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Fabrication of Synthetic Zeolite from Sinabung Mountain Volcanic Ash via Sol-Gel Method

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Abstract. Fabrication of synthetic zeolite from Sinabung Mountain volcanic ash by Sol-Gel method. The zeolite is obtained by extraction of alkalis sodium silicate and sodium aluminate. At first volcanic ash was characterized using XRF and XRD analyses. The XRF analysis shows that silica is 44.8%. In contrast, XRD analysis showed a sharp peak at a 2Ɵ corner area of 27.55o to express bonded with silica mineral salt. At the same time, the silica characterization is done by FT-IR analysis. The FT-IR analysis shows the presence of Si-O-Si groups at wave numbers 1064.71 cm-1, 786.96 cm-1 and Si-OH at wave 3749.62 cm-1 and 3448.72 cm^{-1}, identifying the presence of silica. The synthetic zeolite characterization analysis obtained is FT-IR, XRD, SEM-EDX, and BET analysis. In the FT-IR analysis, the O-Si-O group was obtained at wave 987,85 cm-1 and O-Al-O at wave 447,89-585,30 cm-1, identifying X zeolite. Diffractogram XRD showed a sharp peak at 66.8°, 28.12°, and 45.84°, forming mixed crystalline X and zeolite A. SEM-EDX analysis shows that zeolite morphology is tight and homogeneous and has a high aluminium content of 24.79 and Si 16.12. While for nitrogen desorption, adsorption analysis on pore size, surface area and pore volume are 3,22 nm, 61,86 m2/g and 0,095 cc/g. The result of synthetic zeolite isotherm adsorption-desorption shows type V showing mesoporous size.

Keywords: Synthetic, Zeolite, Volcanic Ash, Sol-Gel.

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1 Introduction

Volcanic ash is usually used as a building material, as a geopolymer material. Besides that, it can be used to manufacture zeolite because it contains silica. Analysis of the chemical composition of Sinabung Mountain volcanic ash, according to Tindaon (2016), is 84.72% SiO2 by weight, 7.12 wt% Al_2O_3; 5.66 wt% MgO; then 0.30% by weight Na_2O; 0.27 wt% K_2O;0.22 wt% CaO; 0.19 wt% Fe_2O_3; 0.1 wt% P_2O_5 and 0.01 wt% MnO.

The raw material for making zeolite is a material that contains silica and alumina. This raw material is taken from nature to reduce the cost of zeolite synthesis and natural utilization (Ulfah

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et al., 2006). But minerals that come from nature are usually not pure because there are still mixtures such as iron, magnesium, manganese, sodium and potassium. So producing a good synthetic zeolite takes a long process (Mathews, 2010).

Synthetic zeolite has many uses because it has several unique properties, namely tiny pore sizes ranging from 0.3 to 0.9 nm (Hamdan, 1992). The nature of this zeolite is essential for use in various fields, such as as an adsorbent, because of the hollow structure of the zeolite so that it can absorb several smaller molecules according to the size of the cavity (Putra, 2003).

Many studies have been carried out on this synthetic zeolite, including Mosoudian (2013) synthesized zeolite using water glass as a source of silica and with the addition of Al_2O_3, the curing process was carried out for 1 hour at room temperature, which was crystallized at 75°C for 4 hours in an oven. The result obtained is pure zeolite X.

Samsul (2015) modified zeolite from Mount Kelud volcanic ash by adding tetraethyl orthosilicate (TEOS) powder and Al_2O_3 using the sol-gel method at 75°C for 4 hours, where the results of the analysis show that the synthesis of zeolite produces a mixture of zeolite X and A.

Febri (2013) has synthesized the use of pumice as a source of silica and the addition of $Al(OH)_3$ using the hydrothermal method at 100°°C for 4 hours. The analysis showed the formation of zeolite A. Suseno (2013) synthesized zeolite from rice husk ash as a source of silica and with the addition of $Al(OH)_3$ using the sol-gel method followed by the hydrothermal method at 100°C for 5 hours. The analysis showed the formation of 4 types, namely zeolite A, Na-A, Na-Y and Sodalite.

The advantages of the sol-gel method over the hydrothermal method are that the homogeneous sol-gel method has better high purity, the temperature is relatively low, and there is no reaction with other compounds. In contrast, the hydrothermal synthesis method depends on the desired material composition, particle size, morphology and synthesis process. Sensitive to many variables such as temperature, pH of silica and alumina sources, types of alkaline and alkaline earth cations, reaction time and surfactants (Fernadez, 2011).

Research on synthetic zeolite from the base material of Sinabung Mountain volcanic ash using aluminate powder (Al_2O_3) and carrying out curing and heating at 100°C is still little reported. This is interesting to the authors to increase the last curing time from only 1 hour to 24 hours. This curing time forms a stronger gel reaction and begins the crystal nucleus's formation. As well as raise the previous temperature was 75 with the sol-gel method for 5 hours, which utilizes silica from the volcanic ash of Sinabung Mountain as a result of alkaline extraction to produce synthetic zeolite through the alkaline reaction of sodium silicate and sodium aluminate; this zeolite will foam at this temperature thereby accelerating the formation of crystals and crystal nuclei.

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2 Materials and Methods

2.1 Equipment

The tools used in this study include analytical balance, universal indicator, furnace control, hotplate stirrer, x-ray diffractometer, Fourier Transform infrared, Brunauer-Emmet Teller adsorpmeter, X-Ray Fluorescence, Scanning Electron Microscope oven, glass vial equipment, pipette, thermometer, filter paper.

2.2 Materials

The materials used in this study included: volcanic ash from Sinabung Mountain, Al_2O_3, HCl, NaOH, Aquadest, and $AgNO_3$.

2.3 Preparation of Sinabung Mountain Volcanic Ash

One hundred fifty g of volcanic ash was dried in an oven for 2 hours at 110°C, sieved using a 100 mesh sieve, and soaked with 1N HCl while stirring using a magnetic stirrer at room temperature for 4 hours. Then it was filtered, and the residue was washed with distilled water to remove the remaining 1N HCl. Then the precipitate was dried and calcined at 900°C for 4 hours and characterized by XRF and XRD analysis (Aritonang, F., 2017).

2.4 Preparation of Sodium Silicate Solution (Na2SiO3)

Twenty-five g of volcanic ash soaked with 8N NaOH and heated at 80°C for 6 hours, stirring using a magnetic stirrer, and then filtered. 7N HCl was added to the filtrate until pH = 7 to form a white precipitate, then filtered. The residue was then washed with hot distilled water several times. Then the precipitate was dried in an oven at 110°C to obtain silica powder and characterized by FT-IR analysis. Furthermore, 5 grams of silica powder was put into 1M NaOH while stirring and heated at 100°C for 2 hours, then allowed to stand for 24 hours to obtain a sodium silicate solution (Aritonang, F., 2017).

2.5 Preparation of Sodium Aluminate Solution

As much as 17 g of NaOH was put into the beaker glass and dissolved in 100 ml of distilled water. The solution was heated at 100°C, added 21.6 grams of Al_2O_3 little by little with stirring, diluted to 250 ml, and allowed to stand for 24 hours.

2.6 Manufacturing of Synthetic Zeolite

20 ml of sodium silicate and 20 mL of sodium aluminate were mixed and stirred using a magnetic stirrer for 2 hours at room temperature. The solution was heated at 100°C for 5 hours in a tightly closed state, then allowed to stand for 24 hours. Furthermore, the sample was washed with distilled water until pH = 7, filtered with Whatman No. 42 then the residue was taken. Then the residue formed was dried at 110°C for 2 hours and characterized using FT-IR, XRD, BET and SEM-EDX analysis.

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3 RESULT AND DISCUSSION

3.1 Preparation of Sinabung Mountain Volcanic Ash

The volcanic ash was sieved using a 100-mesh sieve. Then washed with 1N HCl, it removes metals and non-metals because HCl can bind metal oxides P_2O_5, K_2O, MgO, Na_2O, CaO and Fe_2O3. In non-metal oxide, chlorides will be converted into acidic forms except for silica. Then the volcanic ash is stirred, and the residue obtained is heated to a temperature of 120°C, then calcined at 900°C. Furthermore, it was characterized by XRF and XRD analysis.

3.1.1 XRF Analysis of Sinabung Mountain Volcanic Ash Results

The volcanic ash obtained was analyzed using XRF analysis to determine the minerals contained in the volcanic ash. The XRF results obtained are in Table 1 below:

Table 1. XRF Analysis Results from Mount Sinabung Volcanic Ash in the Sigarang-garang Region, Karo District, North Sumatra

No	Compound	Composition (%)
1	Al_2SO_3	18
2	SiO_2	44.8
3	K_2O	1.55
4	CaO	15.9
5	TiO_2	1.36
6	V_2O_6	0.03
7	Cr_2O_3	0.042
8	MnO	0.33
9	Fe_2O_3	17.33
10	CuO	0.062
11	ZnO	0.049
12	SrO	0.36
13	BaO	0.22
14	Eu_2O_3	0.2
15	Re_2O_7	0.2

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3.1.2 XRD Analysis of Sinabung Mountain Volcanic Ash Results

The volcanic ash obtained was characterized by XRD analysis to identify crystalline and amorphous phases at an angle of 2Θ as shown in Figure 1 XRD below:

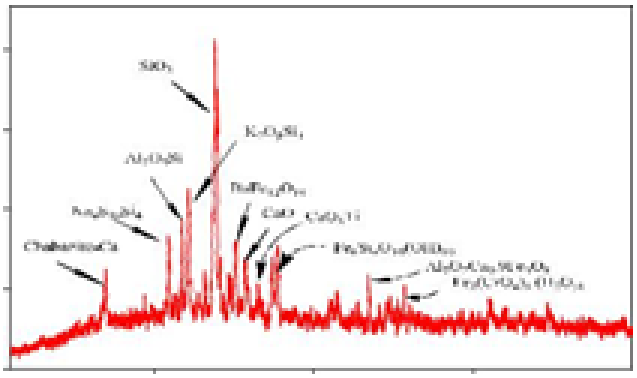

Figure 1. Diffractogram XRD analysis of Sinabung Mountain volcanic ash in the Sigarang-garang, Karo Regency

The XRD diffractogram shown in Figure 1 at an angle of 2Θ indicates several different peaks. That is, there are 12 peaks whose intensity is quite sharp. The sharpest peak is at 2Θ, which is 27.55°, which indicates the presence of SiO_2 in the form of bound minerals, namely Al_2O_5Si, $K_2O_9Si_4$, $6Si_4O_{10}(OH)_{10}$, which corresponds to the XRD peak reported by Hubbard (1981).

3.2 Manufacturing of Sodium Silicate

Silica from Mount Sinabung volcanic ash is obtained by heating 25 grams of volcanic ash in 1L NaOH 8N for 6 hours. It is done to extract silica from volcanic ash because silica dissolves in NaOH solution according to the reaction:

$SiO_{2(s)} + 2NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$ (Basset, et al., 1989)

After that, it was filtered. In this siliceous filtrate, HCl 7N was added to pH 7 and silica gel was formed.

This corresponds to the reaction:

$Na_2SiO_{3(aq)} + 2HCl_{(aq)} \rightarrow H_2SiO_{3(l)} + 2NaCl\ H_2SiO_{3(s)} \rightarrow SiO_2.2H_2O_{(s)}$ (Bakri, 2008)

The silica gel was then washed using hot distilled water to remove the by-product, NaCl, where the test could be carried out qualitatively using $AgNO_3$. Then the silica gel was dried in an oven at 110°C. The silica formed was then characterized by FT-IR analysis.

3.2.1 FTIR Analysis of Silica

The silica obtained was characterized by FT-IR analysis to determine the presence of functional groups. The FT-IR analysis results obtained are shown in Figure 2 below:

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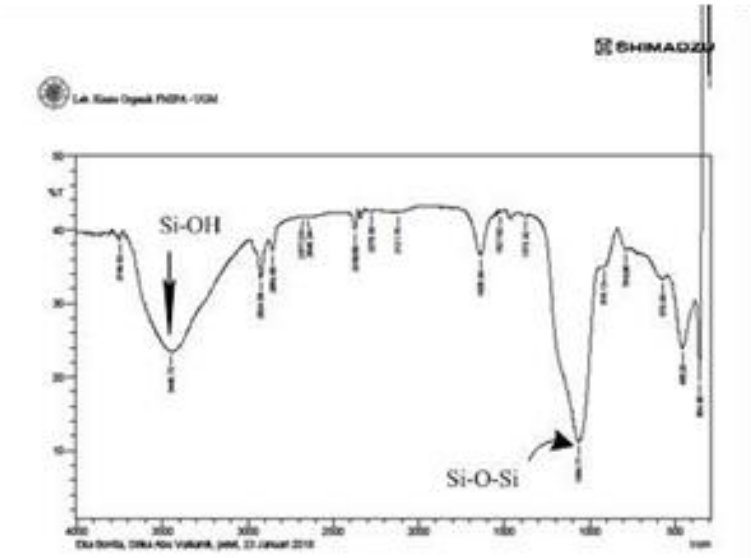
Figure 2. FTIR Spectrum of Silica



The FT-IR spectrum shown in Figure 2 obtained absorption peaks at 3749.62 cm^{-1} and 3448.72 cm^{-1}, indicating the presence of Si-OH groups and at wave numbers 1064.71 cm-1 and 786.96 cm-1 indicating the presence of asymmetry and symmetry groups of Si-O-Si. This difference in peaks is caused by Si-O-Si vibrations. This causes absorption differences between the Si-O-Si asymmetry and symmetry groups (Pavia, 2009).

3.3 Preparation of Sodium Aluminate Solution

The step for making a sodium aluminate solution, NaOH, which is dissolved in distilled water, is added Al_2O_3, so sodium aluminate is formed, a source of Al for synthetic zeolite. Then allowed to stand for 24 hours according to the following reaction:

$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H2O$ (Septia, 2011)

3.4 Preparation of Zeolite Synthesis

The sodium silicate solution and sodium aluminate solution are put into a glass beaker and then stirred with a magnetic stirrer at 100°C; a crystal core is formed, which occurs during stirring to complete the polymerization of zeolite-forming ions (Sholichah et al., 2013). Then leave it for 24 hours. The reaction that occurs is as follows (Ojha et al., 2004):

$NaAlO_{2\,(aq)} + Na_2SiO_{3\,(aq)} \rightarrow [Nax(AlO_2)\,(SiO_2)z.\,H_2O]\,(gel)$

3.4.1 FTIR Analysis of Zeolite Synthesis

The zeolite obtained was characterized by FT-IR analysis to determine the presence of functional groups. The FT-IR analysis results obtained are shown in Figure 3 below:

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Figure 3. FT-IR Spectrum of synthetic zeolite

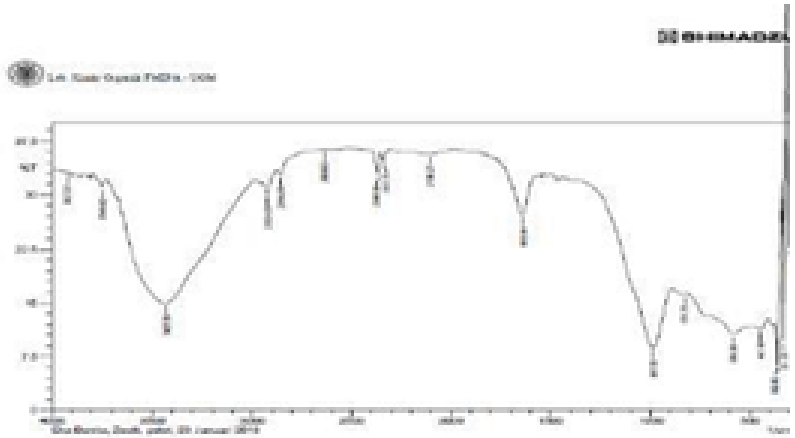

Figure 3 is an image of the zeolite's IR spectrum, which shows a strong IR absorption in the spectral region of 1500 cm^{-1}. A strong peak was observed at the 331.76 cm^{-1} area, which shifted to 447 $cm^{-1,}$ indicating a T-O bond. Another peak observed in the 987 cm^{-1} region indicates an asymmetric T-O bond. Whereas the area of 3425.58 cm-1 indicates the presence of a hydroxyl group –OH, where T is Si or Al (Flanigen, 1991).

3.4.2 XRD Analysis of Zeolite Synthesis

The synthetic zeolite obtained was characterized by XRD analysis to identify crystalline and amorphous phases at an angle of 2Ɵ as shown in Figure 4 XRD below:

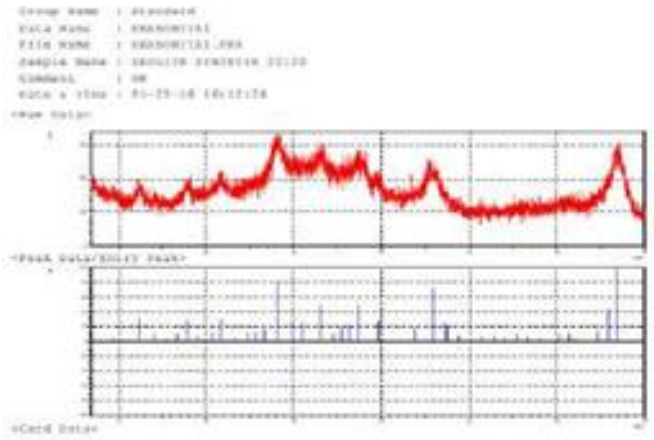

Figure 4. The diffractogram XRD of synthetic zeolite

Based on the results of the diffractogram in Figure 4, it is known that the synthesized zeolite obtained is a mixed zeolite, characterized by the presence of zeolite X peaks (i.e. at an angle of 2Ɵ respectively 23.300°, 26.600°, 33.0300°, 3.500° and 43.800°, respectively) and zeolite A (i.e. at an angle of 2Ɵ 21.6500°, 35.5100°, 47.1800°) so that the synthesized zeolite X is not pure which can be seen in Table 2

Table 2. Comparison of zeolite X and zeolite A with JCPDS data

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Zeolite X	Zeolite X Standart (2θ)	Zeolite A Standard (2θ)	Zeolite A (2Ɵ)
23.300	23.58	21.67	21.650
26.500	26.65	35.75	35.510
33.030	33.59	35.75	35.510
39.590	39.95	47.30	47.180
43.800	43.38	-	-

3.4.3 SEM-EDX Analysis of Zeolite Synthesis

SEM characterization was carried out to identify the morphology of the crystal surface of zeolite X. The SEM characterization results are presented in Figure 5. In zeolite magnification of 1000x and 1500x shows that the zeolite has a tight pore space and looks homogeneous

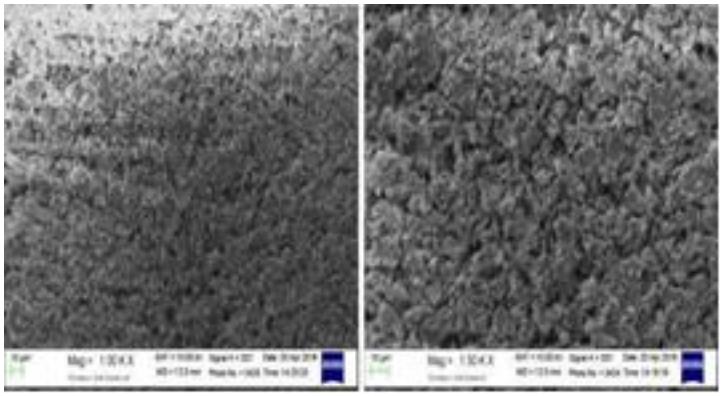

Figure 5. The SEM morphology of zeolite

3.4.4 Nitrogen Adsorption-desorption Isotherms BET

Nitrogen isotherm adsorption-desorption was carried out to determine the porosity of the zeolite and the pore size distribution. This analysis was carried out at 77.3K, and the adsorption-desorption isotherm graphs were obtained after being calculated using the Brunauer-Emmet-Teller method and shown in Figure 6 below:

Figure 6 shows the type V adsorption isotherm according to the classification of IUPAC (International Union of Pure and Applied Chemistry). The graph of adsorption-desorption nitrogen isotherm of synthetic zeolite followed by capillary condensation at a relative pressure (P/Po) between 0.4 - 1.00 atm indicates the formation of multilayers. Type V demonstrates that the porous material subjected to nitrogen gas is included in the mesoporous category (Quercia, 2013)

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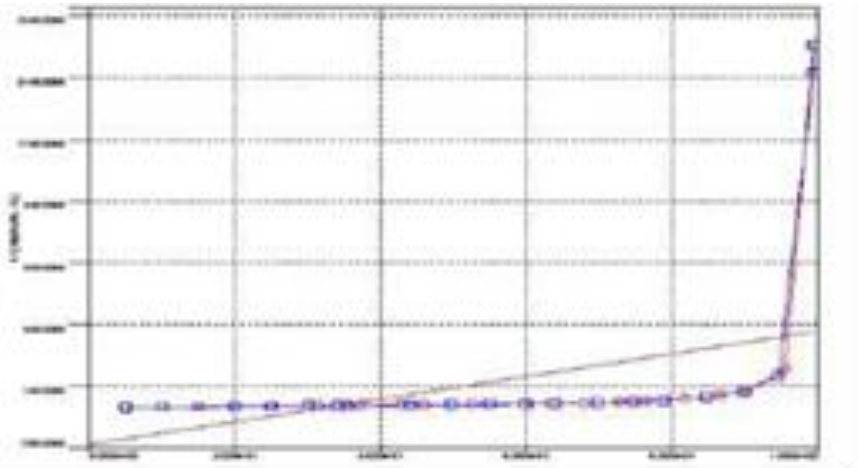

Figure 6. Graph of adsorption and desorption of synthetic zeolite

Pore size distribution was calculated using the Barret-Joyner-Halenda (BJH) method, and the results can be seen in Figure 7 below:

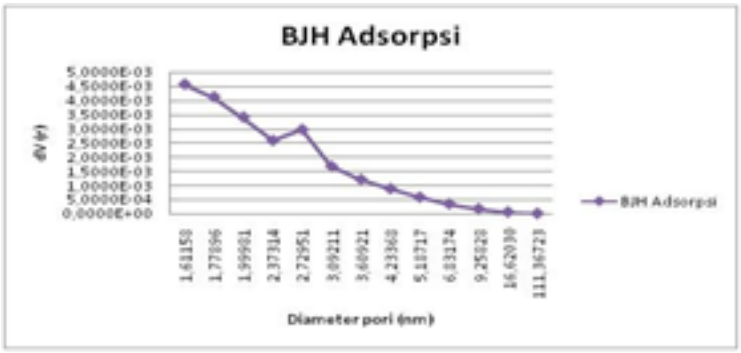

Figure 7. Graph of synthetic zeolite pore size distribution

Based on Figure 7, the pore size distribution of the most dominant synthetic zeolite is 3.22 nm which belongs to the mesoporous size. This study's curing process and synthetic temperature were 24 hours and 100°C, respectively. So in this process, it is predicted that the longer the curing time and the synthetic temperature will cause the pore size and surface area to decrease.

4 Conclusion

Adding sodium silicate and sodium aluminate at 100°C and a curing time of 24 hours in the manufacture of synthetic zeolite affects the type of zeolite produced. The zeolite produced in this study has a high Al content in zeolite X, which can be seen from the SEM-EDX results. In addition, the XRD analysis obtained a high intensity at an angle Θ, namely 66.8816°, indicating the formation of mixed zeolite A and X. Meanwhile, the characteristics of the synthetic zeolite produced in the 24-hour curing process obtained a surface area of 61.863 m^2/g, an average pore diameter of 3.2232 nm, and a pore volume of 0.095 cc/g.

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