

## Enrichment by leaching of kaolin from Tamazert mine (eastern Algeria)

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### Abstract

This article focuses on the development of Tamazert kaolin deposit located in the eastern of Algeria. Recently chemical and mineralogical analyses of representative samples have shown that kaolin contains large amounts of impurities of iron oxide ( $\text{Fe}_2\text{O}_3$ ) and anatase ( $\text{TiO}_2$ ), which adversely affect the quality of the commercial product. In order to improve the kaolin quality, literature search was performed. The aim of the present study was to reduce iron oxide impurities and titanium oxide contained in kaolin. Different particle size fractions of the crude sample were analyzed by XRD. Kaolin, like all clays, has a thin spread of minerals. To supplement the mineralogical characterization of the kaolin sample Tamazert < having a particle size 45  $\mu\text{m}$ , the electron microscope was used (SEM) SEM type 7001F. The point indicating the presence of kaolin was examined by EDX (Energy Dispersive X-ray), with an electron beam with energy of about 10 keV for 37 seconds. The particle size fraction of less than 45  $\mu\text{m}$  corresponding to the liberation mesh was chosen for purification by leaching with different concentrations of hydrochloric acid, heated to a temperature of 85 ° C.

From crude sample, different size fractions of particles were analyzed by XRD. According to the obtained results, it was established that the mineralogical composition comprises: quartz, muscovite, kaolinite, dolomite, albite and orthoclase. Samples of kaolin, treated with HCl, were analyzed by the X-ray fluorescence and by XRD. The results confirm that the iron oxide content ( $\text{Fe}_2\text{O}_3$ ) is reduced from 1.65% to 0.85% with a brightness up to 90% as a result of leaching concentration of hydrochloric acid.

Keywords: KAOLIN, TAMAZERT, LEACHING, SEM, XRD. ALGERIA

### Introduction

Kaolin is known as a white material. It is used as a filler and pigment in various industries such as the paper industry, ceramics, pharmaceuticals, etc. However, to meet the requirements of these industries, the kaolin must first be treated.

The objective of this study is to reduce the coloring impurities (iron and titanium oxides).

The authors Cambier and Picot [4] presented a treatment kaolin method by reductive leaching and

bleaching with acids.

The kaolin brightness, based on the work of the latter, is improved up to the value of 90.6%.

Eze et al [7] have recently considered the treatment of kaolin by hydrochloric acid and its physico-chemical effect. The results obtained show that HCl is a good solvent for impurities removal contained in kaolin.

Dorothy and Starkey [6] have reviewed a variety of clays (montmorillonite, metabentonite, illite, kaoli-

nite and halloysite) and a plurality of solvents suitable for their treatments. The objective of this study is to select the most suitable solvent. The obtained results show that treatment with acids has no detrimental effect on the preparation of the clay to the X-ray diffraction. By contrast, acetic acid is preferred to hydrochloric acid but the latter did not change the iron oxide surfaces of clay minerals, which makes it ineffective in the processing of kaolin.

Cieřla [5] regarding the processing of influence of path length and slurry velocity on the removal of iron from kaolin was using a high gradient magnetic separator.

Raghavan [12] have carried out tests for the purpose to extract iron and titanium oxides. The flotation product measured 84.5% ISO brightness at a clay recovery of 92%. The titania removal is as high as 62.5%. The brightness was further improved to 85.2% by reductive bleaching.

Research has been conducted on kaolin treatment processes by selective flocculation. Among the authors of this research, we quote: Luz et al [9], Larroyd et al [10], Bacon [2],

Pradip et al [11] regarding the processing of kaolin by flotation.

The authors Koster et al [8], were able to improve the whiteness of kaolin for the paper industry.

The aim of our study is to select the most suitable solvent.

## Materials and methods

### Samples characterization

Raw Kaolin sample of 100 Kg obtained from Tamazert deposit located in the north eastern of Algeria. The rock was subjected to crushing, mixing, quartering and dividing to obtain representative samples of 500 g. The Samples from the prepared kaolin were used for chemical analysis, Particle size distribution, Observation by SEM and mineralogical analysis.

For X-ray diffraction analysis we used a powder diffractometer branded « X' Pert Prof Type Panalytical MPD / vertical system  $\theta / \theta$  PDS pass 4 x Accelerator (detector) platforms (Bracket) (sample-stage) » with Cu radiation with a wavelength  $\lambda = 1.5405980 \text{ \AA}$  at  $2\theta$  values between  $10^\circ$  and  $90^\circ$ ,

The observation by SEM was prepared in CREDEG laboratory (Research & Development Centre of Electricity and Gas), Spa (Algeria).

Particle size distribution was conducted using an accessory name Scirocco 2000 (A) in laboratory Process Engineering, Boumerdes University.

The kaolin chemical composition analysis and X-ray diffraction are determined in the laboratory tests CETIM (study center and technology of the con-

struction materials industry services) Boumerdes.

Representative sample of 600g was subjected to sieve analysis using sieve device type RETSCH with a diameter of 200 mm x 50 mm, the particle size measurement range is from 0.045 to 4 mm on a vibratory sieve for 15 min at amplitude of 60 mm.

### Experimental procedure

In this work, we have applied of chemical processes on samples to reduce iron and titanium oxides.

The Particles  $> 45 \mu\text{m}$  in the initial sample are removed by sieving as they represent impurities of silica and mica.

Three kaolin samples of 20 g of particle size  $< 45$  microns were poured into three beakers of equal volume of 500 ml. Each beaker contained 200 ml of one acid: HCl,  $\text{H}_2\text{SO}_4$  and  $\text{OH}_3\text{-COOH}$  of concentration 2 mol / l with a very acidic pH.

Suspension sample N° 1 was stirred for 20 minutes and was then heated to the boiling temperature for each acid for 4 hours (with intermittent stirring for 15 seconds).

The procedure was repeated with samples N°2 and N°3 which were also treated with HCl,  $\text{H}_2\text{SO}_4$  and  $\text{OH}_3\text{-COOH}$ , but with concentrations of 4 mol/l and 6mol/l, and heating times of 6 to 8 hours respectively.

The suspension was filtered and the residue obtained washed three times with potable water, followed by washing with distilled water. These samples were dried at a temperature of  $150^\circ\text{C}$  for 5 hours.

The Samples N°1, N°2 and N°3, treated by chemical attack with HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{OH}_3\text{-COOH}$ , were analyzed by energy dispersive x-ray fluorescence (FX).

## Results and discussion

### Chemical analysis

The analysis of the raw sample by X-ray fluorescence yielded the following results: 68.13% as  $\text{SiO}_2$ , 19.72% as  $\text{Al}_2\text{O}_3$ , 1.65% as  $\text{Fe}_2\text{O}_3$ , 0.14% as CaO, 0.38% as MgO, 0.01% as  $\text{SO}_3$ , 4.34% as  $\text{K}_2\text{O}$ , 0.43% as  $\text{Na}_2\text{O}$ , 0.08% as  $\text{P}_2\text{O}_5$ , 0.35% as  $\text{TiO}_2$  and 9.29% loss to fire.

### Mineralogical analyzes

The samples are finely ground and then analyzed by the X-ray diffraction (XRD). The spectra obtained are composed of several peaks.

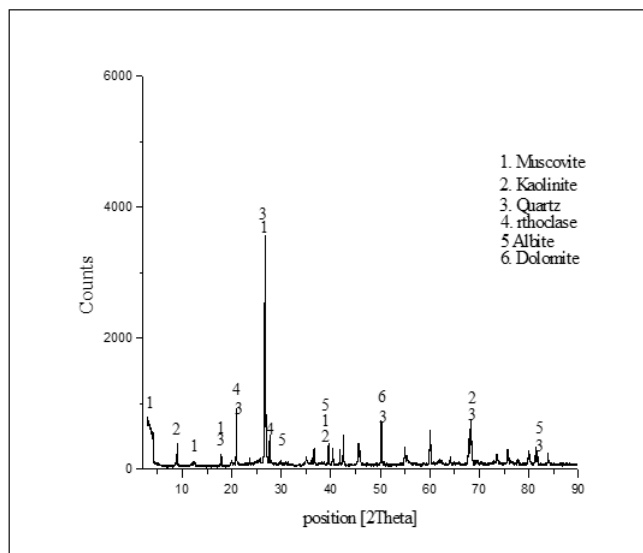
The results relating to the diffraction X-ray spectra of the initial sample are shown in (Fig. 1).

From (Fig.1), we see that the mineralogical composition of the original sample contains the following minerals: kaolinite, muscovite, quartz, dolomite, albite and orthoclase. However, we note:

a) The peaks of quartz and muscovite have a high intensity and are well pronounced, making their identification easier.

b) The peaks of quartz and kaolinite are superimposed with muscovite or aggregate form (quartz and muscovite)

Other chemical analyses were performed for different sized slices for 9 size classes. Their results gave  $Fe_2O_3$  content ranging from 1.27% to 3.



**Figure 1.** X-ray diffraction spectrum of the initial sample

**Table 1.** Results of chemical analysis of the major elements of size fractions of kaolin

Size Classes	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
+4	74.99	15.41	1.68	0.32
-4+2	77.34	14.19	1.27	0.30
-2+1	72.58	17.61	1.44	0.35
-1+0.5	69.50	18.98	1.52	0.35
-0.5+0.25	62.56	23.45	1.97	0.41
-0.25+0.125	58.50	25.86	2.02	0.39
-0.125+0.063	55.63	28.29	2.06	0.37
-0.063+0.045	53.90	29.76	2.13	0.40
-0.045	49.26	31.44	3.00	0.48

The mineralogical distribution curve over different sized sample slices in (Tab.1) shows that the SiO<sub>2</sub> increases gradually from 53.90% for the slice of 0.045 mm thickness to 77.34% for the slice of 2 mm thickness. This confirms that the Tamazert kaolin is siliceous.

And we see that the TiO<sub>2</sub> content is not more than 0.48% for sample < 0.045mm. By contrast the Fe<sub>2</sub>O<sub>3</sub> content reached 3.00% in that slice. From chemical analysis results, Tamazert kaolin raw sample gave a grade of 1.65% Fe<sub>2</sub>O<sub>3</sub>.

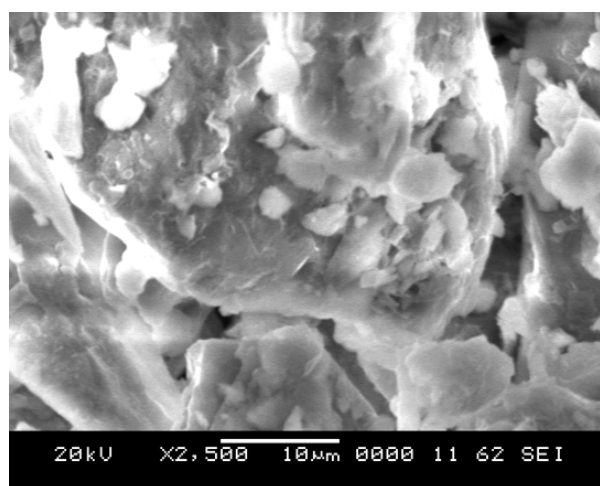
In order to verify and confirm the reliability of the Fe<sub>2</sub>O<sub>3</sub> content results shown in (Fig 3) with respect to the content of Fe<sub>2</sub>O<sub>3</sub> obtained in the initial sample was

applied statistical processing.

The results of statistical analysis for the Fe<sub>2</sub>O<sub>3</sub> contents of the 9 size classes confirm the mean grade of 1.65% Fe<sub>2</sub>O<sub>3</sub> in the raw sample.

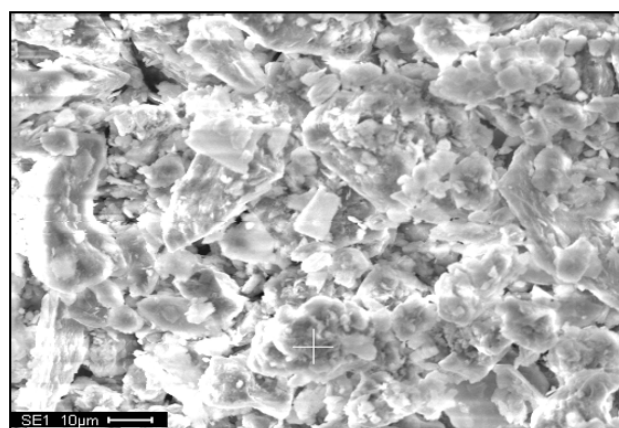
### SEM and EDX analyzes

To complete the mineralogical characterization of the kaolin Tamazert sample having a particle size < 45 μm, we have used a scanning electron microscope (SEM) of 10 μm (see Fig. 2).



**Figure 2.** Observation by electron microscopy

Most clay minerals are monoclinic, kaolinite however is triclinic. These minerals have the form (hexagonal tablets) and basal cleavage (001) mica, but these characteristics are very rarely observed in thin mica.



**Figure 3.** Observation by electron microscopy

The important point indicating the presence of kaolin in Figure 3 was examined by (Energy Dispersive X-ray) EDX, with an electron beam of an energy of about 10 keV during 37 seconds (see Fig. 4).

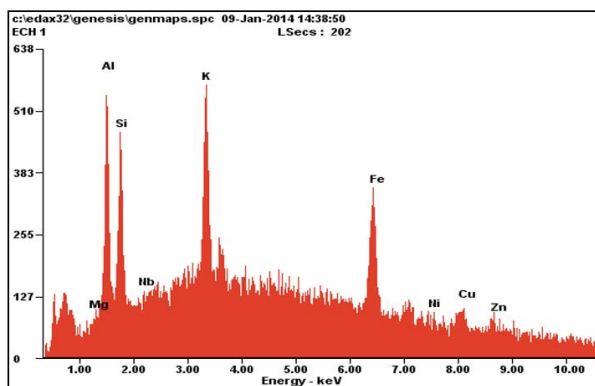
The obtained results are as follows:

a) The peak of Al (1.5 KeV) and K (3.5 KeV) have a high intensity (see Fig. 7). The presence of these two elements confirms the results of the chemical analy-

sis of the initial sample of kaolin.

b) The peak of iron (6.5 KeV) is less intense than the peak of Si (1.8 KeV) (see Fig. 7).

c) The peaks of Mg, Nb, Ni, Cu, and Zn are very low intensities.

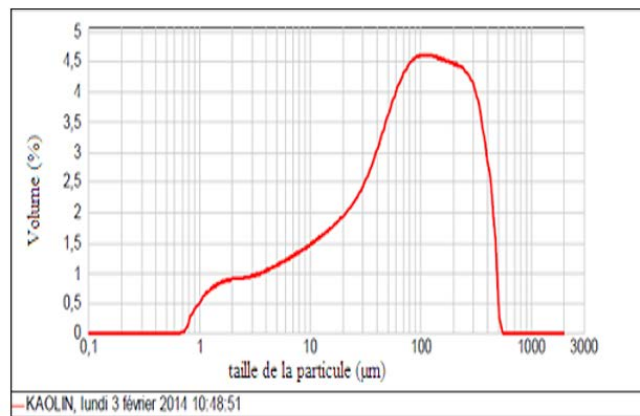


**Figure 4.** Energy Dispersion X-ray

### Particle size analysis

The particle size distribution curve after particle size analysis of the raw sample of Tamazert kaolin, is presented in (Fig 5).

d (0.1): 5,130  $\mu\text{m}$   
 d (0.5): 76,846  $\mu\text{m}$   
 d (0.9): 300,727  $\mu\text{m}$



**Figure 5.** The distribution curve of particle size

### Evaluation of efficiency to removal iron and titanium

The chemical analysis of the main impurities of the Tamazert kaolin, is following presented.

**Table 2.** Efficiency of iron and titanium removal from sample 1 at different concentration and various acids with temperatures boiling of 4 hours

Sample N°	Testing	Acids	Concentration, mol/l							
			1		2		4		6	
			Contents, %							
			Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
1	1	HCl	1.15	0.35	0.98	0.35	0.93	0.34	0.90	0.33
	2	H <sub>2</sub> SO <sub>4</sub>	0.98	0.35	0.80	0.34	0.65	0.33	0.56	0.32
	3	OH <sub>3</sub> -COOH	1.58	0.35	1.49	0.35	1.38	0.35	1.30	0.35

The obtained results shown in (Tab. 2, 3, 4 and 5) confirms the influence of preparation time in sample processing by acids. The content of Fe<sub>2</sub>O<sub>3</sub> is reduced

from 1.65% at the start to 0.85% for HCl, 0.56% for H<sub>2</sub>SO<sub>4</sub> and 1.30% for OH<sub>3</sub>-COOH, for a time heating 4 hours.

**Table 3.** Efficiency of iron and titanium removal from sample 2 at different concentration and various acids with temperatures boiling of 4 hours

Sample N°	Testing	Acids	Concentration, mol/l							
			1		2		4		6	
			Contents, %							
			Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
2	1	HCl	-	-	0.88	0.33	-	-	-	-
	2	H <sub>2</sub> SO <sub>4</sub>	-	-	0.54	0.33	-	-	-	-
	3	OH <sub>3</sub> -COOH	-	-	1.30	0.35	-	-	-	-

The Fe<sub>2</sub>O<sub>3</sub> content is reduced from 1.65% to 0.88% for HCl, 0.54% for H<sub>2</sub>SO<sub>4</sub> and 1.30% for OH<sub>3</sub>-COOH

for a time heating 6 hours.

**Table 4.** Efficiency of iron and titanium removal from sample 3 at different concentration and various acids with temperatures boiling of 8 hours

Sample N°	Testing	Acids	Concentration, mol/l							
			1		2		4		6	
			Contents, %							
			Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
3	1	HCl	-	-	0.85	0.33	-	-	-	-
	2	H <sub>2</sub> SO <sub>4</sub>	-	-	0.50	0.32	-	-	-	-
	3	OH <sub>3</sub> -COOH	-	-	1.25	0.35	-	-	-	-

For a time heating 8 hours, we see that the best results are obtained by the sample N°3, testing 1, during treatment with hydrochloric acid with the following parameters:

HCl concentration: 2 mole / l;

Conditioning time: 8 hours;

Boiling point: 90 °C.

Thereby the iron content decreases from 1.65% to

0.85% with the preservation of the crystal structure of kaolin

As for the content of Fe<sub>2</sub>O<sub>3</sub>, for the sample treated with sulfuric acid, decreases from 1.65% to 0.50%, but this acid is not effective because the latter dissolution of Al<sub>2</sub>O<sub>3</sub>. Furthermore, the influence of acetic acid on Fe<sub>2</sub>O<sub>3</sub> is low.

**Table 5.** Efficiency of iron and titanium removal from sample 1 at different concentration and various acids with temperature ambient of 480 hours (20 days)

Sample N°	Testing	Acids	Concentration, mol/l							
			1		2		4		6	
			Contents, %							
			Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
4	1	HCl	-	-	0.87	0.34	-	-	-	-
	2	H <sub>2</sub> SO <sub>4</sub>	-	-	0.53	0.33	-	-	-	-
	3	OH <sub>3</sub> -COOH	-	-	1.25	0.35	-	-	-	-

The Fe<sub>2</sub>O<sub>3</sub> content is reduced from 1.65% to 0.87% for HCl, 0.53% for H<sub>2</sub>SO<sub>4</sub> and 1.25% for OH<sub>3</sub>-COOH for a time heating 480 hours (20 days).

The obtained results by three acids at different time, we see the influence of the leaching at TiO<sub>2</sub> content remains low and its content does not significantly decrease. A decrease of 35% to 33% for the sample treated with HCl, of 35% to 33% for the sample treated with H<sub>2</sub>SO<sub>4</sub>, and the content remains unchanged for the sample treated by the OH<sub>3</sub>-COOH.

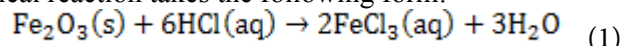
When processing the kaolin at different concentrations of HCl, we notice the color change towards yellow HCl and yellow solubility product to white. By comparison, the color of samples treated with H<sub>2</sub>SO<sub>4</sub> changed from yellow to white and then to gray and this, due to the decreases of Al<sub>2</sub>O<sub>3</sub> in the suspension as shown by the analysis through (FX) and XRD.

This study confirms that, if one increases the conditioning time or the concentration of acid, the content of iron oxide decreases. It was also noted that treating the sample with H<sub>2</sub>SO<sub>4</sub>, also decreases the Al<sub>2</sub>O<sub>3</sub> content.

Therefore, we can say that the treatment of kaolinite

with HCl is more effective compared to H<sub>2</sub>SO<sub>4</sub> and OH<sub>3</sub>-COOH acids.

Under the effect of the dissolution of metal components, mainly Fe<sub>2</sub>O<sub>3</sub> in the HCl solution, the chemical reaction takes the following form:



There are two oxidation states of iron: Fe<sup>2+</sup> and Fe<sup>3+</sup>. This leads us to distinguish two types of iron dichloride (II) and trichloride (III). In the case of

Tamazert kaolin, iron contained in the ore is trichloride.

The risk for the wastewater environment is decisive. Therefore, the potential acid is important because of the leaching of iron and titanium impurities with hydrochloric acid. To overcome this phenomenon which affects the environment, the neutralization quicklime is recommended. On contact of the water with the slaked lime is obtained lime Ca(OH)<sub>2</sub>, which causes an increase in pH. At the industrial level, the neutralization process can be achieved in the settlement of washing tanks [3].

After leaching with hydrochloric acid with a concentration of two moles per liter for a period of 8 hours,

the sample of kaolin concentrate obtained was analyzed by XRD.

### Conclusion

The results of chemical analysis showed that the Tamazert kaolin is siliceous because of the high silica content of up to 68.13%.

The content of the iron oxide, after the HCl acid attack is reduced from 1.65% to 0.85% with the retained crystalline structure, and from 1.65% to 0.50% after the attack by H<sub>2</sub>SO<sub>4</sub>, but with a decrease of Al<sub>2</sub>O<sub>3</sub> content.

The Al<sub>2</sub>O<sub>3</sub> content decreases from 30.13% to 10.80% in the treatment of the kaolin sample by H<sub>2</sub>SO<sub>4</sub> Angus (2012) [1].

In the initial sample, the titanium oxide content is 0.35%. After treatment with acids, it decreased by 0.35% to 0.33% due to a weak influence of acid on TiO<sub>2</sub>.

During the XRD analysis of the concentrate of kaolin sample, Muscovite peaks of kaolinite and albite are clearly expressed relative to the initial sample. The best results are obtained when treating kaolin with HCl to two moles per liter for a period of eight hours.

The results of this study confirm the existence of many structural similarities (impurities, properties, whiteness, etc.) between the treated Tamazert kaolin and kaolin used in the paper industry.

The characteristics of treated kaolin (whose whiteness) in Tamazert mine are similar to the results of the works obtained by Cambier and Picot [4], and Asmatulu [2].

The obtained results by the three acids with ambient temperature for a period of 480 hours, are almost identical. However, the duration of the operation therefore, it is not taken into consideration.

### Acknowledgements

This work was supported by the Laboratory of Valorization of Mining Resources and Environment, Mining Department, Badji Mokhtar University, Annaba, Algeria. I would like to thank Pr. Mohamed Bounouala and Pr. Korichi Talhi for their assistance to carry out this research work.

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