

AN INVESTIGATION OF THE OSMOTIC MODEL OF CEMENT CURING
BY ULTRASONICS

D.D. Lasič and J. Stepišnik
J. Stefan Institute and Department of Physics
E. Kardelj University of Ljubljana
Ljubljana, Yugoslavia

(Communicated by D.M. Roy)
(Received April 6, 1983; in final form Jan. 23, 1984)

ABSTRACT

Ultrasonic measurements were performed in the samples with different water to cement ratios, at different temperatures, and in the samples with added retardants. The results could be qualitatively explained with the osmotic theory of the solidification of cement.

Introduction

According to the osmotic theory of the solidification of cement (1), the silicate grains form a gel coating in contact with water. The silicate begins to dissolve in the gel phase and the concentration of salts in the gel phase increases. The concentration difference of the salts in the liquid and in the gel phase produces the osmotic pressure and the water molecules penetrate into the gel phase. The surface of gel acts as a semipermeable membrane (1). When the necessary amount of water in the gel is reached, the coating bursts and the gel fibrils begin to grow. This is the end of the dormant period (2), and the thixotropy disappears. The crosslinking of the fibrils produces the hardness of the cement. With the application of this theory, the retardation and acceleration effects can be explained (2), using the simple approximation for the osmotic pressure $\pi = \Delta c R T$, where R is gas constant, T the temperature and c the concentration difference of salts in the gel coating and in the bulk liquid phase, $\Delta c = c_g - c_w$. The large and nonpolar molecules of retardants can be dissolved only in the bulk liquid phase and therefore the concentration difference is lowered: $\Delta c = c_g - (c_w + c_{ret})$. Lower osmotic pressure results in slower water penetration rate, growth and crosslinking; i.e. solidifying of fibrils is also slower. According to this model, the high efficiency of the retardants can be understood because the osmotic coefficients, i.e. the factor which determines the real activity of the solvent, is several orders of magnitude bigger in the bulk liquid phase as in the gel phase where there are severe restrictions of mobility and many additional interactions. The effect of the accelerators can be explained in the same way. Because of their ionic character, the cations are attracted by the negatively charged silicate surfaces and the concentration difference increases, $c = (c_g + c_{acc}) - c_w$ (3). However, the lower efficiency of the accelerators can be understood through the low values of the osmotic coefficients of the ions in the very viscous gel phase.

Recently the ultrasonic technique which measures the development of the shear modulus of elasticity in cement pastes has been introduced (4). The experiments show that even slight changes of shear modulus during the cement hydration can be measured which makes this method appropriate for studies of cement hydration. The measurements are based on the shear ultrasonic waves reflected from a hardening cement paste. The reflection coefficient r_0 is determined by the relation

$$r_0 = \frac{Z_2 - Z_1}{Z_2 + Z_1}$$

where the acoustic impedances (Z_1 and Z_2) are determined by the viscoelastic properties of the media. For the case of incident shear waves, it is

$$Z = (\zeta(G + i\eta\omega))^{1/2}$$

where ζ is the mass density, G the shear elastic modulus, η the viscosity, and ω the angular sonic frequency. Since the phase changes of the reflected waves during the hydration of cement pastes are very small (5), the imaginary part of the acoustic impedance can be neglected. A direct relation between the change of the reflection coefficient (in dB) and the shear elastic modulus (5) is

$$y = -20 \log r_0 = 17.376 \frac{(\zeta G)^{1/2}}{Z_1}$$

where Z_1 is the acoustic impedance of the buffer. This relation is valid as long as y is smaller than 5 dB.

Experimental

The measurements were performed at the frequency 16.5 MHz of acoustic waves using the quartz bar as a buffer. The cement paste was spread on the top of the bar in a 4 to 5 mm thick layer and covered with a glass cup with a defined humidity to prevent evaporation.

The time development of r_0 was (i) followed in the samples with different water to cement ratios at different temperatures, and (ii) the retardation effects were studied in the samples with added saccharose and glucose (both 1% o). These molecules are chemically similar, only saccharose has a twice bigger molecular mass. If the permeability characteristics are also similar, the osmotic pressure decrease would be twice bigger in the sample with added glucose which would result in bigger retardation effect.

Results and Discussion

The time dependence of the reflection coefficient which is proportional to the cement hardness is shown in Fig. 1. The different curves correspond to different water to cement ratios and different temperatures. All the curves have a similar shape. The slope of the constant monotonic increase of the negative logarithm of the reflection coefficient with time, increases after the break. By the extrapolation of the second part of the curve to $\log r_0 = 0$, one defines the initiation time of hardening (t_H). This parameter is a function of temperature, but practically not of the w/c ratio. The hardening rate itself increases with decreasing w/c ratio. However, the hardening rate depends strongly on the temperature. In Figure 1, families with different w/c ratios at different temperatures can be distinguished. The hardening rate decreases with increasing w/c ratio. Overall, the families show a decrease in the hardening rate ($d \log r_0 / dt$) with decreasing temperature.

The fact that t_H is a function of temperature but not of w/c ratio, can be

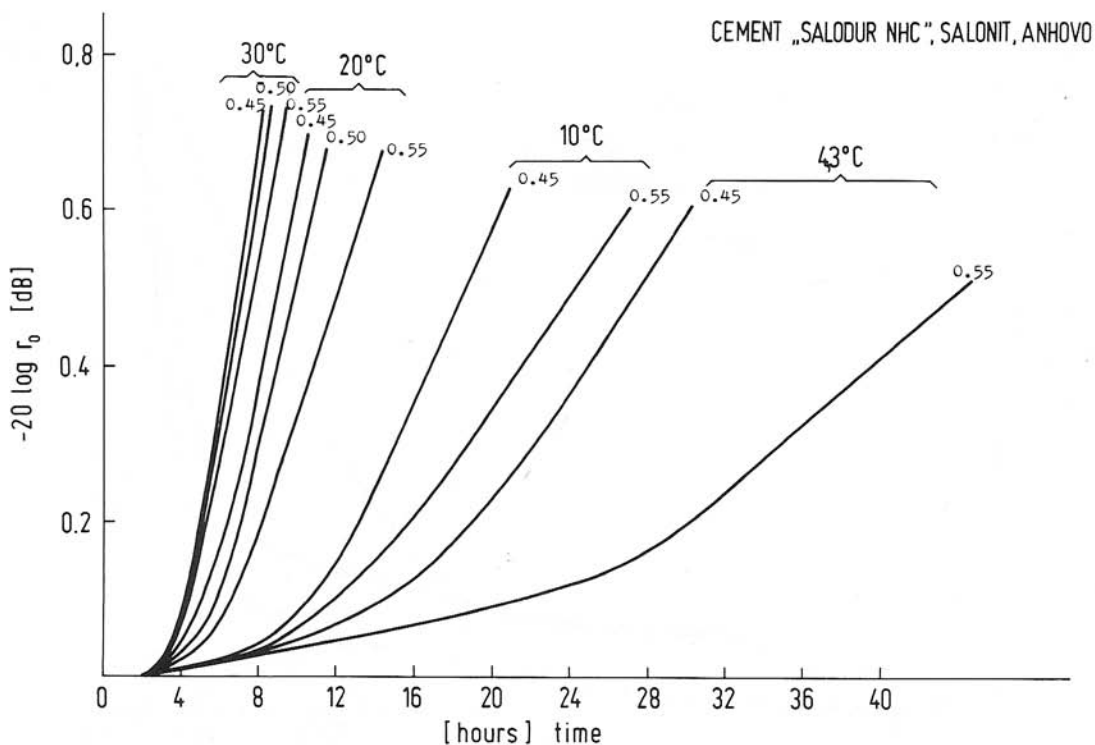


FIG. 1

Variation of the reflection coefficient during the initial stages of Portland PC 550 cement (by "salonit", Anhovo, Yugoslavia), at different temperatures and water to cement ratios.

explained with the osmotic model. The early stage - the gel coating formation and dissolution processes - is independent of the amount of water. Above some critical, minimal water content, the same amount of water is required for wetting the given grain surface. After the gel coatings are formed and the fibrils begin to grow, the samples with the smaller water content harden faster because the fibrils grow through the shorter distances to crosslink at low w/c ratios.

However, the hardening ($d \log r_0 / dt$) as osmotic pressure itself, increases with temperature. In order to obtain some quantitative correlation, one should know more about the geometry of the growing fibrils as well as consider the temperature dependence of the solubilities, water permeability and diffusion coefficients. Probably all these factors contribute to the increase of t_H with decreasing temperature.

Figure 2 shows the effect of the retardants on the time dependence of the reflection coefficient. Retardants increase the t_H value. The "solidification rate," defined as ($d \log r_0 / dt$), is for a sample without any additive 2.17, for a sample with added saccharose 3.13, and for glucose 3.7. The extrapolated t_H values 4, 15 and 20 hours respectively, indicate that glucose is a slightly stronger retardant than saccharose, which may be expected from the inverse proportionality of the osmotic pressure and molecular mass.

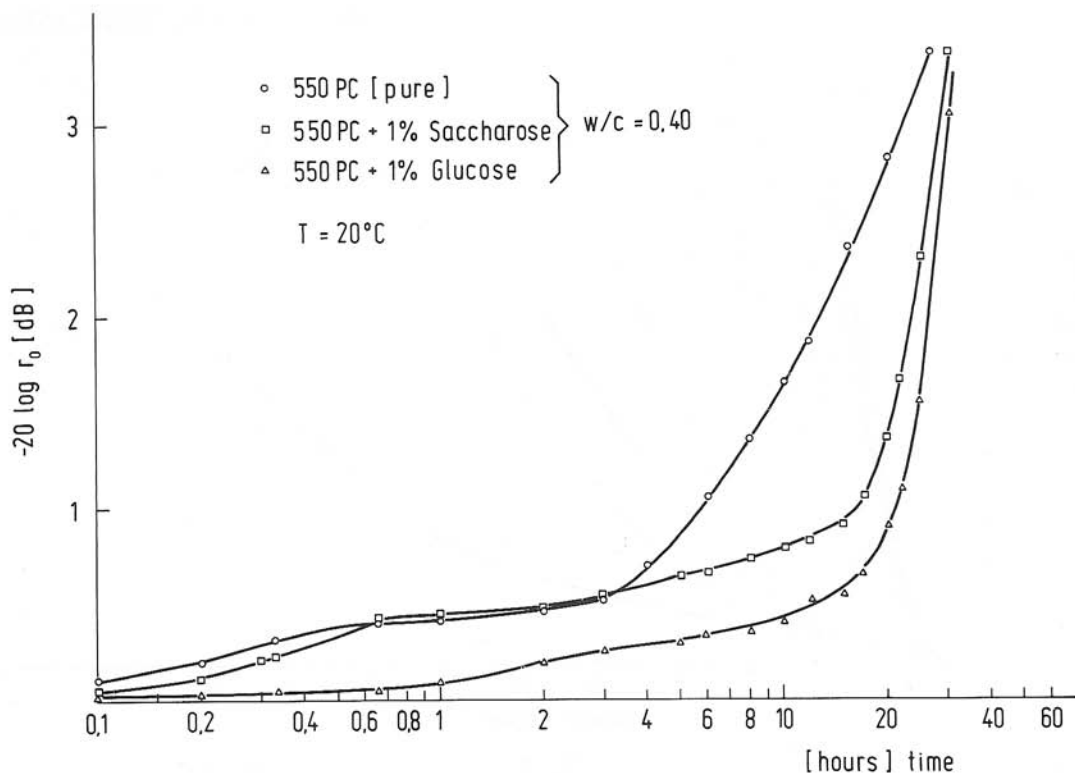


FIG. 2

Effect on cement hydration by addition of saccharose and glucose at 20°C and w/c = 0.4.

References

1. D.D. Double, A. Hellawell, *Nature* **261**, 486 (1976).
2. D.D. Lasič, G. Lahajnar, R. Blinc, I. Kocuvan, *Z. Naturforsch.* **36a**, 203 (1981).
3. P. Triereus, J.P. Verhagen, *Cem. Conc. Res.* **6**, 103 (1976).
4. F.V. Lawrence, J.F. Young, R.L. Bergeer in *Proc. of 6th intl. Congress on Chemistry of Cement, Moscow 1974, Vol. II, part I, p. 134-38.*
5. J. Stepišnik, M. Lukac, I. Kocuvan, *Cer. Bull.* **60**, 481 (1981).