A Nuclear Magnetic Resonance Study of the Water in Calcium Silicate Pastes

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For a better understanding of the setting and hardening processes of cement, it is very significant to study its hydration mechanism. A number of new techniques have been developed in this field.(1-6) However, the application of thermal techniques, such as the methods of vapor pressure and differential thermal analysis, is severely limited, since a sample is degraded by heating. Furthermore, in such techniques as infrared spectra and the dielectric behavior of hydrated water molecules, it is difficult for the measurements to permit a distinct identification of the individual components contributing to the multi-phase hydration system. The use of the proton magnetic resonance technique may be more directly able to resolve these individual components.

The absorption-line width and shape are profoundly influenced by the magnetic environment of the nuclei. The spin-spin relaxation time, T_2, is the line-width parameter associated with the life-time of a given nuclear spin state, and a measure of the interactions between the low frequency component of the local field and the nuclei. Thus, these NMR measurements give us much information about the proton in different states and an important clue to the various hydrated products produced during the hydration process.

The application of this technique to the study of the hydration process of cement has been described by only a few authors.(7-9) Kawachi and his co-workers have reported on the relationship between the absorption line and the mechanical strength of portland cement.(8) Watanabe and Sasaki have observed three absorption lines which can be ascribed to the protons of the free, adsorbed and bounded water respectively, in the order of line width,(9) although they have not confirmed the assignment of these absorption lines satisfactorily.

Under these circumstances, we attempted to shed some light on these problems by making proton magnetic resonance studies of β-di- and tri-calcium silicates, the main constituents of portland cement. Tricalcium silicate, the first hardening constituent of portland cement, has a high hardening rate. β-Dicalcium silicate, the second, has a low hardening rate.

It has been supposed that these calcium silicates react with added water, and that then some hydrates contributing to the hardening process are produced as follows.(10)

$$3CaO\cdot SiO_2+(n+2)H_2O = CaO\cdot SiO_2\cdot nH_2O+2Ca(OH)_2$$

$$2CaO\cdot SiO_2+(n+1)H_2O = CaO\cdot SiO_2\cdot nH_2O+Ca(OH)_2$$

$$aCa(OH)_2+bSiO_2\cdot mH_2O = aCaO\cdot bSiO_2\cdot nH_2O$$

In this work, we will measure the spin-spin relaxation time, T_2, and the temperature dependence of the line width for the two calcium silicates pastes mentioned above; we will also discuss the hydration process for hardening by comparing its data with the data involving $Ca(OH)_2$ powder, $Ca(OH)_2+H_2O$ paste, SiO_2+H_2O paste, and water.

Experimental

The β-di- and tri-calcium silicates used in this investigation were prepared from a mixture of calcium carbonate and silicon dioxide by heating it at 1550°C several times; they were confiremed to be Ca_3SiO_5 and β-Ca_2SiO_4, as had been reported by Sasaki, by X-ray analysis.(11) β-Ca_2SiO_4 is stabilized by adding Na_2O.

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The calcium silicate samples employed in the measurements were of a form of paste prepared with a solid-to-water ratio of 0.4 in weight. The calcium hydroxide and silicon dioxide samples were also paste and had the same mixing ratio. Another calcium hydroxide sample was powder which had been dried for several hours in a vacuum at 80°C. All the samples were sealed in glass tubes about 10 mm. in diameter in order to prevent the vaporization of the added water, and then stored in an air-conditioned room at 20°C. Line-width measurements were carried out from room temperature to −160°C by making use of liquid nitrogen, while T_2-measurements were made at room temperature.

The apparatuses used were Pound-Watkins- and Bridge-type broad-line NMR spectrometers at 30 Mc./sec., and T_2-measurements, a spin-echo NMR spectrometer at 30 Mc./sec., manufactured by the Japan Electron Optics Laboratry Co., Ltd.

Results

In the NMR absorption spectra of the samples of the β-dicalcium silicate, which have various storage periods at room temperature, a single sharp absorption line, the width of which corresponds to the modulation amplitude, was observed at nearly every room temperature. From the results obtained here, it might be considered that real absorption line width of the samples is very narrow, and that a modulation broadening takes place. As the measuring temperature was lowered, the absorption line became broader due to the superposition of more than two absorption lines in a portion of the wing. The temperature dependence of the maximum slope width ($\Delta H_{\mathrm{m.s}}$) of the absorption line for this sample is shown in Fig. 1.

At −70°C, the absorption line became more complex; it had three peaks with widths of about 1, 10 and 17 gauss, hereafter to be referred as the narrow, medium and broad absorption lines respectively. In the lower temperature range, the narrow absorption line, 1 gauss wide, became wider and could not be observed, but the width of the other two remained unchanged down to −160°C. In spite of the different storage periods of the samples, the same temperature dependence was observed. The same result was also obtained in the case of the tricalcium silicate paste.

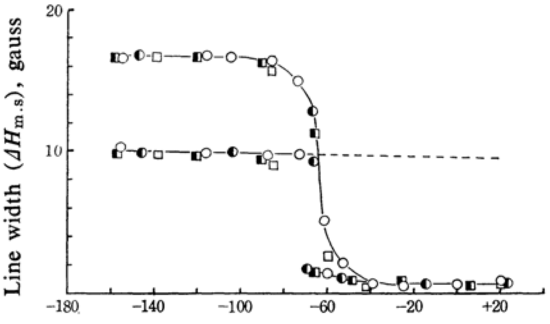

Fig. 1. Line width versus temperature curve for β-di- and tri-calcium silicate.

○ β-Ca_2SiO_4 stored 1 day
◑ β-Ca_2SiO_4 stored 20 days
□ Ca_3SiO_5 stored 1 day
◧ Ca_3SiO_5 stored 20 days

In order to clarify the influence of the storage period on the reacted water, we determined the ratio of the areas of the peaks in the decomposed absorption curves, assuming the gaussian curve for absorption line shape and a proportionality between the area of the absorption line and the fraction of protons in the various hydrated states. The narrow line is much affected by modulation broadening and so is not included in Table I, which gives the results for the broad and medium absorption lines, though the decomposition of the absorption line was not simple.

TABLE I. THE RATIO OF THE DECOMPOSED ABSORPTION LINES FOR β-DICALCIUM SILICATE PASTE AT −70°C

Storage periods	1 day	20 days
The broad line	23%	7.8%
The medium line	77%	92.2%

Furthermore, in order to clarify the details of the storage effect, the spin-spin relaxation time, T_2, was measured at room temperature. The relation of the storage period to T_2 in each case of β-di- and tri-calcium silicate pastes is shown in Fig. 2. As this figure shows, the T_2-value of β-dicalcium silicate paste decreases very slowly, whereas that of tricalcium silicate decreases very rapidly, as the storage period increases.

To make clear what proton states correspond

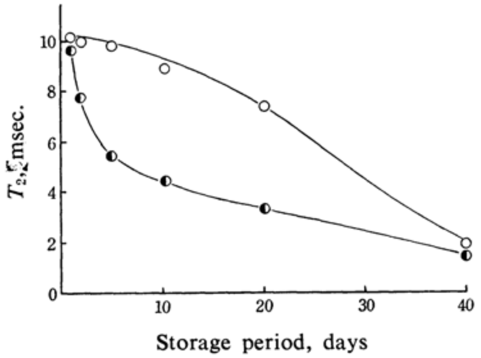

Fig. 2. T_2-Value versus storage period at room temperature.

○ β-Ca_2SiO_4 ◑ Ca_3SiO_5

to the three absorption lines observed in the low temperature region, we carried out broad-line NMR measurements of $Ca(OH)_2$ powder, $Ca(OH)_2+H_2O$, SiO_2+H_2O paste, and water. The results are shown in Fig. 3.

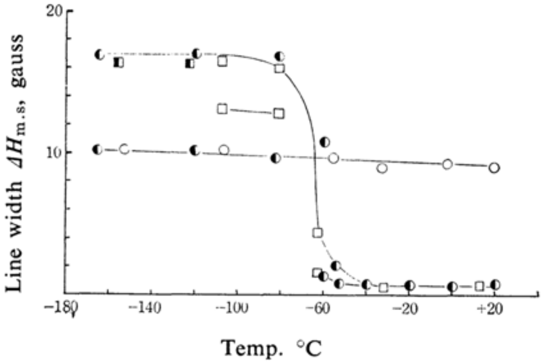

Fig. 3. Line width versus temperature curve for various reference samples.
○ $Ca(OH)_2$ powder ◐ $Ca(OH)_2$ paste
□ SiO_2 paste ◧ H_2O

The absorption line of water has a width of 16.5 gauss in the low temperature range, a value which is compatible with the results reported by other authors.[12,13]

Calcium hydroxide powder gives an absorption line 9.5 gauss wide, even at room temperature. On the other hand, the paste sample gives the same sharp absorption line as the calcium silicate pastes at room temperature, and also gives the superimposed absorption lines, with widths of 10 and 17 gauss, in the low temperature range.

The absorption line of silicon dioxide paste shows a temperature dependence similar to that of both calcium silicates and calcium hydroxide paste, with line widths of 13 and 17 gauss in the low temperature range.

It is of interest that an absorption line 17 gauss wide is observed in all the paste samples and water studied in this work.

Discussion

As shown in Fig. 1, the same temperature dependence of the absorption line width was observed for each paste of the two calcium silicates, even when they were stored for different periods. In agreement with the assumption that both silicates form a similar hydrated gel in the hydration process of cement,[10] this result may indicate that the two calcium silicates form similar hydration products.

Table I shows the ratio of the area of the medium absorption line to that of the broad line for storage periods of 1 day and 20 days. The ratio seems to represent the amount of water in the hydrated gel state and in the nonhydrated state, because the area of the medium line increases as the storage period becomes longer. These results show that the hydration process of the samples can be followed from the temperature dependence of the line width. However, it is difficult to investigate their hydration process by the broad line method without setting the samples at a lower temperature, because all the samples give a single sharp absorption line in the room temperature range, regardless of the kinds of silicate and the storage periods of the pastes.

The T_2-value obtained at room temperature may be ascribed to some relaxation mechanisms of the protons of the adsorbed or free water.[14] It is a measure of the molecular motion in the corresponding states in which the added water suffers restriction by the ions eluted in the hydration process. Therefore, the change in T_2-value may be correlated with the hardening rate of calcium silicates. Namely, T_2-value decreases with the progress of hardening. The result in Fig. 2 corresponds to the facts that tricalcium silicate is the first hardening constituent of portland cement and has a high hardening rate, while β-dicalcium silicate is the second one and has a low hardening rate. The fact that both samples, when stored for forty days, have the same T_2-value, 2.5 msec., may be considered, from the viewpoint of nuclear magnetic resonance, to show that the added water is restricted to a similar extent in both the samples.

Let us now consider the three absorption lines observed in the low temperature range. The broad absorption line observed in the calcium silicate pastes is ascribed to the protons in a more immobile state of free water; thus, they do not take part in hydration directly. This absorption line corresponds to the one hitherto ascribed to the protons of the hydrated water in cement paste by some of the present authors.[8] It it reasonable to infer, however, that the broad absorption line is associated with the protons of the free water with an ice structure at the lower temperature, as is shown in the data on ice given by Bloembergen et al.,[12] by Kume[13] and by us.

The medium absorption line, 10 gauss wide at a low temperature, can be ascribed to the protons of a solid chemical structure, such as hydroxyl ion or hydrated water, formed by the reaction between the silicates and added water. This medium absorption line could not

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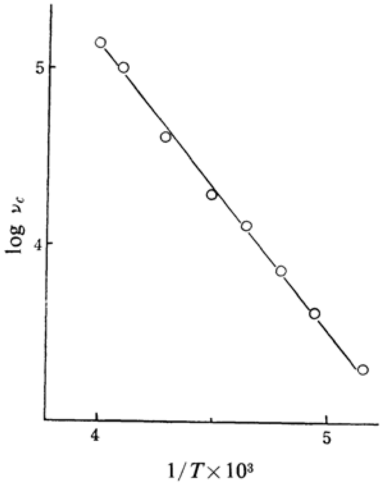

Fig. 4. The temperature dependence of the correlation frequency for the broad absorption line.

be observed at room temperature because the signal of unhydrated water is highyl intense at room temperature. However, this line is considered to appear even in the room temperature range, as is shown in Fig. 1 with an extrapolated broken line.

The narrow absorption line observable at temperatures as low as -70°C may be associated with the freely-moving protons in ice, because the lattice defects in ice crystals produced by various ionic impurities would facilitate the motion of protons, as has been reported by Kume.[13]

An attempt has been made to relate the absorption line width to the motional correlation time of the protons by means of the B.P.P. relaxation theory.[12] The activation energy, V, for the motion of the proton is estimated by applying Eyring's theory of rate process as follows;[15]

$$\nu_c=\nu_o\exp(-V/\boldsymbol{R}T)$$

where ν_c is the correlation frequency. Figure 4 shows the temperature dependence on ν_c for the broad absorption line. The slope yields $V=6.53$ kcal./mol. This is in agreement with the activation energy for the proton motion in ice,[13] and supports the abovementioned assignment of the absorption lines.

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