

Inelastic neutron scattering study of the hydration of tricalcium silicate

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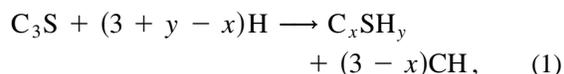
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Inelastic neutron scattering is applied for the first time to monitor directly the concentration of calcium hydroxide formed during the hydration of tricalcium silicate. Results taken between 10 and 40 °C show that the onset of calcium hydroxide formation is delayed at lower temperatures but that the final quantity formed appears to be converging to a temperature-independent value. At 20 °C, the 28 day value is 1.3 moles per mole of tricalcium silicate. Combining these results with previous measurements of the free water index made using quasielastic neutron scattering reveals that the hydrogen content of the C–S–H gel decreases significantly at increased curing temperature.

I. INTRODUCTION

The reaction between tricalcium silicate (C₃S)¹ and water is the principal factor in the setting and hardening of Portland cement. Given its importance, this reaction has been studied by numerous investigators with the aim of obtaining a detailed understanding of the development of strength in concrete. However, the kinetics of the reaction and the stoichiometry of the products are at best poorly known.

The overall hydration process which proceeds in several different reaction steps can be summarized as²



where x determines both the number of moles of calcium hydroxide (CH) formed and the C/S ratio of the C–S–H gel. Various techniques such as electron probe microanalysis, SEM/energy dispersive x-ray analyses,³ chemical extraction,^{4,5} quantitative x-ray diffraction,⁶ and thermal methods^{7,8} have all been used to determine the CH content. In general, chemical extraction tends to yield higher values, which may be a result of excess lime being extracted from the C–S–H phase, while diffraction analysis yields lower values which has been attributed to a small fraction of the CH being noncrystalline. Values for x tend to range from 1.4 to 1.7 with more recent findings favoring the larger number.⁹

In almost all of the cases listed above, the work was done on mature pastes or samples that had been quenched and then processed. It is only recently, with the introduction of synchrotron x-ray sources,¹⁰ and the advancement in neutron diffraction,¹¹ that attempts

have been made to perform continuous *in situ* measurements on the CH content of a curing sample. In this paper we introduce the first application of inelastic neutron scattering to monitor directly the formation of CH throughout the hydration process. This technique allows data to be acquired *in situ*, on a continuous basis, without disturbing the sample, and it provides a direct measure of the absolute CH quantity formed regardless of whether the product is crystalline or amorphous.

In addition to the historical lack of real time data on the CH content, there is an even greater uncertainty over the evolving water content of the C–S–H gel phase. Values for y in Eq. (1) vary widely from 1.2 to 2.5, and there is the question of whether different techniques include bound water, interlayer water, and structural water in their analysis of hydroxyl ions and water molecules incorporated into the C–S–H structure. Neutron spectroscopy allows one to measure both the calcium hydroxide content and the quantity of unreacted free water (i.e., water molecules moving on a time scale of $\leq 10^{-10}$ s, corresponding to the spectrometer's neutron energy resolution of 0.15 meV). If the remaining water is assumed to be in the C–S–H gel, then its quantity can also be determined as a function of time.

Inelastic neutron spectroscopy uses the change in a scattered neutron's energy to probe a sample's vibrational modes. By comparing the sample's spectrum to that of various reference materials, it is possible to associate specific peaks in the spectrum with specific substances in the sample. Calibrating the intensity of the peak with a known mass of reference material allows one to determine the absolute quantity of that material in the sample. Of particular interest to this

study is CH which has a characteristic mode at 41 meV associated with the oscillation of the hydroxyl group.¹²⁻¹⁴ Because the neutron technique, like Raman or infrared spectroscopy, probes the local interactions of atoms and molecules, it can be used to investigate both crystalline and amorphous materials. Thus, the intensity of the peak at 41 meV reflects any amorphous calcium hydroxide formed, in addition to the crystalline material observed using diffraction techniques.

The next section contains a brief description of the measurements. In the results section we demonstrate how the formation of CH is monitored throughout the hydration process. The data show that after an initial dormant period, CH is formed in a rapid growth process which is followed by a much slower diffusion limited behavior. The extracted diffusion constants are found to be largely temperature independent and quite similar to previous results obtained from Free Water measurements.¹⁵ Although the onset of CH formation occurs earlier at higher temperatures, the final quantity formed appears to be independent of temperature. In a similar way we show how our previous quasi-elastic scattering results are used to determine the total amount of bound hydrogen present in the sample. Assuming that all the water associated with the C-S-H phase is bound on a neutron time scale, then it is a simple matter of combining the results from these two techniques to extract out the hydrogen content of the C-S-H phase as a function of time.

II. EXPERIMENTAL PROCEDURE AND ANALYSIS TECHNIQUE

The C_3S powder (with a Blaine specific surface area of $390 \text{ m}^2/\text{kg}$) obtained with Construction Technology Laboratories¹⁶ is mixed with distilled water to produce a paste with a 0.4 water/ C_3S ratio by mass. Approximately 8 g of the mixed material are spread into a 30 by 60 mm thin layer (2.0 mm thick for the inelastic measurements and 0.5 mm for the quasi-elastic) on an aluminum cell. The sample is weighed and then immediately sealed using an indium gasket. The cell is lined with Teflon to prevent the sample from reacting with the aluminum sample holder, which has been shown to delay the hydration process.¹⁷ The material is mixed at ambient temperature but thereafter is maintained at a constant temperature throughout the experiment. Spectra take on average 35 min to complete and are obtained continually for the first 48 h and thereafter at specified intervals for the 20 °C cured sample.

The inelastic data were obtained using the NIST Center for Neutron Research filter analyzer spectrometer at BT-4. The instrument was configured for a 90° scattering angle with an energy resolution of 3 meV. The reference spectra were measured for 3.0 g of pure

CH powder placed in an identical cell and constrained to the same lateral dimensions as that of the sample material. Care was taken to ensure that the sample and reference spectra were obtained under nominally identical conditions such that a precise calibration of the absolute mass of CH formed during the hydration process was possible.

III. RESULTS

Figure 1 shows the inelastic neutron spectra obtained for the various components which are present throughout the hydration process. Of the two initial ingredients, namely water and C_3S , the water spectrum has by far the higher scattered intensity. This is because hydrogen has a much higher scattering cross section than any other element present in our system. Thus, neutron scattering is extremely sensitive to any vibration involving large-amplitude motion of hydrogen. The spectrum of the resulting C_3S paste cured for 28 days is shown in bold. The most obvious feature is the sharp peak centered at 41 meV. It is known from both infrared and Raman spectroscopy,^{12,14} and more recently inelastic neutron spectroscopy,¹³ that one of CH's main phonon modes occurs at an energy of 41 meV. The large intensity of the mode occurs due to the oscillation of the OH group as shown in the spectrum for a pure CH sample. In contrast, the spectrum of the synthetic C-S-H, which contains no

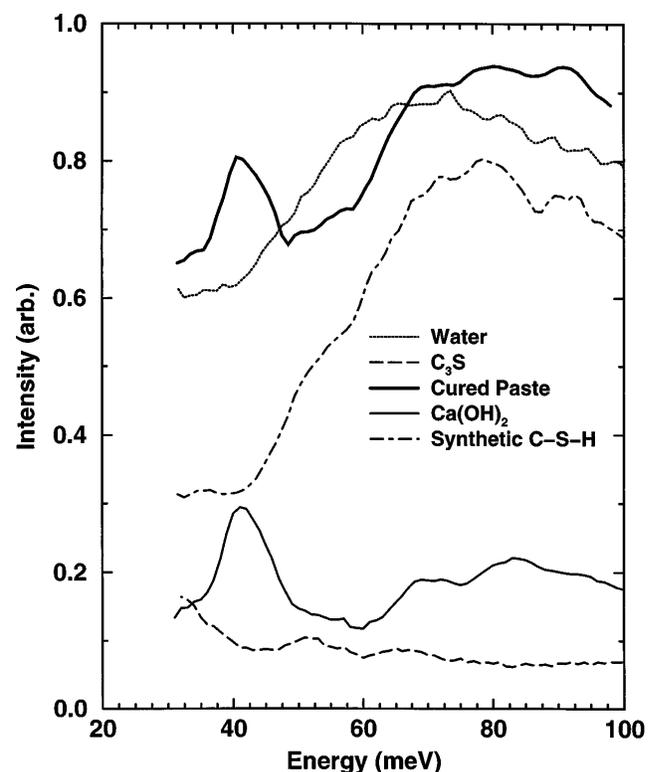


FIG. 1. Inelastic neutron scattering spectra for the ingredients and proposed products of the hydration of C_3S .

CH, shows no evidence of a peak at 41 meV. The sample was made by progressive hydration of β - C_3S combined progressive removal and replacement of solution.¹⁸

By measuring the integrated intensity of the 41 meV peak as a function of hydration time, it is possible to monitor the absolute quantity of CH that is being formed throughout the hydration process. Figure 2 shows the quantity of CH formed for a series of four samples which were cured at temperatures ranging from 10 to 40 °C. The data are expressed in terms of the number of moles of CH formed relative to the initial number of moles of C_3S . It can be seen that the onset of CH formation is systematically delayed with decreasing temperature. At 40 °C we observe a significant quantity of CH within the first 2 h of hydration, while at 10 °C more than 10 h elapse before a measurable amount of CH is detected. In an earlier paper¹⁵ we observed a similar temperature dependence in the duration of the dormant period as measured by the sudden reduction in the amount of Free Water. A comparison of the two techniques indicates that the sudden reduction in Free Water occurs at slightly earlier hydration times than the onset of CH formation. This is consistent with the findings of Brown *et al.*¹⁹ that the beginning of the acceleratory period precedes the precipitation of CH.

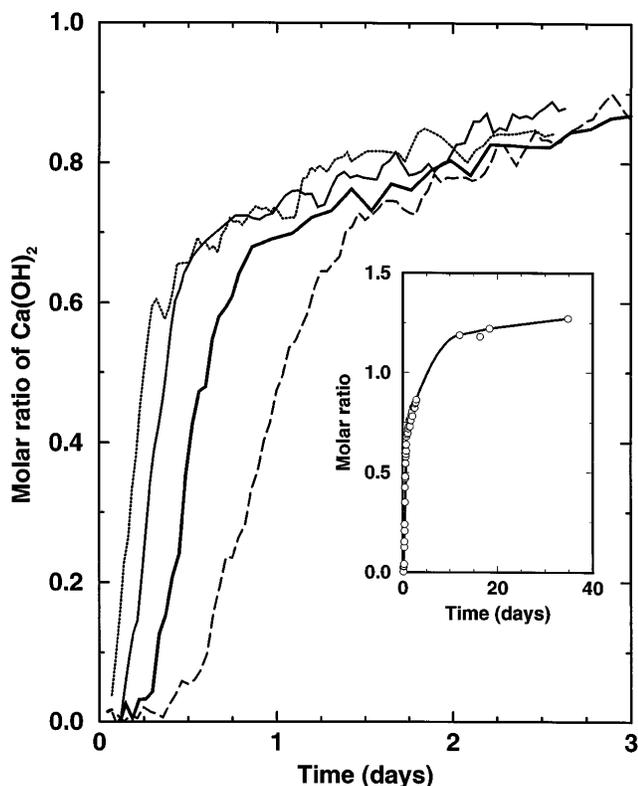


FIG. 2. The number of moles of CH formed normalized to the initial number of moles of C_3S in the cured sample. Dashed line 10 °C; bold line 20 °C; solid line 30 °C; dotted line 40 °C. The inset shows the results for the 20 °C sample extended to 35 days.

Previously we showed that following on the dormant period the initial decrease in the Free Water content of the system could be fit to an Avrami behavior,¹⁵

$$[CH] = [CH_{\infty}] \exp[-k(t - t_i)^n], \quad (2)$$

where k the rate constant, t_i the delay time, and n depends on the dimensionality of the product and the type of growth. Our present CH concentration data also follow (within the noise) an Avrami behavior with n ranging from 1.2 to 1.4. Given the level of noise in the CH data and the high sensitivity of the fit parameters to the exact choice of t_i , it is difficult to make any direct comparisons other than noting that the values for n obtained through the CH measurements are significantly lower and show a weaker temperature dependence than the Free Water values, which increase with temperature from 1.9 to 2.6.

As shown in Fig. 2 this rapid rise in the CH concentration is followed by a much slower reaction rate at later hydration times. This is thought to occur because all the available surface area of the C_3S grains has reacted and hydration can now proceed only by diffusion of the water through the product layer coating the C_3S grains. In the model originally proposed by Fujii and Kondo,²⁰ it is assumed that the grains are spherical with an unreacted radius r , and that the complex reactions occurring at the grain surface can be analyzed in terms of a very simplified diffusion-limited behavior,

$$dr/dt = D/(r - r_d) \quad (3a)$$

$$\rightarrow r_d - r = (2D)^{1/2}(t - t_d)^{1/2}, \quad (3b)$$

where D is the appropriate diffusion constant and r_d is the radius of the C_3S at the time t_d when diffusion becomes the rate-limiting step. If we further assume that throughout this period the quantity of CH formed is proportional to the volume of C_3S consumed, then we can rewrite Eq. (3) as

$$[CH]_N^{1/3} = [CH_d]_N^{1/3} + R^{-1}(2D^*)^{1/2}(t - t_d)^{1/2}, \quad (4)$$

where R is the original radius of the C_3S grain, $[CH]_N$ is the number of moles of CH formed relative to the initial number of moles water,²¹ and D^* is the effective diffusion constant related to D via the normalized CH concentration formed per unit volume of C_3S consumed. Figure 3 shows the data for the diffusion limited period plotted in terms of Eq. (4). We observe a linear dependence at each temperature. Their values are listed in Table I along with the results obtained from Free Water measurements using the same analysis technique.¹⁵ The analysis we have used is greatly simplified, and factors such as the initial surface concentration of products, the large change in volume during the diffusion process, and the large distribution of initial grain sizes are not

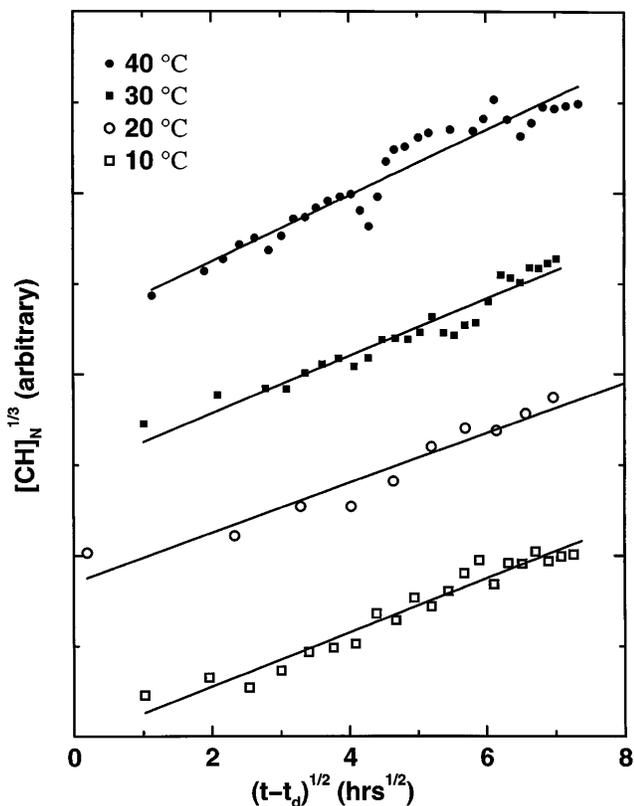


FIG. 3. Calcium hydroxide concentration at later hydration times fit to a diffusion-limited behavior. The curves for each temperature have been displaced for clarity. The values of t_d are listed in Table I.

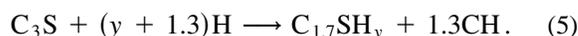
TABLE I. Parameters for the diffusion-limited process.

T (°C)	Calcium hydroxide		Free Water	
	t_d (h)	$D^* \times 10^{15}$ (m ² h ⁻¹)	t_d (h)	$D^* \times 10^{15}$ (m ² h ⁻¹)
40	7.5	2.2	6.5	1.7
30	12.5	1.7	11.0	2.4
20	20.5	1.5	21.5	1.8
10	35.0	1.5

considered. However, the use of a consistent analysis method allows us to compare directly the results of the two experimental techniques and the behavior at different temperatures. The results from both techniques show no significant (within the errors of $\sim 10\%$ for the slope which is equivalent to 20% for D^*) temperature dependence in the effective diffusion constants. The similarity in the results of the two experimental probes indicates that the same physical process, presumably the diffusion of water through the product layer and into the C_3S grains, is controlling both the formation of CH and the consumption of Free Water. The lack of any gross temperature dependence is thought to arise because at higher temperature a more impervious coating is formed

around the C_3S grain which offsets the faster intrinsic diffusion due to the elevated temperature. Finally we note that the times for the onset of diffusion-limited behavior are very similar for both Free Water consumption and CH formation. This is as expected since in both cases it is the exhaustion of the available C_3S surface area that triggers the onset of diffusion limited behavior.

Although the duration of the initial dormant period and the time to reach a diffusion-limited regime change significantly with temperature, the final CH quantity formed appears to converge to a temperature-independent value. The inset in Fig. 2 shows the result for the 20 °C sample which was maintained for 35 days. The data curve is converging to a limiting value and has reached a 28 day concentration of 1.3 moles of CH per initial mole of C_3S . This is consistent with a consensus view that the overall reaction can be written as⁹



Since there is no apparent variation in the long-term quantity of CH formed at different temperatures, the reaction represented by Eq. (5) should hold true for all temperatures between 10 and 40 °C.

The major unknown in Eq. (5) is the quantity of water associated with the product gel of C–S–H. To determine this we take advantage of our earlier results obtained from quasi-elastic scattering.¹⁵ This technique uses the principle that the elastic spectrum of neutrons scattered by a fixed (solid) material is distinctly different from that of neutrons scattered by a mobile (liquid) material. Such mobile scatterers produce a broadening in the elastic spectrum which increases with increasing mobility.²² It is easy to separate out the fixed and mobile contributions to a spectrum and hence determine what fraction arises from solid material and what fraction from mobile, liquid-like material.

Due to hydrogen's extremely large incoherent scattering cross section, it tends to dominate neutron measurements in hydrogenous materials. Since all of these atoms originated from the initial water mixed with the C_3S , our technique allows us to focus on the water and determine the fraction of molecules which are liquid-like on a neutron time scale of $\leq 10^{-10}$ s and the fraction which has chemically reacted to form CH or become "bound" in the C–S–H gel-like structure.

Figure 4 shows these results expressed in terms of the bound hydrogen ratio. This refers to the number of atoms which have become bound relative to the initial number of C_3S molecules. We use the term "bound hydrogen" rather than "bound water" because the measured quantity includes both structural water and hydroxyl groups. It can be seen that this number is not converging to a common value for the three temperatures. There is a systematic trend of a larger fraction of hydrogen becoming bound at lower temperatures. We were able

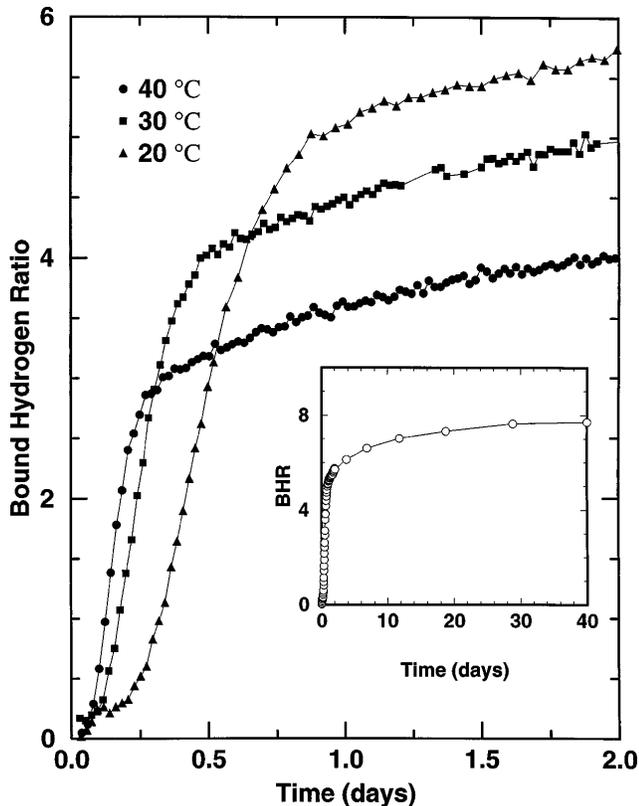


FIG. 4. Results from quasi-elastic scattering showing the number of moles of hydrogen atoms (all initially in the form of water) which have become bound on a neutron time scale of 10^{-10} s. The data are plotted relative to the initial number of moles of C_3S . The inset shows the results for the 20 °C sample. If all the free water reacted, the final bound value would be 10.2.

to measure the 20 °C sample over an extended time period, and the inset shows that a BHR of 7.9 is reached after 28 days. For a water to C_3S ratio of 0.4 by mass, there are initially 5.1 moles of water for every mole of C_3S , and thus if all the water reacts and becomes bound the final BHR should be 10.2. At 20 °C it appears that slightly more than 20% of the initial water is still free after more than four weeks of curing.

The two neutron techniques allow us to determine (i) the total number of bound hydrogen atoms, and (ii) the total number of CH molecules formed. Working on the assumption that the final products consist wholly of either CH or C–S–H, it is thus a simple matter of subtracting the CH content from the total bound hydrogen content to determine the amount of hydrogen bound within the C–S–H gel.

$$[H_y] \text{ in C-S-H} = 2(\text{BHR} \times [H]_{t=0} - [\text{CH}]). \quad (6)$$

Figure 5 shows the hydrogen distribution expressed in terms of the relative number of moles of hydrogen atoms associated with each phase as a function of time. It can be seen that the amount of unreacted free water

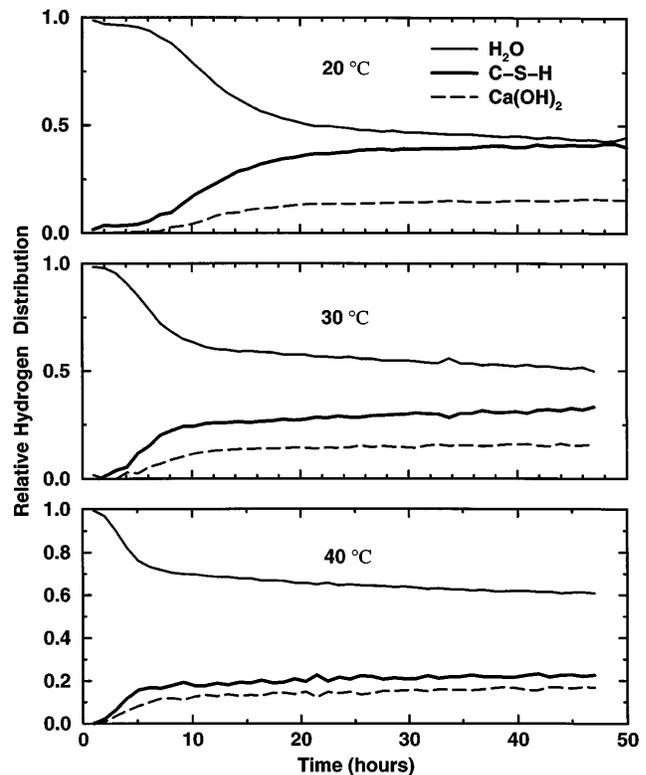


FIG. 5. The relative distribution of hydrogen in the phases of water, C–S–H gel, and calcium hydroxide. The data show that the amount of hydrogen in the C–S–H phase decreases with increased curing temperature.

increases with increasing temperature. In a similar way there is a systematic decrease in the water content of the C–S–H phase formed at higher temperature. This is consistent with the weak temperature dependence of the diffusion constant which indicates that the C–S–H product formed at higher temperature is more impervious to the diffusion of water. In the case of the 20 °C, the data indicate a 28 day value of 2.7 moles of water incorporated into the C–S–H gel per mole of C_3S .

IV. CONCLUSION

We have shown for the first time that inelastic neutron spectroscopy can be used to continuously monitor the CH content of a curing C_3S paste. Although the onset of CH formation is delayed at lower temperature, the amount formed becomes largely temperature independent, reaching a 28 day value of 1.3 moles per mole of C_3S . In contrast, our Free Water measurements show a systematic variation with temperature which indicates that the hydrogen content of the C–S–H phase decreases significantly with increasing temperature. At longer times both Free Water and CH formation proceed at the same kinetic rate, which is consistent with a single controlling mechanism of diffusion-limited behavior.

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