Evaluation of the pozzolanic reactivity of two clays from Côte d'Ivoire for substitution of clinker in cement

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Abstract: Developing new building materials with low environmental impact is a challenge in the current situation linked to global warming. This study, therefore, contributes to the valorization of local clays as natural pozzolans for the substitution of clinker in cement. Two clays, ME1 and ME2, from the city of Man in the western region of Côte d'Ivoire, which were calcined at 710°C, were used to conduct this study. The chemical analysis of the raw samples by ICP_AES revealed that they mainly comprise three oxides, namely, silica, alumina, and iron, with contents more significant than 70 wt.% of the sum of these three elements. The crystalline phases highlighted by X-ray diffraction showed the presence of quartz, kaolinite, and iron compounds (goethite and hematite) in the raw samples and only quartz and hematite in the calcined samples ME1_710°C and ME2_710°C following the dehydroxylation of kaolinite and goethite. Laser particle size testing highlighted a spread distribution of 3 populations centered at approximately 2, 10, and 39 µm for the raw samples and a single population centered at 39.23 and 133 µm for ME1_710°C and ME2_710°C, respectively. The results of the pozzolanic activity carried out by the saturated lime test showed a significant reactivity for the calcined samples with a $Ca(OH)_2$ consumption capacity of more than 80 wt.% after 7 days compared to approximately 48 wt.% for the raw samples. The evaluation of the quantities of remaining Ca^{2+} and OH^- ions showed that the concentrations of these two elements were below the solubility curve, indicating good pozzolanic reactivity of the calcined samples.

Keywords: Clays; clinker; pozzolans; saturated lime test.

1. Introduction

Portland cement, the main constituent of concrete, remains the most widely used construction material worldwide. It is used to construct buildings, road infrastructure, and many other structures. With the increasing urbanization accompanying economic development, global consumption has increased tenfold over the last 65 years [1]. This high demand for cement is not without consequences for our environment. Indeed, the cement industry is very energy-intensive, which produces a significant amount of carbon dioxide and other greenhouse gases whose direct impact on our planet is global warming. According to estimates, cement is responsible for 36 wt.% of the construction industry's 7.7 billion tons of CO2 emissions annually by the construction industry [2].

Additionally, according to the International Energy Agency [3], building construction and operation are responsible for approximately 40 wt.% of CO_2 emissions over the entire lifespan, which are often estimated at approximately 60-75 years in most life cycle analyses. For these reasons, alternatives must be found to reduce the environmental impact of buildings that use cement as their main binder. To do this, much scientific research focuses on new, innovative, and ecologically friendly materials that can partially or wholly replace cement. In this respect, some studies have focused on the use of glass powder in concrete [4,5], and others have focused on the partial substitution of cement by the addition of aluminosilicate mineral materials with pozzolanic properties such as silica fume, fly ash, and metakaolin [6–8]. Substitution by mineral additions has proven to be very interesting since these materials are available locally and, therefore, at a lower cost. They are of ecological interest and have outstanding performances close to those of cementitious materials [6,8,9]. Metakaolin, a pozzolan obtained after heat treatment of kaolinitic

clay between 500 and 900°C, is of great interest to the scientific community. Indeed, its production allows, on the one hand, the production of binders with exciting properties and is less expensive not only because the availability of clay raw materials locally but also because it is relatively easy to produce compared with clinker, which requires a lot of energy (the production temperature is 4,500°C); on the other hand, its production reduces CO2 emissions, which makes it an ecologically friendly material.

Côte d'Ivoire is experiencing rapid population growth. This strong growth implies constructing an extensive infrastructure to meet the population's needs. Faced with the high cost of cement-type construction materials, which are generally imported, the valorization of local raw materials proves to be a rather exciting solution due to their availability in large quantities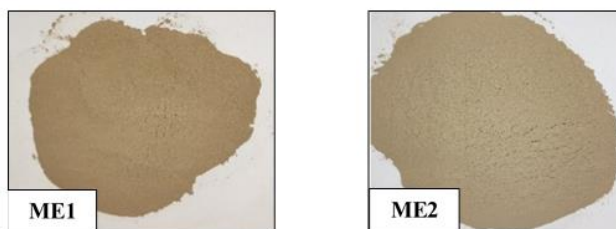 throughout the country. This study is part of the general framework of valorizing local clays in eco-construction [10,11]. This work aims first to evaluate the suitability of two clays for the production of metakaolin and second to study the reactivity of these raw and calcined clays concerning Ca^{2+} ions to estimate their potential as a raw material to replace clinker in cement production.

2. Materials and Methods

2.1. Raw materials

The clayey raw materials ME1 and ME2 used in this study were collected in the village of Delobly, in Man, located in the western region of Côte d'Ivoire. The geographical coordinates of the sampling site are 6°52'N, 7°24'W. The two samples were crushed and sieved at 100 µm, as shown in Fig.1.

Fig.1. Raw samples

To evaluate the pozzolanic activity of the samples, 98% of the extra pure slaked lime $Ca(OH)_2$ supplied by the Merck laboratory was used. The diffractogram of this lime, presented in Fig.2, shows that it is partially carbonated.
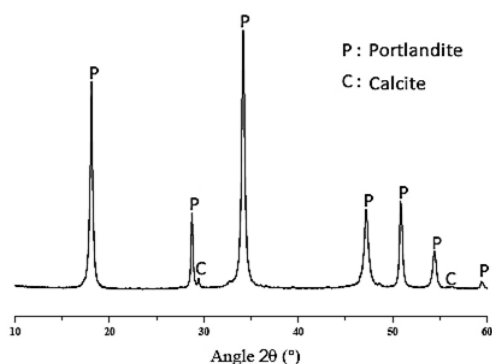
In addition to X-ray diffraction, differential thermal and thermogravimetric analyses (DTA/ATG) carried out on the lime show approximately 1% by mass of calcite ($CaCO_3$) in the lime used in this study. Fig.3 presents the different thermograms.
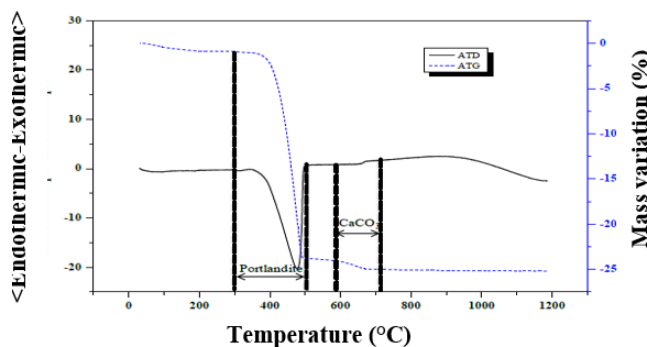

Fig.2. Diffractogram of the slaked lime used

Fig.3. ATD/ATG thermograms of lime

2.2 Methods
2.2.1 Pozzolan production
The clay samples were calcined at 710°C to evaluate pozzolanic activity using a CERADEL furnace.

Calcination was performed from room temperature to 710°C with a temperature increase rate of 5°C/min. Calcined samples ME1 and ME2, named ME1_710°C and ME2_710°C respectively, are shown in Fig.4.

Fig.4. Clay samples calcined at 710°C

2.2.2 Physicochemical characterization of the raw and calcined clays

The chemical composition of the raw clay samples was determined by inductively coupled plasma atomic emission spectrometry (ICP_AES). Before analysis, 30 mg of each sample was crushed to 100 μm, dried at 110°C for 24 hours, and dissolved using an ANTON Paar microwave.

X-ray diffraction using a Bruker D8 ADVANCE diffractometer determined the powder's crystalline phases. Phase identification was performed by comparing the diffractograms obtained with the International Centre for Diffraction Data (ICDD) international database using EVA software (Bruker AXS).

The specific surface areas of the raw and calcined samples at 710°C were measured by the BET method. The measurements were carried out using a Micromerictis Tristar II device on powders sieved at 100 μm and degassed at 200°C for 16 hours.

The particle size analysis of the raw and calcined clays was performed using a Mastersizer 3000 laser particle size analyzer. The study was conducted with 2 g of each sample dispersed in 30 mL of distilled water subjected to ultrasonication for deagglomeration.

2.2.3 Evaluation of pozzolanic activity: Saturated lime test

The saturated lime test evaluated the pozzolanic activity for the raw and calcined samples at 710°C. A saturated lime solution was prepared by dissolving 2.2 g of lime in 1 L of distilled water. Then, 1 g of each sample was placed in a plastic bottle containing 75 mL of the saturated lime solution, and the mixture was sealed and then stored for 1, 3, or 7 days in an oven maintained at 40°C. After filtration, the Ca^{2+} ions contained in the filtrate were titrated with a concentrated EDTA solution at 0.03 mol/L after adjusting the pH to 12.5 with a NaOH solution (2.5 mol/L) using the Patten and Reeders color indicator. OH^- ions were titrated in the filtrate with a 0.1 mol/L HCl solution using methyl orange as a colored indicator. The results are illustrated by a graph showing the concentration of Ca^{2+} ions expressed in mmol/L, equivalent to the amount of CaO as a function of the concentration of OH^- ions also expressed in mmol/L. Thus, the amount of calcium ions in the initial mixture determined the amount of CaO fixed by the raw and calcined clays.

3. Results and Discussion

3.1.1 Physicochemical characterization of the samples

The results of the chemical analysis of the raw clay samples ME1 and ME2 are presented in Table 1.

Table 1. Chemical composition of the raw clay samples (wt.%).

| Oxides	SiO₂	Al₂O₃	Fe₂O₃	CaO	K₂O	MgO	Na₂O	TiO₂	SiO₂/Al₂O₃
ME1	69.94	14.47	12.11	0.41	0.27	0.33	0.17	2.3	4.83
ME2	71.21	16.47	9.94	0	0.29	0	0.16	1.89	4.32

The chemical composition highlights the presence of three significant oxides in the two raw samples, namely, silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). The two samples have similar chemical compositions, which is explained by the fact that they originate from the same sediment. The silica and alumina contents show that they are aluminosilicates. In addition, the SiO_2/Al_2O_3 mass ratios of 4.83 and 4.32 for ME1 and ME2, respectively, suggest the presence of clay minerals of types 1:1 and 2:1 and free silica, which could be quartz. Furthermore, the chemical composition of the samples shows that they can be used as pozzolans. Indeed, according to the ASTM C 618 standard, a material can be used as a

pozzolan if the sum of the SiO_2, Al_2O_3, and Fe_2O_3 oxides is greater than 70% by mass of the oxides [12], which is the case for the two raw samples whose sum of their oxides are 96.52 wt.% and 97.62 wt.% for ME1 and ME2, respectively.

Fig.5 presents the diffractograms obtained for the four samples. The prominent peaks of the identified crystalline phases were referenced using the JCPDS sheets.

The diffractograms of the raw samples highlighted the presence of kaolinite ($Si_2Al_2O_5(OH)_4$), quartz (SiO_2), goethite (α-FeOOH), and hematite (α-Fe_2O_3). On the diffractograms of the samples calcined at 710°C,

quartz and hematite are still observed. On the other hand, the peaks representative of kaolinite and goethite no longer appear on the diffractograms of the calcined samples. This could be because the calcination temperature (710°C) is much higher than the decomposition temperature of these two minerals. Indeed, for kaolinite, the dehydroxylation temperature corresponding to the departure of structural hydroxyls is generally between 500 and 650°C[13], forming an amorphous phase called metakaolinite. The reaction is written according to **equation 1**:

$$Si_2Al_2O_5(OH)_4 \rightarrow Si_2Al_2O_7 + 2H_2O \tag{1}$$
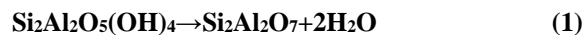
The resulting metakaolinite has good pozzolanic properties due to its amorphous structure [13]. The disappearance of the goethite peak can be explained by its dehydroxylation into hematite, a transformation that generally occurs at approximately 300°C [14,15]. This dehydroxylation reaction is written according to eq.2.
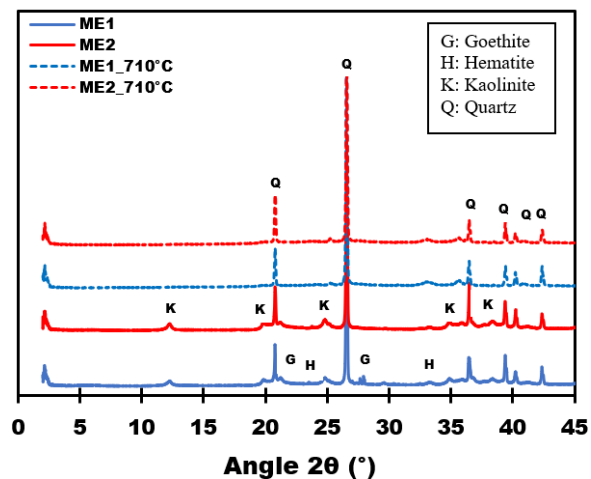
$$2FeOOH \rightarrow Fe_2O_3 + H_2O \tag{2}$$

Fig.5. Diffractograms of the raw and calcined samples

The mineralogical composition of the raw samples was determined via chemical analysis and X-ray diffraction. This semiquantitative composition was determined by calculations using (eq.3) [16].

$$T(a) = \sum M_i P_i(a) \tag{3}$$

T(a): Content (wt.%) of oxide of the chemical element "a"

Mi: Content (wt.%) of mineral "i" in the studied material containing element "i"

Pi(a): Proportion of element "a" in mineral "i"

The results obtained after the different calculations are summarized in Table 2. Kaolinite and quartz are the major minerals present in the two raw samples. These two minerals are associated with iron compounds (goethite and hematite).

Table 2. Semiquantitative mineralogical composition of the raw samples (wt.%)

	Kaolinite	**Quartz**	**Iron compounds (Goethite, Hématite)**
ME1	36.6	52.91	13.47
ME2	41.67	51.72	11.6

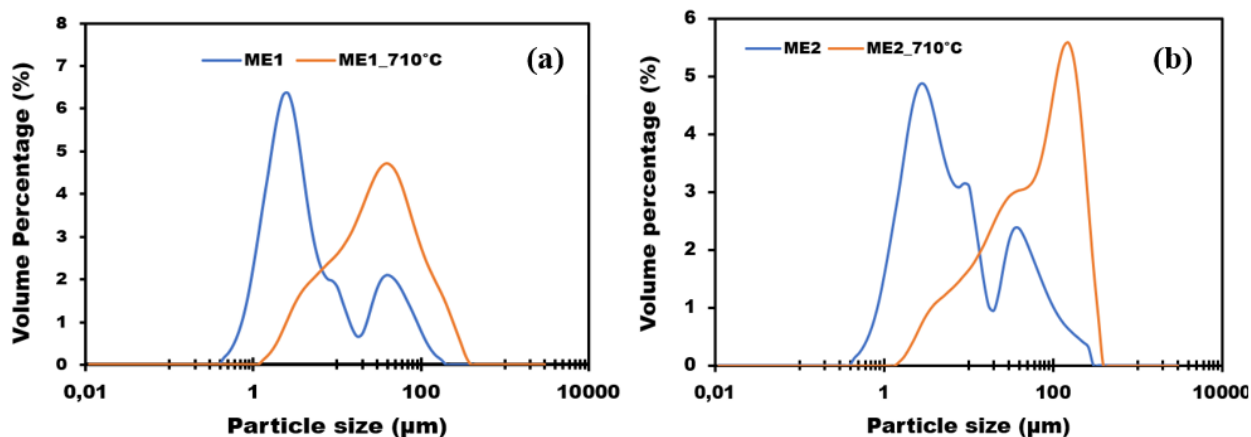The results of the granulometric analyses of the raw and 710°C calcined samples are presented in Fig.6.

Fig.6. Particle size distribution of ME1 and ME1_710°C (a) and ME2 and ME2_710°C (b)

From the analysis of the results, the raw samples are composed of three populations centered at 2.6, 10 and 39 µm for ME1 and at 2.97, 10.09, and 39.23 µm for ME2.

These results show that both samples are acceptable. The different intervals in which the particle size fractions are located allow us to conclude that the samples are rich in fine and coarse silt. For the metakaolins ME1_710°C and ME2_710°C, we detected a single population centered at 39.23 and 133 µm, respectively. The maximum diameters corresponding to cumulative volumes of 10%, 50%, and 90% are reported in Table 3. These results show an evolution of the particle size toward larger particles after calcination at 710°C for both raw samples. This increase in particle size can be explained by a decrease in the clay fraction following the decomposition of kaolinite and has been widely observed in the literature [17,18]. Additionally, the d_{50} values show that the raw and calcined ME1 samples are finer than the raw and calcined ME2 samples.

Table 3. Particle size distribution and specific surface area of the samples.

Sample	Particle size distribution			Specific surface
	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)	Specific surface (m^2/g)
ME1	1.15	3.12	43.5	34.6
ME1_710°C	3.18	17.6	65.4	29.9
ME2	1.36	4.9	55.03	29
ME2_710°C	4.81	37.5	109	31.1

The specific surface areas measured by the BET method are also reported in Table 3. The results show a greater specific surface area for ME1 (34.6 m^2/g). This higher value could be explained by, on the one hand, a greater quantity of fine elements in this sample and, on the other hand, the high level of iron oxides. Indeed, the literature shows a linear evolution of the specific surface area of clays as a function of the iron content, and the particle size is one of the factors influencing the specific surface area [19]. After calcination at 710°C, a decrease in the specific surface area was observed for the metakaolin obtained in ME1, which could be explained by better dehydroxylation during calcination leading to coalescence of the particles. For sample ME2, the surface area increased slightly for the metakaolin obtained, which could be explained by poor dehydroxylation of kaolinite, which is more important in this sample (51.72 wt.%). However, it is essential to note that the values of the specific surfaces obtained for metakaolins ME1_710°C and ME2_710°C are much greater than those found in some studies, which may be due to the texture of the raw materials [20,21].

3.2 Chemical analysis of the pozzolanic activity of the samples: lime saturation test

The saturated lime test evaluated the pozzolanic activity of the raw and 710°C calcined samples. The lime used was slaked lime supplied by the Merck laboratory. The results of the lime saturation tests for the different samples are presented in Fig.7. The amount of lime fixed by the various samples increases over time. The results highlight a low pozzolanic activity for the raw samples because the lime fixation rate did not change substantially from the 1st to the 7th day, i.e., approximately 11 wt.% with ME1 compared to 6 wt.% with ME2.
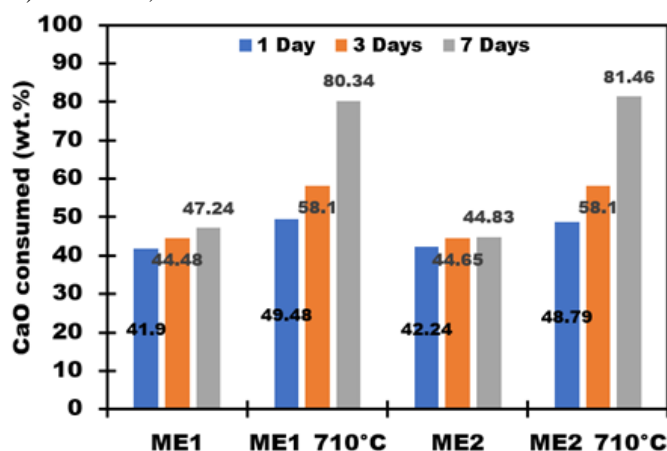
Fig.7. Saturation of lime samples

On the other hand, with the metakaolins obtained after calcination of the raw samples at 710°C (ME1_710°C and ME2_710°C), the lime consumption capacity is high with more than 80% of the lime consumed after 7 days. The rapid increase in the amount of calcium hydroxide consumed by the calcined samples may be

due to the appearance of surface defects and/or the increase in the amount of adsorbed surface material. According to Walker [22], the dominant factor determining pozzolanic activity is the amorphous nature of the material. Therefore, these samples' reactivity was due to amorphous silica. These results allow us to conclude that the clayey raw materials ME1 and ME2 calcined at 710°C have good pozzolanic reactivity and could be used in new types of cement.

The amount of $[Ca^{2+}]$ ions remaining as a function of the number of hydroxide ions $[OH^-]$ remaining in solution on the 1st, 3rd, and 7th days and the solubility curve of portlandite are presented in Fig.8. The $Ca(OH)_2$ solubility curve demarcates the pozzolanic zone below this curve and the non-pozzolanic zone above the curve. The results show that all four samples exhibit pozzolanic activity below the $Ca(OH)_2$ solubility curve. However, ME1_710°C and ME2_710°C exhibited a higher reactivity after 7 days, indicating that the calcined clays consumed some $Ca(OH)_2$ following a pozzolanic reaction. This pozzolanic reactivity observed for the calcined samples could be explained by the presence of amorphous silica, one of the dominant factors determining pozzolanic activity[22] because of the relatively large specific surface area compared to metakaolins.

Given the results obtained, the ME1 and ME2 clays calcined at 710°C present good pozzolanic reactivity; therefore, they could be used as a raw material to substitute for clinker in cement production.
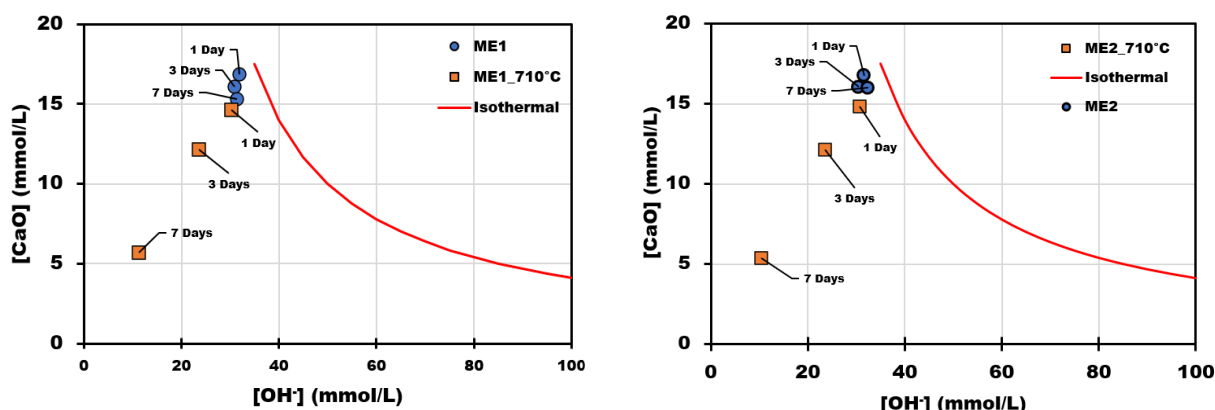

Fig.8. Remaining $[Ca^{2+}]$ concentration as a function of $[OH^-]$ for the different samples

4. Conclusion

The current global warming situation is linked to greenhouse gas emissions, for which the building sector is partly responsible and encourages the development of new building materials with low environmental impact. We have resorted to valorizing clay raw materials with ecological solid potential in recent years. Therefore, the main objective of this study was to evaluate the pozzolanic reactivity of two local clays to use as a substitute for clinker in cement. To do this, two samples, ME1 and ME2, were taken from the city of Man, located in the western region of Côte d'Ivoire, and then calcined at 710°C. The results of the chemical analysis of the raw samples showed that they are mainly composed of silica (SiO_2), alumina (Al_2O_3), and iron oxides (Fe_2O_3), whose sum is more significant than 96 wt.% for both samples. Quartz, kaolinite, and iron oxides (goethite and hematite) are the main crystalline phases in terms of mineralogical composition. In terms of the particle size distribution, the raw samples ME1 and ME2 present three populations centered at 2.6, 10, and 39 µm for ME1 and 2.97, 10.09, and 39.23 µm for ME2. For ME1_710°C and ME2_710°C, the samples had smaller particle sizes consisting of a single population centered at 39.23 and 133 µm, respectively. The specific surfaces measured are relatively large for both the raw and calcined samples, which suggests good reactivity. The pozzolanic activity of the raw and calcined samples was studied through the saturated lime test. The results of this test highlighted the good pozzolanic reactivity of the calcined samples, with a $Ca(OH)_2$ consumption of more than 80 wt.% after 7 days compared to approximately 10 wt.% for the raw samples. Furthermore, the OH^- and Ca^{2+} ions remaining in solution for the calcined samples had concentrations well below the portlandite solubility curve on the 1st, 3rd, and 7th days, highlighting a pozzolanic reaction. This study showed that the two samples, ME1 710°C and ME2_710°C, could be used as pozzolans to substitute cement clinker due to their excellent reactivity.

Conflicts of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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