\text{ZrO}_3$  (NZ). This can be attributed to a decrease in the inter-planar distance of the crystalline structure of  $\text{Na}_2\text{ZrO}_3$  assuming a substitution of some of the Na by Li atoms in the overall structure. XRD results also points out that all Li content sorbents appear to alter the crystalline structure of  $\text{Na}_2\text{ZrO}_3$ .



**Figure 1.** XRD analysis of  $\text{Na}_2\text{ZrO}_3$  Set 1 Prepared Samples

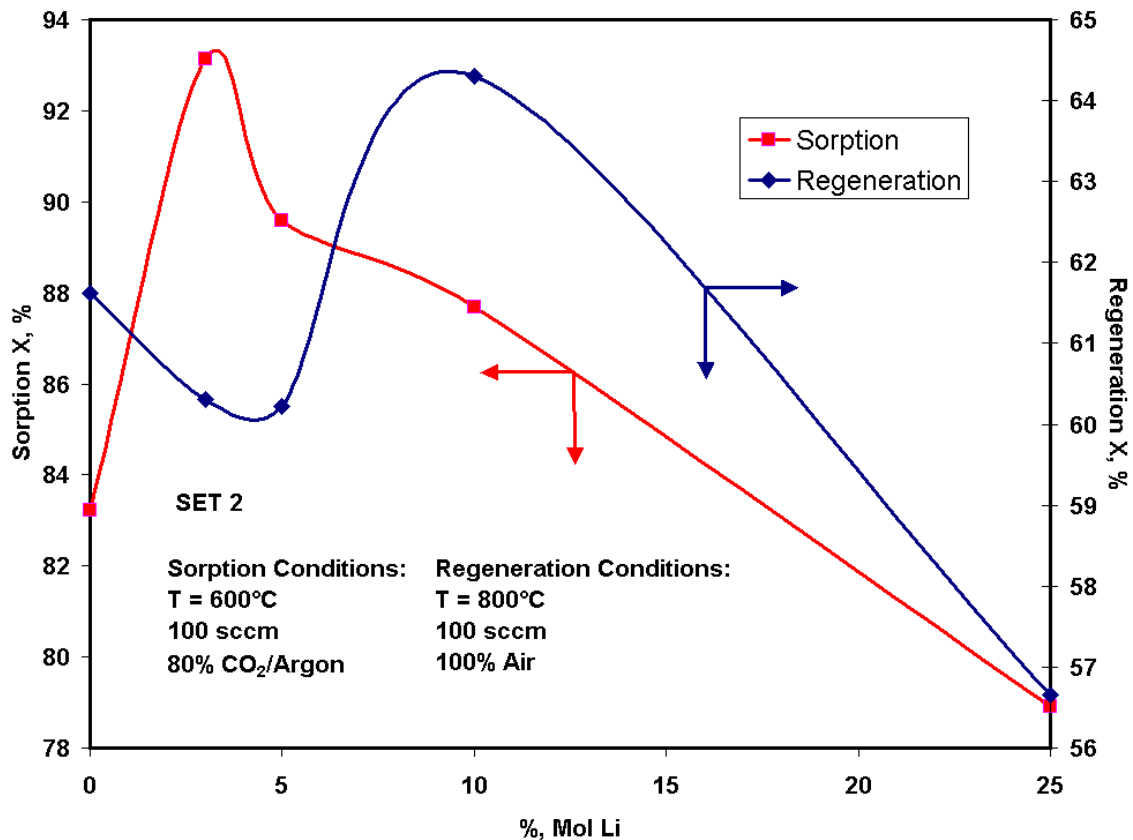
SEM images were taken to explore the morphology of the doped and non-doped  $\text{Na}_2\text{ZrO}_3$  particles. Figure 2 shows SEM micrographs of (non-doped) NZ and NZL25 (25% Li-doped) samples.

Non-doped NZ sample presented a flake-like shaped morphology, while the doped samples showed a gradual increase of a rectangular wedge-like shaped morphology as the lithium content increased. This behavior is evident for sample NZL25 shown in Figure 2. This last wedge-like shape is characteristic of a  $\text{Na}_2\text{ZrO}_3/\text{Li}_2\text{ZrO}_3$  solid mixtures since previous experiments in our laboratory where  $\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$  were combined in 50% mol presented an enhanced morphology of this kind.



**Figure 2.** SEM micrographs of non doped NZ (left) and NZL25 (right) samples

Figure 3 shows TGA results of the sorption/regeneration behavior of samples described in Table 1. In this Figure the sorption and regeneration conversions are plotted against lithium content in  $\text{Na}_2\text{ZrO}_3$  (% mol). Sorption conversions were taken when the weight change in the TGA was stable. However, due to the fact that each regeneration resulted in evident differences in regeneration rates of each sample, it was decided to evaluate the regeneration conversion at a time where kinetic differences were enhanced (after 12.3 minutes).



**Figure 3.** Sorption/Regeneration Conversion versus % Mol Li content for TGA Tests

TGA results presented a strong doping effect of Li in  $\text{Na}_2\text{ZrO}_3$  on the  $\text{CO}_2$  sorption capacity and kinetics. A maximum in  $\text{CO}_2$  sorption conversion and kinetics was observed with sample NZL3, which achieved a 11.9% conversion increase over the non-doped  $\text{Na}_2\text{ZrO}_3$  (NZ), samples NZL5 and NZL10 showed higher conversions than non-doped NZ, with 7.7% and 5.4% increase, respectively. However, there is a gradual decrease of sorption conversion as the Li content increased from 3% to 25% mol Li with sample NZL25 presenting a decrease of 5.2% with respect to NZ.

Regeneration conversions showed a maximum between 5 and 10% mol Li. Greater and lower Li content than this range resulted, surprisingly in lower regeneration conversions with a conversion reduction of 12.5% for 1NZL25 compared to non-doped 1NZ. It is important to note that when the sorption conversion was maximum the conversion of regeneration showed a minimum and vice versa.

Results suggest that the presence of Li in amounts greater than 5% in  $\text{Na}_2\text{ZrO}_3$  produce a competition between Li and Na for Zr to reach the morphology of the mixture  $\text{Na}_2\text{ZrO}_3/\text{Li}_2\text{ZrO}_2$  that is evident from SEM images shown above. XRD results also indicate that Li atoms substitute some of the Na atoms in the crystalline structure of  $\text{Na}_2\text{ZrO}_3$ . The proposed substitution of Na by Li atoms is confirmed through the shifting of the XRD peaks in the doped samples and in the evident change in morphology observed in the SEM images. Once the mixture of  $\text{Na}_2\text{ZrO}_3/\text{Li}_2\text{ZrO}_2$  is present in the system, generates a decrease in the  $\text{CO}_2$  sorption kinetics, since it is well known that sorption kinetics for  $\text{Li}_2\text{ZrO}_3$  is much slower than for  $\text{Na}_2\text{ZrO}_3$  (Lopez-Ortiz et al., 2004). While, it is known from previous experience (Lopez-Ortiz et al., 2004) that  $\text{Li}_2\text{ZrO}_3$  exhibits faster regeneration kinetics than  $\text{Na}_2\text{ZrO}_3$ . From this, it is suggested that there should exist an optimal Li doping amount that may produce a doped- $\text{Na}_2\text{ZrO}_3$  with reasonable fast sorption and regeneration kinetics with respect to the non-doped  $\text{Na}_2\text{ZrO}_3$ . From Figure 3 it is evident that this optimal amount of Li is located between 3 and 10% mol Li.

The fact that greater Li content resulted in lower  $\text{CO}_2$  sorption kinetics is associated with the theory that Li, that substitutes some of the Na in the  $\text{Na}_2\text{ZrO}_2$  structure, results in the formation of a small amount of  $\text{Li}_2\text{ZrO}_3$  instead of  $\text{Na}_2\text{ZrO}_3$ . Therefore, during sorption of a high Li-content sample such as NZL25,  $\text{Li}_2\text{ZrO}_3$  present in small amounts diminishes the overall kinetics, which agrees with the fact that  $\text{Li}_2\text{ZrO}_3$  sorption kinetics is considerably slower than  $\text{Na}_2\text{ZrO}_3$  as shown in Lopez-Ortiz et al (2004).

Finally, to test the stability of this doped-sorbent during a multicycle scheme, preliminary sorption/regeneration results using sample NZL10 indicate a great consistency of 90% conversion during 9 cycles. While, previously reported non-doped  $\text{Na}_2\text{ZrO}_3$  (Lopez-Ortiz et al., 2004) showed a continuous decrease in regeneration conversion as the number of cycles increased.

## CONCLUSIONS

A strong doping effect was found by adding Li to  $\text{Na}_2\text{ZrO}_3$ . This effect resulted in evident changes of sorption/regeneration kinetics and conversions of doped  $\text{Na}_2\text{ZrO}_3$

compared to non-doped samples. Bests sorption conversion and kinetics results were found with sample NZL3, while sample NZL10 presented the best regeneration features. It is concluded that optimal doping amount of Li must be between 3 and 10% mol in Na<sub>2</sub>ZrO<sub>3</sub>.

The theory of competition of Na and Li atoms for the ZrO<sub>2</sub> helps to explain the results obtained in the sorption/regeneration experiments.

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