# Influence of Modified Coal Fly Ash on Its Cation Exchange Capacities

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## Abstract

Fly ash modified with sodium hydroxide calcination-hydrothermal was used to treat ammonia-nitrogen wastewater. The mount of alkali, the solid-liquid ratio, and the temperature of calcination were investigated in the process of modification. The best modified condition was when the ratio of sodium hydroxide and fly ash was 0.4:1, the ratio of solid and liquid was 1:1, and the temperature of calcination was 400ºC. After modification, the zeolite-like substances were produced from the fly ash and the cation exchange capacities (CEC) increased from 5 to 81 mmol/100 g. The separation efficiency of the ammonia-nitrogen was up to 90%.

## Introduction

Fly ash is one of the main wastes from coal-fired power plants [1]. With the rapid development of the electrical industry, the emission of fly ash has increased rapidly. It has become the largest single emission source in China [2]. The huge amounts of coal fly ash, the serious environmental pollution caused by coal fly ash, and the current situation of exhausted mineral resources have attracted the attentions of researchers in this field.

Ammonia-nitrogen is an important pollutant in water. If there is more nitrogen in water than the standard content, then it can cause eutrophicate ion and become harmful to humans and animals [3, 4]. Ionization was used to remove the harmful hydronium (ions) in a way that the convertible hydronium of insolubility anonym was substituted by the hydronium of the same surname in the solution. Ionization was a special process of absorption [5]. The zeolite was generally used as the ions switch to remove the ammonia-nitrogen. Fly ash has surface-activated groups, and the component of fly ash was similar to zeolite [6]. Researchers, both at home and abroad, have suggested that fly ash can be used to treat the ammonia-nitrogen wastewater [7].

Given that the purification efficiency of raw fly ash was low, it cannot satisfy the actual requirement of effluent treatment. The modified fly ash was used as the absorbent to treat the wastewater [8]. Currently, there is little research on employing modified fly ash to treat ammonia-nitrogen wastewater, and the treatment efficiency was not ideal [9]. In order to improve the efficiency of ammonia-nitrogen wastewater treatment by fly ash, the sodium hydroxide calcination-hydrothermal treatment was adopted to modify the fly ash and the best modified method was found out. Prepare the modified fly ash with high efficiency and low cost accordingly. This paper has proved the feasibility of ammonia-nitrogen wastewater treatment by fly ash.

## Experimental

### Experimental Procedure

The sodium hydroxide (AR, ≥96.0%) and coal fly ash (from a coal-burning power plant in Taiyuan, Shanxi,

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China) were mixed by a certain ratio (0.2-1.2:1). The sample was then calcinated at a certain temperature (200-800ºC) for 1 h. After cooling, it was ground and filtered through a 60-mesh sieve. The calcined sample and distilled water were mixed by a certain ratio (1-5). We stopped stirring when temperature reached 70ºC after 2 h of thermostatic heating in a water bath. The temperature was then increased to 100ºC. Hydrothermal synthesis was conducted under constant temperature and pressure for 4 h. Finally, the mixture was subjected to extraction filtration. The filter cake was washed until it reached neutral pH (Seven-Multi, Mettler Toledo), dried at 105ºC, and then filtered through a 200-mesh sieve after cooling. The CEC (mmol/100 g) of the fly ash before and after modification were calculated by Nessler's reagent colorimetry method [10].

## Analysis and Characterization

A D8 Advance X-ray powder diffractometer (Bruker, Germany) was used to analyze the phase of the coal fly ash before and after modification. The sample was pressed into a tablet by a mold with 2 cm diameter. The following conditions were required: Cu-Ka radiation, 40 kV voltages, 40 mA current, step length 0.02º, retention time 0.2 sec per step, and 2θ range 10º-50º.

## The Adsorption of Ammonia-Nitrogen from Wastewater

Modified fly ash (4 g) was mixed with 50 mL amonia-nitrogen wastewater (prepared from ammonium chloride (≥99.8%) and distilled water), and reacted for 1 h. Then they were separated by centrifuge. The filtrate was used to determine CEC of the modified fly ash, and the calculation formula was as follows:

$$CEC = \frac{V(C_0 - C_e)}{m} \times \frac{1}{18} \times \frac{1}{1000} \times 100 \qquad (1)$$

...where $C_e$ was the residual ammonia-nitrogen concentration in solution at equilibrium (mg·L$^{-1}$), $C_0$ was the initial ammonia-nitrogen concentration (mg·L$^{-1}$), $V$ was the solution volume (mL), m was the weight of modified fly ash (g), 18 was the molecular weight of ammonia-nitrogen, 1,000 was the ratio of L and mL, and 100 was the weight of modified fly ash. Each aforementioned experiment was repeated three times and the following data were given as average.

## Results and Analysis

### Influence of Alkali Content on Performance

#### *XRD Analysis*

The raw fly ash was mixed with alkali and calcine at 800ºC for 1 h (Fig. 1). When the content of alkali was 0.2, the peak of 2θ in the range of 20º-30º disappeared and the

$Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$ and nepheline were generated. When the content of alkali was 0.4, the peak of $Na_2SiO_3$ appeared when the 2θ were 16.836º and 29.350º. When the content of alkali was 0.8, $Fe_{5.36}Si_{0.64}O_8$ and $Ca_2Al(AlSi)O_7$ were generated. When the content of alkali was 1.2, the strength of the peak of $Fe_{5.36}Si_{0.64}O_8$ and $Ca_2Al(AlSi)O_7$ increased, while the peak of $Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$ was undermined and changed into $Na_{1.52}(AlO_2)_{1.45}(SiO_2)_{0.55}$ and more nepheline.

Sodium hydroxide acted as flux in the reaction. It could destroy the crystal structure of mullite and quartz and make the system of glass dissolve, and then generated the activated $SiO_2$ and $Al_2O_3$. With the content of alkali increasing, sodium hydroxide can destroy the other crystal structures – such as haematite, magnetite, $CaSO_4$ – of fly ash. It could further react with the active $SiO_2$ and $Al_2O_3$, and then generate new phases, which explains why the color of the product of the calcination was light green.

After calcination and hydrothermal, the XRD of fly ash was shown in Fig. 2. When the content of alkali was 0.4, zeolite-like substances were generated in the range of 16.534º and 26.077º. When the content of alkali was 0.8, the original zeolite-like substances had a stronger peak and when 2θ was 18.444º they would generate more zeolite-like substances. Fig. 2 shows that with increasing alkali content there would be more zeolite-like substances as well as different kinds. In the process of calcination the sodium hydroxide served as flux. Besides, sodium hydroxide joint in the following hydrothermal and the quantity of zeolite-like substances increased further [11]. The products were different under different content of alkali [12]. Therefore, the content of sodium hydroxide played an important role in the process of reaction, which not only affected the quantity of zeolite-like substances, but also the kinds of the product.
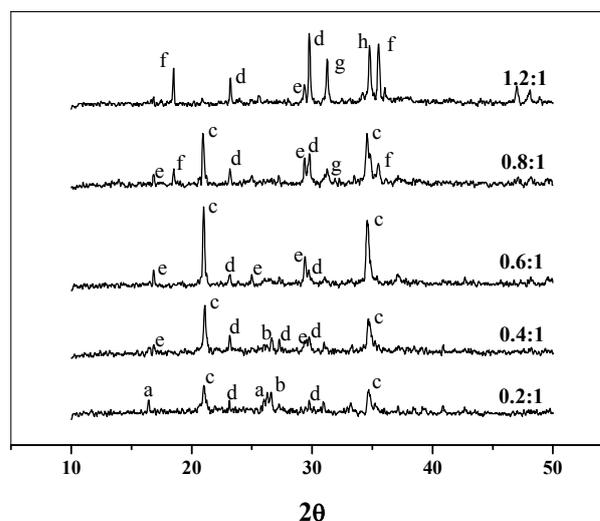


Fig. 1. XRD pattern of fly ash with different alkali content. a – Mullite, b – Quartz, c – $Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$, d – Nephelinee – $Na_2SiO_3$, f – $Fe_{5.36}Si_{0.64}O_8$, g – $Ca_2Al(AlSi)O_7$, h – $Na_{1.52}(AlO_2)_{1.45}(SiO_2)_{0.55}$

*CEC of Modified Fly Ash with Different Content of Alkali*

CEC of different content of alkali of modified fly ash (the temperature of calcination was 800ºC, the ratio was 1:5) and the separation percent of ammonia-nitrogen in the wastewater were shown in Fig. 3.

CEC could reflect the exchange ability of cation, which was an important indicator. Fig. 3 showed that with the content of alkali increasing, the CEC of modified fly ash increased. When the content of alkali was 0.4, the CEC of modified fly ash was 13 mmol/100 g, and there was a clear increase compared with raw fly ash, as a result of the generation of zeolite-like substances. When the content of alkali is 0.8, CEC of modified fly ash was up to 41 mmol/100 g, 8 times of raw fly ash. The reason was that with the content of alkali increasing, there were more zeolite-like substances, then increased the CEC of fly ash. When the con-
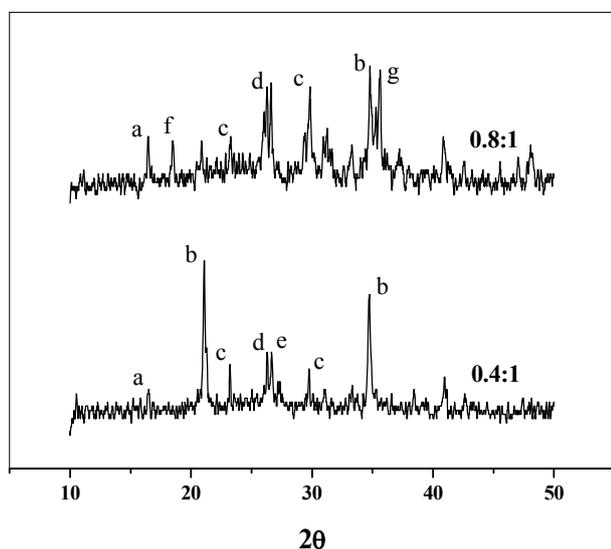


Fig. 2. XRD pattern of fly ash after calcination and hydrothermal.
a – $Na_4KAl_5Si_{11}O_{32} \cdot 10H_2O$, b – $Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$, c – Nepheline, d – $Na_3Al_3Si_3O_{12} \cdot 1.8H_2O$, e – $Na_2Al_2Si_5O_{14}$, f – $Na_2Al_2Si_{2.5}O_9 \cdot 6.2(H_2O)$, g – $NaAl_2(Si_3Al)O_{10}(OH)_2$
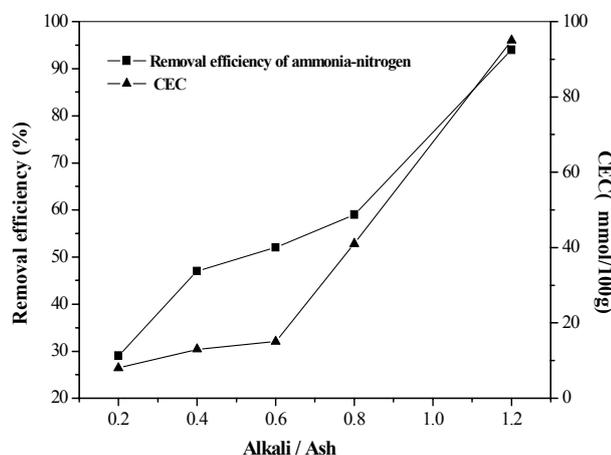


Fig. 3. CEC of different content of alkali and ammonia-nitrogen removal efficiency.
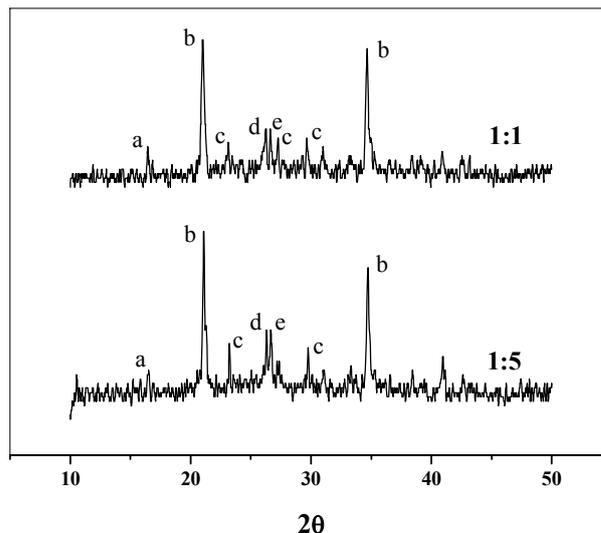


Fig. 4. The XRD pattern of modified fly ash with different solid-liquid ratios.
a – $Na_4KAl_5Si_{11}O_{32} \cdot 10H_2O$, b – $Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$, c – Nepheline, d – $Na_3Al_3Si_3O_{12} \cdot 1.8H_2O$, e – $Na_2Al_2Si_5O_{14}$

tent of alkali was 1.2, CEC of modified fly ash could be up to 95 mmol/100 g, which corresponded with the XRD analysis of Fig. 2.

The regularity of separation percent of ammonia-nitrogen in the wastewater corresponded to the regularity of the CEC. With the content of alkali increased, the separation percent of ammonia-nitrogen in the wastewater increasing. When the content of sodium hydroxide increased from 0.2:1 to 1.2:1, the separation percent of ammonia-nitrogen increased from 29% to 94%, which showed that CEC could reflect its ability of ammonia-nitrogen treatment. Therefore, ion exchange was the main process of a separation percentage of ammonia-nitrogen in the wastewater.

The CEC of raw fly ash was 5 mmol/100 g. The separation efficiency of ammonia-nitrogen wastewater by raw fly ash was 14%. In summary, with the content of alkali, separation percent of ammonia-nitrogen in the wastewater can be improved, while in fact the cost should be considered. Therefore, the content of alkali was 0.4:1, because when the content of alkali was 0.4, the mullite mainly disappeared and the zeolite-like substances were generated after hydrothermal. Compared with the situation when alkali content was 0.2, the modified fly ash had a well treatment effect to ammonia-nitrogen wastewater.

## Effect of Solid-Liquid Ratio on Performance

*XRD Analysis*

NaOH and coal fly ash were blended under the weight ratio of 0.4:1, and calcined at 800ºC. Then the calcined fly ash (solid) and distilled water (liquid) was synthesized at different solid-liquid ratio. Fig. 4 shows the XRD pattern of modified fly ash with a different solid-liquid ratio. When the solid-liquid ratio decreased from 1:5 to 1:1, the characteristic peak of modified fly ash did not change significantly.

The peak of $Na_4KAl_5Si_{11}O_{32} \cdot 10H_2O$ increased a little, and the peak of $Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$ decreased slightly. Maybe the alkali blended in coal fly ash (in the ratio of 0.4:1) was mostly consumed in the calcined process. There was little alkali follow-up to participate in the alkali hydrothermal reaction. So when the solid-liquid ratio changed, little changed in the concentration of sodium hydroxide, and the products were less affected.

### Ammonia Removal and CEC Analysis

As can be seen in Fig. 5, as the solid-liquid ratio decreased, the variation of the modified fly ash's CEC and the modified fly ash on the removal of ammonia nitrogen from wastewater were the same; namely, oscillation increased. The CEC of modified fly ash increased from 13 mmol/100 g to 24 mmol/100 g, the removal of ammonia nitrogen wastewater from 47% to 55%. The changes of the solid-liquid ratio in the hydrothermal process, in fact, were to change the sodium hydroxide concentration to participate in hydrothermal synthesis. The smaller the ratio, or to say, the smaller the amount of water in the reaction, the higher the concentration of sodium hydroxide and the more favorable the formation of zeolite materials. The CEC of modified fly ash and its effect on ammonia nitrogen removal ratio of wastewater were markedly improved. According to the determination of CEC and the results of ammonia removal efficiency, the best solid-liquid ratio of modification of calcined fly ash is 1:1.

## Effect of Calcination Temperature on Performance

### XRD Analysis

Mix the original fly ash with sodium hydroxide by 0.4:1 under different temperatures, and the XRD results of calcined 1h are shown in Fig. 6. It can be seen that as the calcination temperature increased from 200 to 800ºC, mullite and quartz peak decreased intensively, indicating that the higher the temperature, the more damage is conducive to
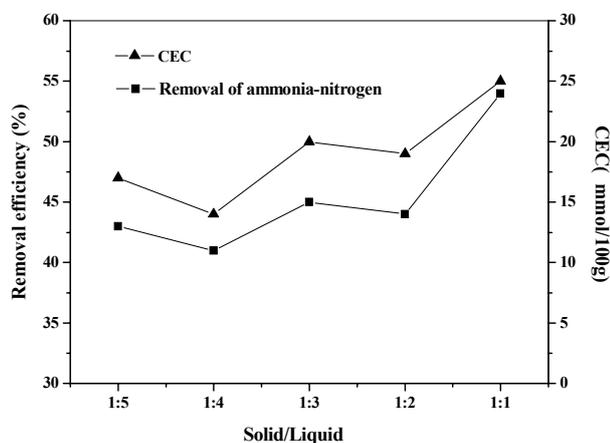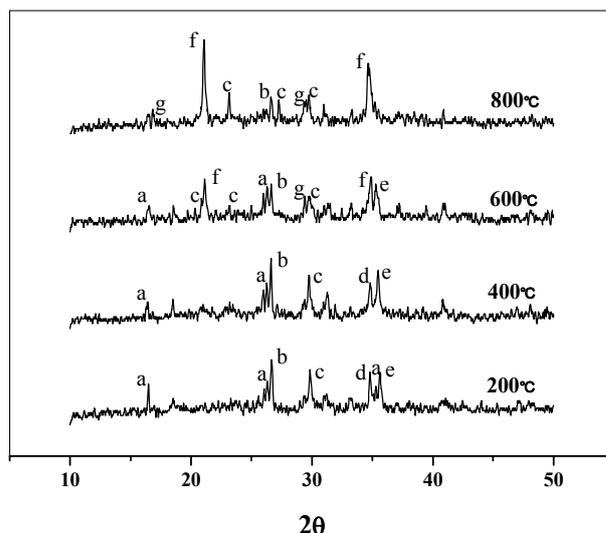


Fig. 6. The XRD pattern of calcined fly ash at different calcination temperatures.
a – Mullite, b – Quartz, c – Nepheline, d – $Na_{17}Al_5O_{16}$, e – $NaAl_2(Si_3Al)O_{10}(OH)_2$, f – $Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$, g – $Na_2SiO_3$

mullite and quartz crystal structure, and the more the sodium hydroxide and the reaction of $SiO_2$ and $Al_2O_3$ Alumina sodium of active substances. This may be because Si-O triangular tetrahedron and aluminum oxide polymer body with high temperature could fully grow a chain, forming a large number of the free-end of the breaking point. Particles could no longer be arranged according to certain rules and generate the active sodium alumina material to achieve the purpose of activation.

Calcined fly ash was taken into the follow-up hydrothermal synthesis (solid-liquid ratio of 1:1). The XRD was shown in Fig. 7, from which we could see different modified fly ash products after hydrothermal synthesis under different



Fig. 5. CEC and removal efficiency of modified fly ash in different solid-liquid ratios.



a-$Na_4KAl_5Si_{11}O_{32} \cdot 10H_2O$
b-$Na_{1.65}(AlO_2)_{1.65}(SiO_2)_{0.35}$
c-Nepheline
d-$Na_3Al_3Si_3O_{12} \cdot 1.8H_2O$
e-$Na_2Al_2Si_5O_{14}$
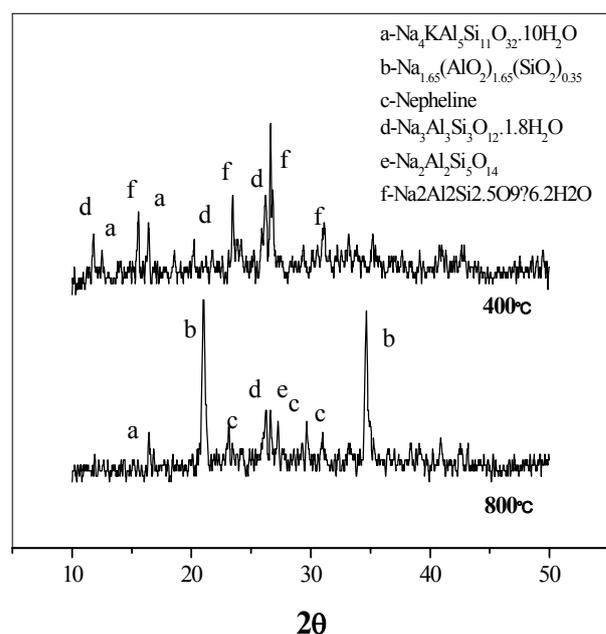f-Na2Al2Si2.5O9?6.2H2O

Fig. 7. The XRD pattern of hydrothermal synthesis fly ash at different calcination temperatures.
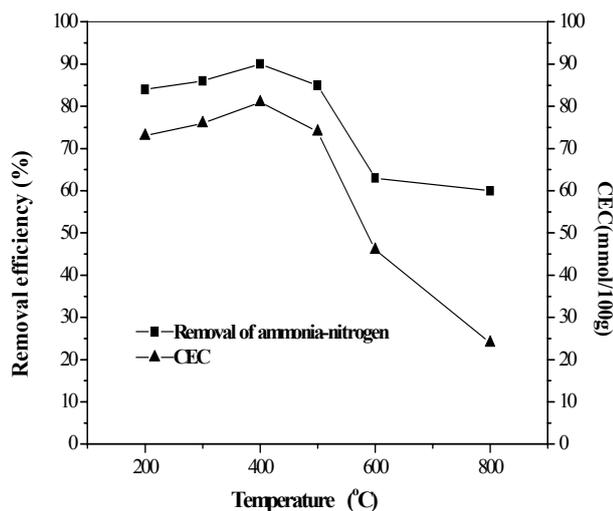
Fig. 8. Ammonia removal efficiency and CEC of modified fly ash at different calcination temperatures.

temperatures. With the low dosage of sodium hydroxide, the high temperature calcination would consume most of the sodium hydroxide in the hydrothermal synthesis of the follow-up small amounts of sodium hydroxide, which were not conducive to the formation of zeolite materials. Thus, with a small dosage of sodium hydroxide and after low-temperature calcination, hydrothermal synthesis of zeolite was more conducive to the formation of substances.

### *Ammonia Removal and CEC Analysis*

It can be seen from Fig. 8 that when the calcination temperature is 400ºC, the modified fly ash in the CEC and its effect on ammonia nitrogen removal ratio reached the maximum 81mmol/100 g and 90%, respectively. As the calcination temperature first decreased and then increased, CEC and ammonia nitrogen removal were tested to show a downward trend. This was because the low-temperature was not conducive to the formation of the active alumina substances, so that there was less alumina to participate in the follow-up hydrothermal reaction, reducing the amount of zeolite-like substances produced. When there was a small amount of sodium hydroxide, as the calcination temperature increased, sodium hydroxide and fly ash had more reaction in the calcination process. Thus, less sodium hydroxide participated in the follow-up hydrothermal reaction and fewer zeolite-like substances were produced. Whether the temperature increased or not, there were little amount of zeolite-like substances produced, which affected the cation exchange capacity of modified fly ash and removed less ammonia nitrogen. Therefore, when the alkali content was low, the best calcination temperature of modified fly ash was 400ºC.

### Conclusions

Coal fly ash was modified using the sodium hydroxide calcination-hydrothermal method. Given efficiency and cost, the amount of alkali should be set as 0.4:1, the

amount of alkali should be set at 0.4:1, the solid-liquid ratio of modified fly ash ratio should be set at 1:1, and the best calcination temperature should be 400ºC. Through modification, the zeolite-like substances were produced and the cation exchange capacities (CEC) increased from 5 to 81 mmol/100 g. The modified fly ash could be treated with heat and HCl solution or NaOH solution in order to remove ammonium efficiently [13]. The modified fly ash in this paper was cheap and effective, providing a theoretical basis for ammonia-nitrogen wastewater treatment. Future studies could focus on the use of this modified coal fly ash for adsorption of other pollutants.

### Acknowledgements

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