

Crystallization Behavior of Synthesized Zeolite-A from Iraqi Kaolin

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ABSTRACT

In this study, Iraqi kaolin deposits were used as starting materials in synthesis of zeolite-A. The kaolin was converted into metakaolin by a process of calcinations at 582 °C for 90 min. The amorphous aluminum silicate of metakaolin was mixed hydrothermally with 3M of NaOH solution via two tools (autoclave and condenser) for different reaction times. XRD, FTIR, and SEM techniques were applied to specify the crystalline phases appeared during the reaction time. The alkalinity environment, pressure, and the stirring action were played the principal role in crystallization of zeolite-A. In an autoclave instrument, the zeolite-A was grown at early time of reaction and gradually faded in subsequent times of reaction. On the other hand, the reaction in a condenser tool showed an opposite state of crystallization of zeolite-A. The only drawback was the appearance of quartz as an impurity phase throughout the reaction times.

Keywords: Iraqi Kaolin, Zeolite-A, Hydrothermal Synthesis.

1. INTRODUCTION

The zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline and alkaline earth metals. They are frameworks of $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetrahedral, which corner-share to form different open structures. These tetrahedral are linked together to form cages by pore opening of range sizes 3-10 Å^o [1]. Naturally, the zeolites have been thought of as well-crystallized minerals found in cavities and veins in basic igneous rocks. They are fuse readily with marked intumescences which results when water is expelled during heating [2]. The structure formula of zeolite is based on the crystallographic unit cell: $M_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] w\text{H}_2\text{O}$, where M is an alkaline or alkaline earth cation, n is the valence of the cation, x and y are the total number of tetrahedral per unit cell, and w is the number of water molecules per unit cell, and the ratio y/x usually has values of 1 to 5, but for silica zeolite y/x can be ranging from 10 to 100.

Synthetic zeolite is named by International Zeolite-A is characterized by their absorption, adsorption, ion exchange, and catalyst due to their unique porous structure. So, there are many applications of zeolite-A in agriculture, water treatment, and oil industries [4,5]. Many sources have been used to synthesized zeolite-A such as fly ash [6], kaolin deposits [7,8,9], inorganic wastes [10], and alumatrane with silatrane precursors [11]. In this article, the synthesis of zeolite-A was isothermally done using the Iraqi kaolin ore and a simple, low cost apparatus which built in our laboratory. The synthesized zeolite-A was characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and fourier transmission infrared (FTIR), to know of its crystallization behavior route.

2. EXPERIMENTAL

Zeolite Association (IZA) which is frequently published and updated any new product and assigns it as three letter code to be used for a known topology. Zeolite-A which is concerned here, is known as a Linde Type A according to IZA. It is classified into different categories when potassium and

calcium ions are replaced the sodium ion in M site. Zeolite-A is characterized by the following features: It has a 3-dimensional pore structure with pore running perpendicular to each other in the x,y, and z planes. It is made of secondary building units 4, 6, 8, and 4-4. The pore diameter is defined by an eight member oxygen ring and is small at 4.2 Å^o. This leads into a large cavity of minimum free diameter 11.4 Å^o. The cavity is surrounded by eight sodalite cages [truncated octahedron] connected by their square faces in a cubic structure [3]. So, the unit cell is cubic (a=24.1661 Å^o). It has space group of Fm3c and the ratio of Si/Al = 1.

Table. 1 Chemical and Mineralogical Analysis of Iraqi Kaolin before and After Calcinations.

Oxide	Kaolin before calcinations	Kaolin after calcinations
SiO ₂	51.07	56.07
Al ₂ O ₃	31.67	35.7
TiO ₂	1.26	1.48
Fe ₂ O ₃	1.37	1.56
MgO	0.09	0.11
CaO	1.37	1.60
Na ₂ O	0.13	0.15
K ₂ O	0.43	0.5
L.O.I	12.32	2.64
Minerals content of kaolin		
Before calcinations		After calcinations
Kaolinite = 91.49 %		Metakaoline=86.5%
Quartz = 7.21 %		Quartz = 7 %
Orthoclase = 1.3 %		Orthoclase = 6.5 %

2.2 Hydrothermal synthesis of zeolite-A

Three gram of metakaolin was mixed with 75 ml of 3M sodium hydroxide solution. The mixture was stirred for one hour to obtain a homogeneous solution. The hydrothermal treatment for the solution was achieved by two tools, the first was a Teflon lined stainless steel autoclave, and the other was a condenser. The mixture reaction in the autoclave apparatus is kept at 110 °C for various times (3, 6, 12, 24, and 48) hour. Then the solution was left over 24 hour to be cooled and aged at room temperature. After that, the solid powder was separated from the liquid by centrifuging device, and washed with distilled water three times to remove any excess of alkali. Finally, the synthesized powder was dried at 85 °C for 24 hour. On the other hand, the mixture reaction in the condenser set tracks the same procedure as that follows in an autoclave excepting the temperature was 100 °C. Figure 2 illustrates both of autoclave device and a condenser set in which the hydrothermal process was achieved.

2.3 Instrumental

Calcinations temperature of Iraqi kaolin was detected using differential scanning calorimetry (DSC) type-131, evo, Setaram, France. Platinum pan containing 10 mg of kaolin sample was used in DSC analysis, in which the sample and the crystalline of phase product was characterized by X-ray diffraction (XRD) using Shimadzu 6000 (Japan) diffractometer at a scanning speed of 5° /min and Ni as a filter and $Cu\alpha$ as a source radiation of 40 kV and 30 mA . The diffraction data were recorded after 20 scans in the range 5-40°.A Fourier transform infrared (FTIR) spectrum was detected using a 8400s Perkin-Elmer spectrophotometer (Shimadzu, Japan) in 4000-400 cm^{-1} region. The solid samples were prepared by the KBr disc technique.

Scanning electron microscope (SEM) micrographs were obtained with inspect 550 type at 1500 kV to characterize the morphology of the product samples.

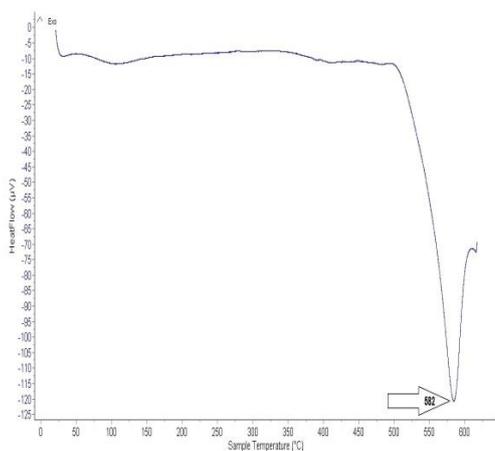


Fig.1 DSC analysis of Iraqi kaolin.

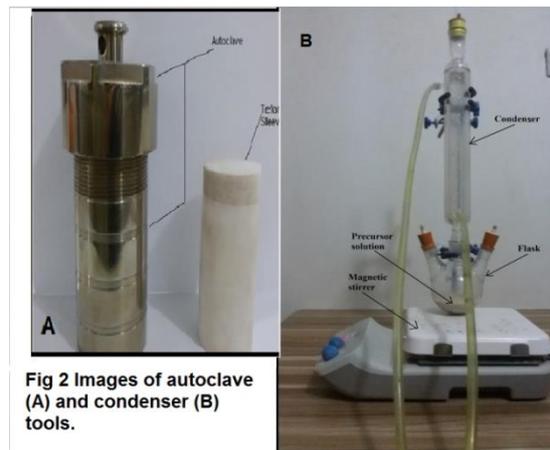


Fig 2 Images of autoclave (A) and condenser (B) tools.

3. RESULTS AND DISCUSSION

The kaolinite is considered the main phase in the Iraqi kaolin besides quartz phase (table 1). The calcinations process of kaolinite at 582°C (fig.1) will permit to existence the amorphous aluminum silicates (metakaolin), which is regarded the background of SiO_4 and AlO_4 tetrahedral network for synthesis of zeolit-A.

Figure (3) shows the XRD patterns of Iraqi kaolin illustrates both of autoclave device and a condenser set in which the hydrothermal process was achieved.

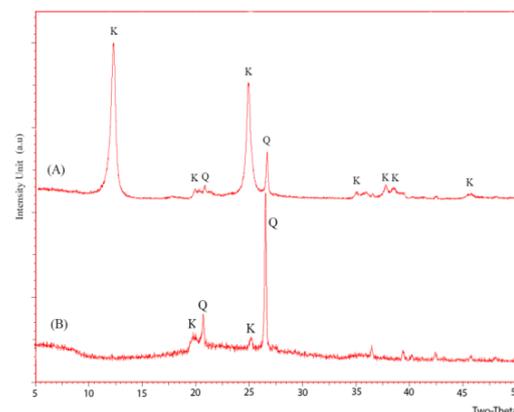


Fig. 3 XRD patterns of Iraqi kaolin (A) and metakaolin (B) at 582°C. k=kaolinite, Q=quartz.

The difference in temperature between the hydrothermal treatment in an autoclave and condenser was ten centigrade. This difference was necessary to be suitable for heat treatment agreement between autoclave tool and a condenser set. Figure 4 shows the relation between the temperature in Kelvin and time in hours for the heat transfer in an autoclave device using Cosmal program. The curve in this figure explains the heat flow steady in an autoclave device after fourteen hours, and this behavior coincidence with the choice of different heat treatment in an autoclave and a condenser.

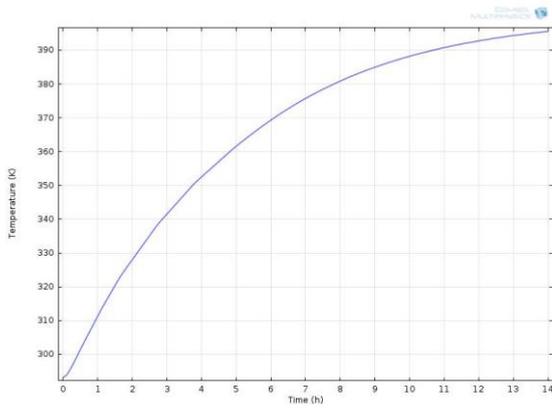


Fig. 4 Cosmal program chart for insulation in an autoclave device.

3.1 Crystallization path of zeolite-A

Figure 5 illustrates the X-ray diffraction patterns of the reaction products of zeolite-A by hydrothermal process in an autoclave tool. The time of reaction was done on several stages started from 3 hrs. and go on up to 48 hrs. At early stage of reaction as shown in fig. (5e), the cations of Si^{4+} , Al^{3+} , and Na^+ to oxygen anion ratio were feasible to well grow of both zeolite-A (z) and another modification of zeolite (z_1). Whereas, quartz phase remains as inherent impurity to the products of the reaction. This situation of crystallization stay on the same fashion until the time reaction reaches 6 hrs. (fig. 5d). When the reaction of mixture approaches 12 hrs. some deviations in diffraction angles inasmuch as $1.05^\circ 2\theta$ will happen for each zeolite-A (z) and zeolite (z_1) as shown in figure 5c. At a great distance in reaction time of 24 and 48 hrs. (fig.5 b,a), zeolite-A (z) will be gradually fade away in greater amount in comparison with that happened for zeolite phase (z_1). The alkalinity environment of the mixture could be considered as a guided for crystalline of zeolite-A. So, low ratio of Na/H_2O (~0.5) permits to develop the zeolite-A as a major phase at early stage of reaction. With proceeding time of reaction, the upgrade of alkalinity index up to 1.5 will cause prevailing of zeolite (z_1) at the expense of zeolite-A (z) which is going to gradually disappear.

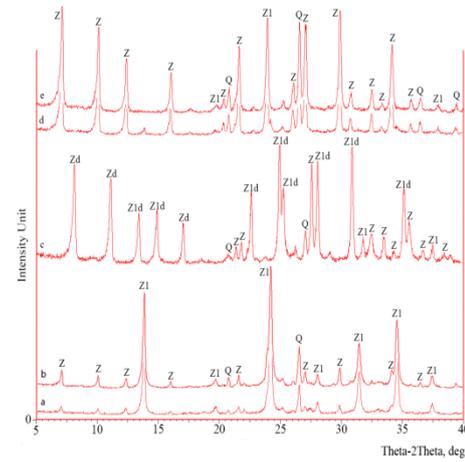


Fig. 5 XRD patterns of zeolite-A and quartz attendant resulted by autoclave hydrothermal process. (a) 48 h., (b) 24 h., (c) 12 h., (d) 6 h., and (e) 3 h. [z = zeolite-A ($NaAlSi_3O_8 \cdot 2.25H_2O$), $z_1 = (Na_{1.5}Al_{1.5}Si_{1.5}O_6 \cdot H_2O)$, Q = quartz, zd = deviation peak of zeolite-A, z_{1d} = deviation peak of zeolite z_1].

3.2 FTIR analysis

Figure 7 shows the IR spectra of the unreacted metakaolin, synthesized powder of zeolite-A by hydrothermal in an autoclave device at 6, 12, and 48 hrs. reaction times, and the reference zeolite-A sample given for comparison^[10]. The hydrothermal process in an autoclave tool. The time of reaction was done on several stages started from 3 hrs. and go on up to 48 hrs. At early stage of reaction as

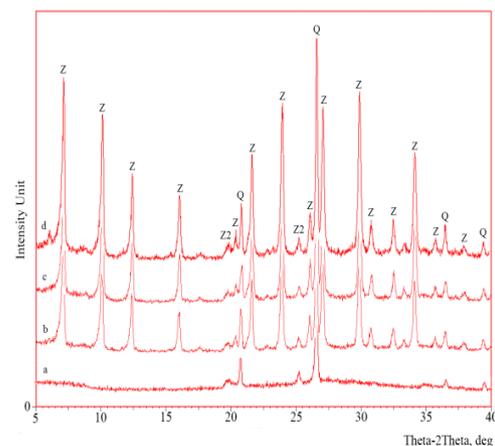


Fig. 6 XRD patterns of zeolite-A and associated phases obtained by condenser hydrothermal process. (a) 6 hrs., (b) 12 hrs., (c) 24 hrs., (d) 48 hrs. z = zeolite-A ($NaAlSi_3O_8 \cdot 2.25 H_2O$), $z_2 = (NaAlSi_{1.4}O_{4.7} \cdot 2.25 H_2O)$, Q = quartz.

Figure 6 shows the X-ray diffraction of zeolite powder which is prepared by hydrothermal process in a condenser device. It is obvious that there is not crystallization of zeolite-A at early stage of reaction (as far as 6 hrs.), in spite of appearance a little crystallization of another mode of zeolite (z_2) which has the same alkalinity index but differs in Si/Al ratio. Quartz mineral was occurred at the beginning time of the reaction and stays all

during further reaction as an accompanying impurity (fig 6a). At 12 hrs. of reaction and above, zeolite-A was started to develop as a major and well crystallized phase as shown in figure (6b, 6c, and 6d).

The pressure and stirring action play a main role for crystallization of zeolite-A in both of autoclave device and a condenser set. The presence of pressure and absence the stirring action in an autoclave device cause the appearance of zeolite-A at early time of reaction and gradually faded in subsequent times of reactions. While, it is found the opposite situation of crystallization of zeolite-A in a condenser tool, where little pressure and an effective stirring action were occurred.

characteristic metakaolin bands were observed at 3475.73, 1639.49, 1060, 798.53, and 482.20 cm^{-1} (spectrum a). The band 482.20 cm^{-1} is related to the tetrahedral T-O (T=Si or Al) bending vibration. The broad band of metakaolin at 798.53 cm^{-1} represents Al-O bonds in Al_2O_3 . The band of metakaolin at 1060 cm^{-1} which could be contributed to asymmetric stretching of T-O bonds was shifted to 1000, 1000, and 990 cm^{-1} as shown in spectra b, c, and d respectively. This amount of deviation in band vibration was caused by the transformation of amorphous metakaolin to crystallized aluminosilicates of zeolite-A structure [8]. The other bands of metakaolin at 1639.49 and 3475.73 cm^{-1} are assigned to O-H group [11]. The characteristic bands of zeolite-A which is synthesized by an autoclave, are well defined at 460.99, 464.84, and 457.13 cm^{-1} for reaction times of 6, 12, and 48 hrs. respectively. These particularly bands are referred to the internal vibration of T-O bending modes [11,12] as shown in fig 7b, c, and d. While, the bands at 563.21 and 555.50 cm^{-1} for the reaction times of 6 and 12 hrs. (Fig 7b and 7c) were assigned for the external vibration of double four rings [7]. These bands represent the beginning of zeolite crystallization [8]. Whereas, the zeolite product by a reaction time of 48 h shows a weak band at 540 cm^{-1} (Fig 7d) whereof reflects there is a weakness in crystalline of zeolite-A. This result is confirmed by XRD analysis in which zeolite-A reveals a tendency to be faded at later times of reaction. The bands at 663.51, 647, and 659.66 cm^{-1} are belonging to the internal vibration of tetrahedral T-O symmetric stretching, whereas the bands at 1000, 1000, 990 cm^{-1} and the sequence at 1365, 1300, and 1360 cm^{-1} are specified to the internal vibration of T-O asymmetric stretching [8,11]. The two packages of bands at 1635, 1645, 1649.14 cm^{-1} and the broad band's at 3445, 3483.44, 3537.45 cm^{-1} represent the O-H group as shown in figures 7b, 7c, and 7d.

Figure 8 illustrates the IR spectra of the unreacted metakaolin, synthesized powder of zeolite-A by hydrothermal in a condenser at 6, 12, and 48 hrs. reaction times, and the reference zeolite-A sample given for a comparison. It is evident that there are a similar peaks patterns and behavior with that noticed at

figure 7, excepting the continuous appearing of absorption bands for zeolite-A at beginning time of reaction other than observed in powder product of zeolite-A by autoclave device which are vanished at the later times of reaction.

3.3 Scanning electron microscopy (SEM)

Figure 9 shows the images of the zeolite-A produced after hydrothermal treatment in an autoclave and condenser devices. Image (a) reveals the morphology of the zeolitic grains obtained after 3h of reaction in an autoclave tool. It is obvious that the grains of zeolite-A have a habit of cubic forms with approximately crystal size of 1.7 μm . The microstructure of this stage of reaction displays a good crystallization of zeolite which agree with mineralogical and XRD results. Image (b) illustrates the progress in reaction of 12h in an autoclave instrument. It can be noticed that the grains of zeolite began in deformation from the perfect cubic habit to semi-spherical particles and this stage has confirmed by the deviation in diffraction angle of XRD analysis. Image (c) showed the zeolitic product after 6h in a condenser tool. It is clear that there are no characteristic cubes forms of zeolite but there is a random distribution of irregular grains of aluminosilicates. Hence, the reaction at early times have no any crystallization of zeolite-A. The progress in reaction time more than 6h will yield well defined cube crystals of zeolite-A as shown in image (d). The results of microstructure were coincidence with that obtained by XRD and FTIR analyses.

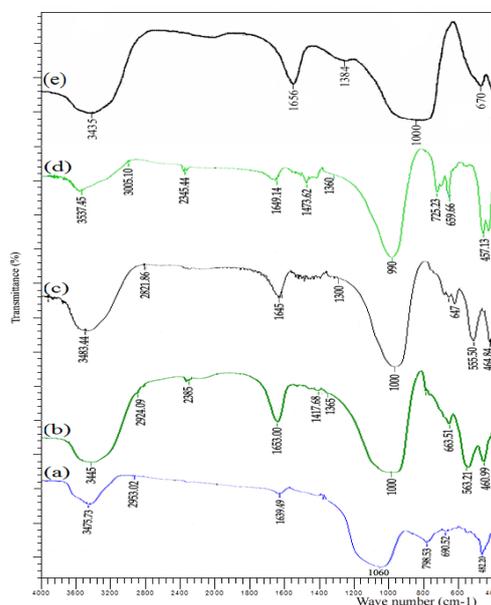


Fig.7 FTIR spectra of zeolite-A synthesized by hydrothermal in an autoclave at several reaction times. (a) unreacted metakaolin, (b) 6 hrs. (c) 12 hrs. (d) 48 hrs. (e) Reference of zeolite-A.

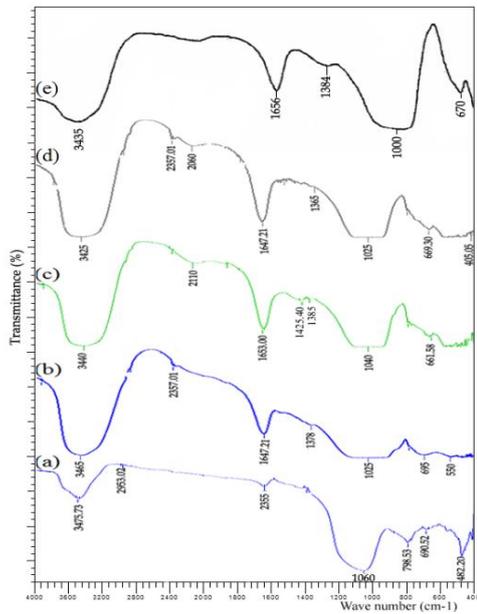


Fig.8 FTIR spectra of zeolite-A synthesized by hydrothermal in a condenser at several reaction times. (a) unreacted metakaolin, (b) 6 hrs. (c) 12 hrs. (d) 48 hrs. (e) Reference of zeolite-A.

CONCLUSIONS

The present work has been made to convert available Iraqi kaolin into zeolite-A using a hydrothermal treatment via two tools: an autoclave device and condenser one. The obtained results by XRD, FTIR, and SEM show the following observations:

- The pressure and stirring action have been played the main role in synthesis of zeolite-A.
- The presence of pressure and absence of stirring action in an autoclave tool derive the reaction to appearance of the zeolite-A at early times of reaction.
- On the contrary, little pressure and an effective stirring action in a condenser instrument were the reason for rising the crystalline phase of zeolite-A at later times of reaction.
- Iraqi kaolin was a proper and a cheaper raw material for synthesis of zeolite-A. On the other hand, quartz phase appears as an inherent impurity throughout the time of reaction.

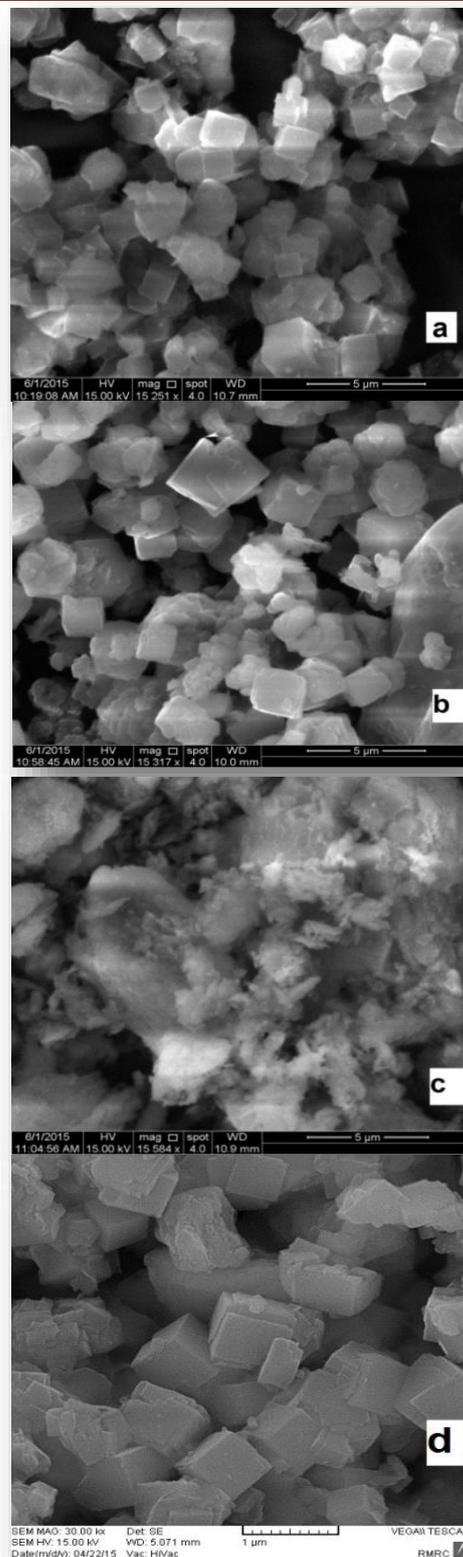


Figure 9 SEM micrographs show the microstructure of synthesized zeolite-A, (a) 3h[autoclave], (b) 12h [autoclave], (c) 6h [condenser], and (d) 48h [condenser].

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