EPR Study of Hydration of Portland Cement

D. D. Lasič, G. Lahajnar, and R. Blinc
J. Stefan Institute, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia

and I. Kocuvan
"Salonit", Anhova, Yugoslavia

Z. Naturforsch. **36a**, 203–204 (1981); received December 16, 1980

The microscopic nature of the solidification of cement was studied via a measurement of the time dependence of the fraction of freely rotating spin probes by electron paramagnetic resonance with and without added retardants.

The results seem to support the osmotic theory of cement hydration.

In spite of many investigations the microscopic nature of the hydration of cement is still not completely clear [1]. There is a controversy [2] to whether the dormant period is due to delayed nucleation of the major hydration products or to the formation of a semipermeable protective gel coating around the cement grains [2, 3]. Here we report on an electron paramagnetic resonance (EPR) study of the solidification of cement which seems to support the protective coating and osmosis model of cement hydration and explains the action of accelerators and retardants with osmotic effects.

The EPR spectra of cement pastes labelled with the spin label TEMPO (1-oxyl-2,2,6,6 tetramethyl piperidine) show a characteristic isotropic triplet spectrum (Fig. 1) due to motionally averaged hyperfine interaction of the unpaired electron with the $^{14}N(I=1)$ nucleus). The intensity I of the observed isotropic spectrum is proportional to the number of spin probes freely ($\tau_c \leqq 10^{-9}$ s) rotating in micro-domains of the fluid phase which are bigger than a few diameters of spin probe ($r_{s.p.} \sim 6$ Å) (Figure 2).

The intensity I of the isotropic EPR spectrum at room temperature linearly decreases with time in the first 10–15 minutes after the water-spin label solution ($0.4 \times 10^{-2}\%$ of spin label) was mixed with cement and sealed in capillary tubes. The data show that in this period about 10% of the water-spin label solution enters the silicate hydrate

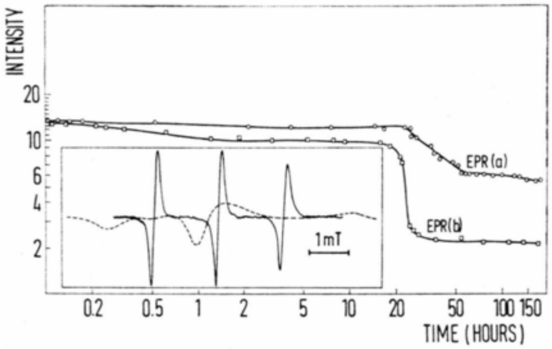

Fig. 1. Dependence of the intensity of the motionally averaged isotropic EPR spectrum of the nitroxide spin probe TEMPO on the solidification time of a Pc550 paste with a cement/water ratio of 100/40 in the presence of a retardant, 1‰ saccharose (curve EPR(a)) and without the retardant (curve EPR(b)). The insert shows the shape of the isotropic EPR spectrum for freely rotating spin probes (full line) and the spectrum of immobilized spin probes (dotted line), where however the receiver gain has been greatly enhanced.

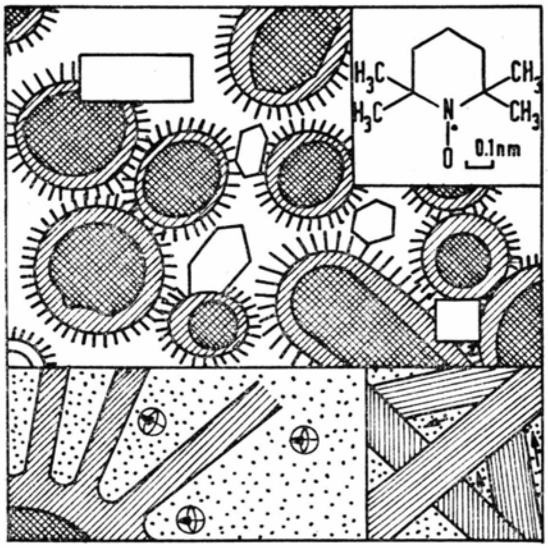

Fig. 2. Schematic illustration of the progressive cross-linking of a solidifying cement paste due to the growth of gel fibers from the gel coating (hatched area) of the cement minerals (crosshatched area). When the dimensions of the fluid micro-domains become smaller than a few diameters of the spin probe (insert) the free rotation of the spin probes (down left) is inhibited and the probes become immobilized (down right).

Reprint requests to Dr. D. D. Lasič, Solid State Physics Dept., Institute Josef Stefan, University of Ljubljana, Jamova 39, 61000 Ljubljana, Yugoslavia.

0340-4811 / 81 / 0200-0203 $ 01.00/0. — Please order a reprint rather than making your own copy.

gel coating around the cement grains and becomes immobilized. After that a dormant period sets in (Fig. 1) with I slowly decreasing with time. After about 20 hours I rapidly decreases by a factor of about five. After this sharp drop I decreases very slowly with time and the isotropic EPR spectrum could — in a sample with a water/cement ratio 0.4 — still be observed after half a year. The intensity loss due to the degradation of the probe is negligible.

The dependence of I on time is drastically affected by adding a retardant, $1\,{}^0/_{00}$ of saccharose, to the water-spin label solution. The decrease of I with time is now much slower (Fig. 1) and the sharp drop after 20 hours is greatly reduced and spread out over the whole period between 20 and 30 hours. When a charged spin label such as Mn^{++} — which acts as an accelerator — is used it becomes quickly adsorbed and immobilized on the surface of the cement minerals and in the gel coating.

These effects are easy to understand if the osmotic mechanism for the gel fibril growth is accepted [3]. Here one assumes that the hydration of cement occurs in two stages involving i) the formation of an initial gel hydrate coating around the anhydrous cement grains inhibiting the access of water to the unreacted material and ii) the local rupture of this semipermeable gel membrane — i.e. the end of the "dormant period" — and the subsequent growth of tubular fibrils [3] interpenetrating into the region between adjacent cement grains, blocking the free rotation of spin probes and finally creating a rigid matrix. The concentration of the various mineral salts in the gel coating, c_{gel}, always exceeds the concentration of these salts in the bulk water, c_{bulk}, inside the microdomains of the fluid phase. The resulting concentration difference, $\Delta c = c_{\text{gel}} - c_{\text{bulk}}$, which produces the osmotic pressure and provides the driving force for the penetration of water into the gel, is greatly reduced if a retardant is added. The uncharged saccharose molecules, which are well soluble in water and cannot penetrate through the semipermeable membrane, are concentrating in the fluid micro-domains thus changing c_{bulk} into $c'_{\text{bulk}} = c_{\text{bulk}} + c_{\text{saccharose}}$ and reducing Δc. The smaller slope of the curve EPR (a) of Fig. 1 in the time interval $20 \leqq t \leqq 50$ hours — as compared to the slope of the curve EPR (b) at $t \sim 20$ hours — directly measures the slower growth of fibrils in the presence of a retardant. The high efficiency of the retardants is explained by the fact that the osmotic coefficient in the bulk water solution can be several orders of magnitude bigger than in the gel state.

The same mechanism also explains the acceleration effects of ionic accelerators such as $CaCl_2$. Because of their ionic character they will — as the Mn^{++} spin labels — dissolve in the hydrated gel or become attached to the mineral surface thus increasing Δc and the osmotic pressure. In view of the low osmotic coefficient in the gel — as compared to the fluid phase — they are, however, less effective in small concentrations than retardants.

[1] J. D. Birchall, A. J. Howard, and J. E. Bailey, Proc. Roy. Soc. London **A 360**, 448 (1978) and references therein.

[2] J. Skalny, I. Jawed, and H. F. W. Taylor, World Cement Technology, p. 183, September 1978.

[3] D. D. Double and A. Hellawell, Nature London **261**, 486 (1976).

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg