Surface tension skrinkage and strength of hardened cement paste

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SESSION 2

Surface tension skrinkage and strength of hardened cement paste

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RÉSUMÉ

La tension superficielle et l'énergie superficielle d'un solide se trouvent diminuées par la présence d'une pellicule d'eau adsorbée. Quand la tension superficielle d'un matériau poreux à grande surface interne est diminuée, la longueur augmente tandis que la résistance diminue. En s'appuyant sur la théorie de la propagation des fissures de Griffith, il est possible de calculer l'énergie superficielle. Pour une pâte de ciment durcie ayant un rapport eau/ciment de 0,45 et de 0,6, l'énergie superficielle se révèle être de 1 370 erg/cm² et de 657 erg/cm² respectivement. On a laissé la pâte de ciment s'hydrater durant 28 jours sans perdre d'humidité à une température de 20 °C. Ces résultats concordent avec l'énergie superficielle du verre poreux possédant une surface similaire.

SUMMARY

The surface tension and the surface energy of a solid is reduced by the presence of an adsorbed water film. When the surface tension of a porous material with a large interior surface is reduced, the length increases whereas the strength decreases. With the help of Griffith's theory of crack propagation it is possible to calculate the surface energy. For hardened cement paste with a water cement ratio of 0.45 and 0.6 the surface energy is found to be 1370 erg/cm² and 657 erg/cm² respectively. The cement paste was allowed to hydrate for 28 days without loss of moisture at a temperature of 20 °C. These results are in agreement with the surface energy of porous glass with a similar interior surface.

1. INTRODUCTION

In a liquid the attractive and repulsive forces which interact with a molecule compensate one another. When a molecule approaches the surface at a distance which is less than the range of the molecular forces ($R \approx 10^{-7}$ cm) a force results which is directed towards the center. In order to bring a molecule to the surface, it is necessary to do work to overcome the resulting force. When the surface area of a given liquid is enlarged the total energy increases as a result. The difference in energy related to the increase in the surface area is called specific surface energy. The specific surface energy is usually measured in erg/cm². In a liquid the surface energy and the surface tension which is usually measured in dyn/cm are numerically equal. Gibbs has pointed out that in a solid material the surface tension and the surface energy F are related in the following way [1].

$$\gamma = F + A \cdot dF/dA \qquad (1)$$

In equation (1) A stands for the surface area. In a liquid dF/dA is zero. Calculations have shown that in a solid material the surface tension can be three times greater than the surface energy [2, 3]. This means, however, that $A \cdot dF/dA$ is in the same order of magnitude as F. For a long time the physical significance of surface tension was the subject of much controversy. As late as 1947 it was therefore possible for L. Prandtl to quote two physics textbooks in which surface tension is simply describ-

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ed as " a convenient means of calculation " [4] (see also [5]). Udin and his co-workers then showed that a thin copper wire contracts under the influence of surface tension when it is heated near to melting point [6].

Their experiments established the following value for the surface tension of copper: 1,400 dyn/cm. In comparison with this, water has a value of 72,9 dyn/cm.

Using the method described by Birke and Friedman [7], Nicolson prepared MgO and NaCl crystals with diameters between 100 Å and 3,000 Å. With such small particles it is not possible to ignore the number of molecules lying near the surface. By means of X-ray diffraction patterns Nicolson could show a deformation of the lattice due to surface tension. This is another convincing proof of the existence of surface forces.

The increasing influence of surface tension, with the particle radius growing continually smaller, has been demonstrated recently by means of the Mössbauer effect. These experiments were carried out with finely divided $\alpha\text{-Fe}_2\text{O}_3$ [8, 9]. Burton and his colleagues also succeeded in measuring, with the help of the Mössbauer effect, the difference in binding mechanism of the surface molecules in tungsten [10]. This method has proved to be particularly successful when studying the molecular reactions near the surface of a solid.

Powers, whose experiments have contributed a great deal to the knowledge of the structure of cement gel, was the first to recognize the importance of surface tension for the physical properties of hardened cement paste [11].

2. THE INFLUENCE OF AN ADSORBED LIQUID FILM

A liquid film which is adsorbed on a surface is able to some extent to neutralize the forces which act on the surface molecules. In this way the surface energy is reduced by ΔF. Bangham and his colleagues have been able to show that spreading pressure π can also be calculated for solids with the help of Gibb's adsorption isotherm [12, 13]:

$$\pi = \frac{RT}{M \cdot O} \int_0^P \frac{v}{p}\, dp \qquad (2)$$

In equation (2) M stands for the molar volume, O for the surface and v for the volume of gas adsorbed at pressure π. Equation (2) does not lead to exact values of spreading pressure π because the measurements are not precise enough for small values of p.

Bangham also showed that the decrease in surface tension is the same as the decrease in surface energy and both values are equal to the spreading pressure. These considerations are based on the assumption that the adsorbed molecules move on the surface of the adsorbent like a two dimensional gas [12] (see also [14]):

$$\pi = -\Delta F = \gamma_0 - \gamma \qquad (3)$$

Here ΔF stands for the decrease in surface energy and γ_0 represents the surface tension without adsorbed film and γ the surface tension of the solid with adsorbed film. In this case the activation energy necessary to move an adsorbed particle on the surface must be smaller than the activation energy which is necessary to remove the particle from the surface. In connection with experiments on crystal growth, Volmer and Adhikari [15] were able to prove that an adsorbed liquid film has high mobility along the surface. Except in the case of low temperatures, we must presume two translatory degrees of freedom in the surface plane [16].

When the surface tension is reduced, a solid which has been compressed can expand. Bangham and Fakhoury found the following equation relating the expansion $\Delta l/l$ to the decrease in surface tension or surface energy [17, 18]:

$$\Delta l/l = \lambda(F_0 - F) \qquad (4)$$

In experiments on porous glass, the so-called Bangham equation was confirmed [19]. Bangham deduced the constant λ from the elastic properties of a thin non-porous rod [20]. Hiller modified this equation for a porous material with pores orientated at random [21]:

$$E = \frac{O\rho}{3\lambda} \qquad (5)$$

In equation (5) E is the elastic modulus, O the interior surface of the porous material and ρ the density of the non porous material. Yates derived a similar relation between the modulus of compression and λ [22]:

$$K = \frac{2}{9} \frac{O\rho}{\lambda} \qquad (6)$$

Equation (5) and Equation (6) are identical with $\mu = 0,25$.

For a brittle material with surface energy F, the ultimate stress σ is expressed by the Griffith equation [23] (see also [24]):

$$\sigma = \sqrt{\frac{2E \cdot F}{\pi c}} \qquad (7)$$

in which c is the length of the crack which induces the fracture. When the surface energy decreases, the ultimate stress is also reduced. From equation (7) it follows that:

$$\left(\frac{\sigma}{\sigma_0}\right)^2 = \frac{F}{F_0} \qquad (8)$$

In this case σ_0 stands for the ultimate stress of a material in vacuo. When F in equation (8) is replaced by equation (4), the following function between the relative ultimate stress and the expansion is found:

$$\left(\frac{\sigma}{\sigma_0}\right)^2 = 1 - \frac{1}{\lambda F_0} \frac{\Delta l}{l} \qquad (9)$$

It must be kept in mind that equation (9) applies only to brittle materials when the fracture is induced by tensile stress. In our experiments the relative compressive strength S/S_0 is approximately equal to the relative tensile strength σ/σ_0 [21]. In addition equation (9) is only applicable when the experiment is carried out on a material with a large internal surface. When the decrease in the ultimate stress and the expansion of the porous body are plotted as in equation (9) on a diagram the result must be a straight line with the following inclination:

$$tg\,\alpha = -1/\lambda F_0 \qquad (10)$$

Equations (9) and (10) were confirmed by Hiller with experiments on porous glass which possesses a similar internal surface to hardened cement paste
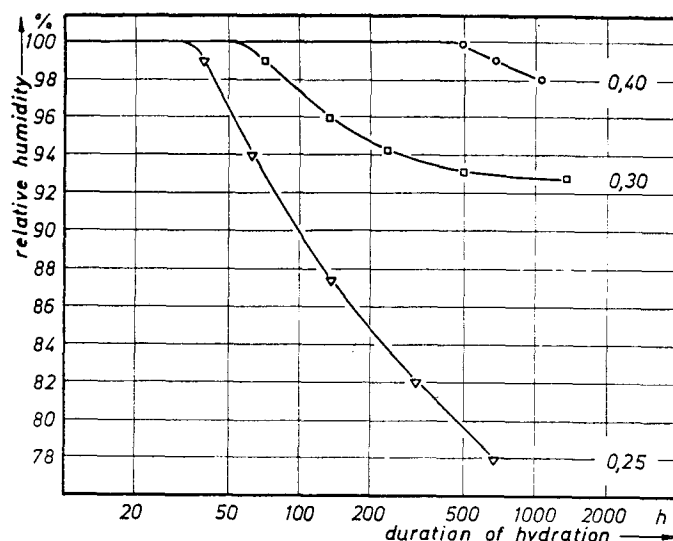
FIG. 1. — Relative humidity of the air around hardened cement paste as a function of the duration of hydration. The experiments were carried out with three different water/cement ratios: 0.25; 0.3 and 0.4.

(150-200 m²/g) [21]. However divergencies are observed when capillary condensation occurs.

The pressure which is created by the surface tension in a macroscopic body is usually neglegible. On the other hand colloidal particles as found in cement gel react quite differently. The pressure P increases rapidly with decreasing radius r of the particles [3, 22, 25]:

$$P = \frac{2\gamma}{r} \qquad (11)$$

Brunauer and his colleagues measured the surface energy of tobermorite which is a main constituent of hydrated cement paste [26-29]. The most recent result published by this group is 450 erg/cm² [30]. If we presume that the average gel particle has a radius of 100 Å, and if we presume the surface tension is three times the surface energy we find with equation (11) a pressure of $2.7 \cdot 10^9$ dyn/cm² = $2.66 \cdot 10^3$ atm. This considerable pressure acts on a gel particle when the adsorbed layer has been removed completely. This result may throw new light on the mechanism of deformation of colloidal systems such as cement paste. The adsorbed water reduces surface tension and therefore lowers the hydrostatic pressure of the gel particles. In particular, the surface layers of the hydration products become more mobile as a result. Thus it is possible to explain the low creep velocity of dried cement specimens. In this case, however, water does not play an active role in the deformation process, as is often claimed, but only influences the creep mechanism by lowering the surface energy.

3. EXPERIMENTS

The influence of the water content on the strength of concrete has been described and discussed in detail by Pihlajavaara [31 to 34]. When a concrete specimen is dried, its strength increases. Pihlajavaara terms this process drying-strengthening. On the other hand, the strength decreases when concrete adsorbs water. This is known as wetting-weakening. The decrease of strength of hardened cement paste resulting from the rising water content was first studied systematically by Sereda and his colleagues [35]. The strength of hardened cement

paste increases when oven-dried (110 ⁰C), by about 25 % [35, 36]. With mortar specimens an increase of about 40 % was observed [36]. Fischer found that there is an increase in strength of over a 100 % in concrete which was heated up to 200 ⁰C before the test [37].

Before the actual experiments are described, it should be mentioned that an increase in strength is not solely caused by an external drying process. An increasing amount of water is removed from the capillaries of the hardened cement paste as hydration continues. This is usually called self-desiccation [38]. The relative humidity of the air, as was measured around cement stone stored at 20 ⁰C, is shown in figure 1. These experiments were carried out with 3 different water/cement ratios. Cement paste which contains very little water after hydrating for 500 hours dries to such a degree that it influences the strength to some extent. The result shown in figure 1 condradicts the generally accepted opinion that the hydration of hardened cement paste does not continue below 80 % relative humidity.

The preparation of the samples is described in detail in another paper [36]. The samples were cylindrical in form, 60 mm long, with a diameter of 11.3 mm. When the specimens had been stored for 28 days without loss of moisture, they were oven-dried (116 ⁰C) up to constant weight. The resulting loss of weight enabled us to estimate the amount of chemically-bound water and the degree of hydration. The dried specimens were then put in desiccators in which the relative humidity was kept constant with hydrostatic liquids: 10 % (LiCl), 22 % (CH₂COOK), 33 % (MgCl)₂, 42 % (NaCl) and 100 % (aqua dest.). While the samples were being stored in the desiccators, the swelling was measured. In figure 2 the result of this experiment is shown for samples which were prepared with a water/cement ratio of 0.45 and 0.6. The deformation due to swelling is almost identical in both cases. The difference cannot be considered statistically significant. As soon as the equilibrium with the relative humidity had been reached, the samples were loaded to breaking point. All samples exploded when the ultimate load was reached. The dependence of the breaking stress on the relative humidity of the air in which the samples had been stored to reach equilibrium is shown in figure 3. The strength of the hardened cement paste before the
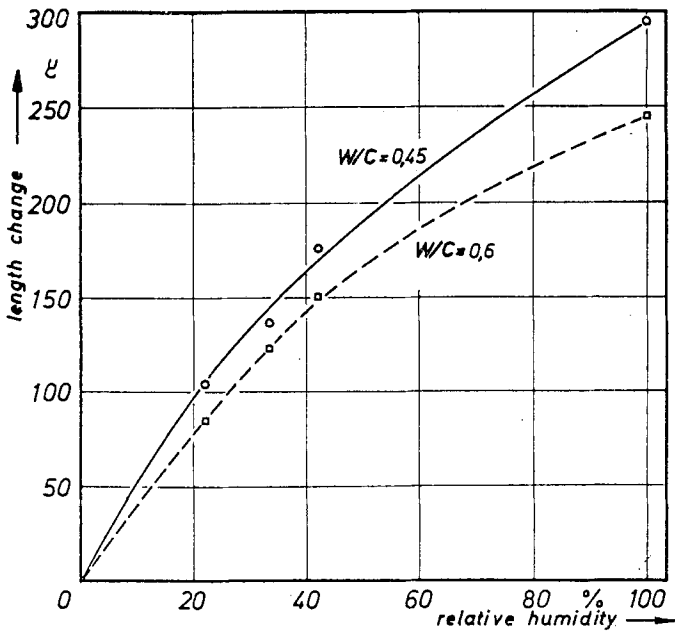
FIG. 2. — Deformation due to swelling of hardened cement paste as a function of the relative humidity of the surrounding air.

FIG. 3. — Ultimate load of small cement stone cylinders as a function of the relative humidity of the air in which the samples were stored to reach equilibrium. The ultimate load of the samples when they were stored for 28 days without loss of moisture is shown by a dotted line.
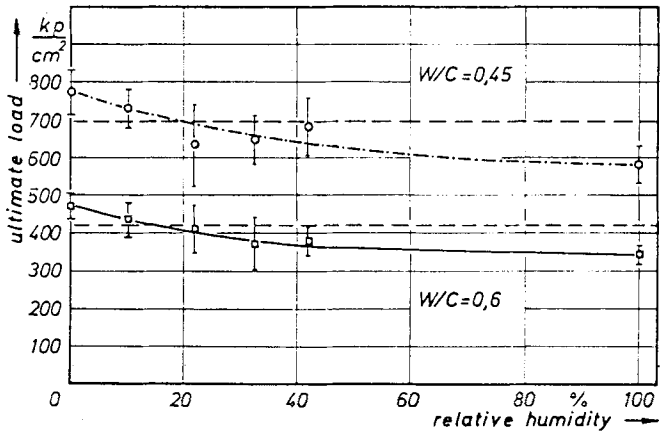
FIG. 4. — The square of the relative ultimate load as a function of the deformation due to swelling.
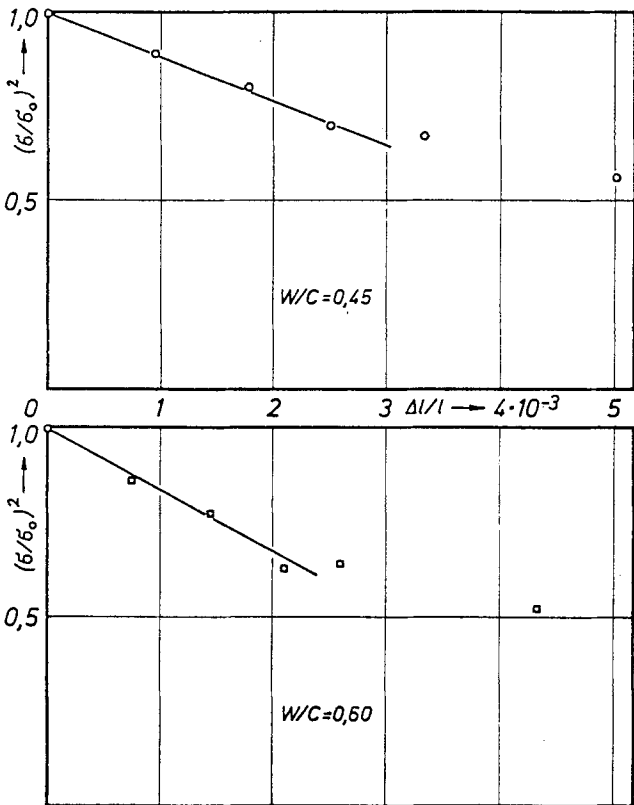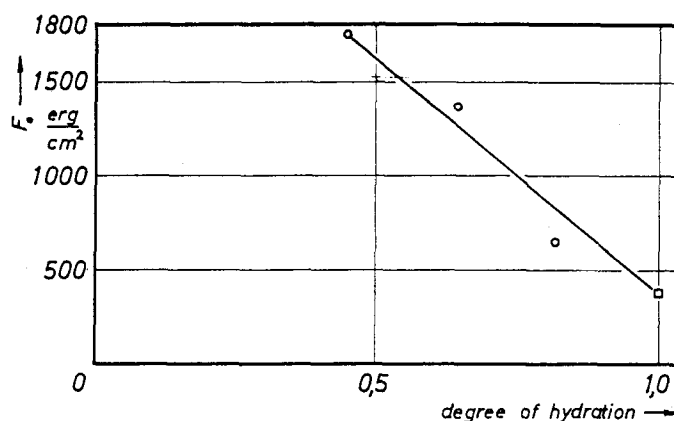
Fig. 5. — Surface energy of hardened cement paste as a function of the degree of hydration.

drying process is shown in figure 3 by a dotted line. The decrease in the strength and the deformation due to swelling agrees in the main with the results of Sereda and his colleagues [35, 39].

4. RESULTS

The graph of the square of the relative ultimate load as a function of the length change due to swelling is shown in figure 4. The values up to a relative humidity of about 40 % can be linked approximately by a straight line. When the relative humidity of the surrounding air rises, water can enter cement stone as interlayer hydrate water. In addition, new tensions arise due to capillary condensation. Both effects contribute to the change in length. Therefore it could not be expected that equation (9) is also valid for the region of high relative humidity.

When λ is known, the surface energy F_o of the cement gel can be calculated with the help of equation (10). According to equation (5) λ can be calculated when some physical values of the porous system are known. In table I the corresponding values have been entered. The modulus of elasticity and the internal surface in column 2 and 3 have been taken from earlier papers [40, 41]. The density was first of all calculated following a method described by Czernin [42]. And then it was measured directly with a Fekrumeter. The two sets of results obtained in this way agree completely and have been entered in column 4. The degree of hydration which appears in column 5 has been calculated on the basis of the amount of water lost during the drying process. With the values of table I equation (5) leads to $\lambda = 6.23 \cdot 10^{-6}$ cm/dyn for hardened cement paste with a water/cement ratio of 0.45 and $\lambda = 9.42 \cdot 10^{-6}$ cm/dyn for w/c = 0.6. These results are in agreement with values obtained for porous glass with a similar internal surface by Hiller [21] (5.33·10⁻⁶ cm/dyn) and by Amberg and McIntosh [19] (9.1·10⁻⁶ cm/dyn).

TABLE I. — Modulus of elasticity, internal surface, density, and degree of hydration of hardened cement paste with w/c = 0.45 and w/c = 0.6 which was tested.

W/C	E kp/cm^2	0 cm^2/g	ρ g/cm^3	α %
0.45	$1.92 \cdot 10^5$	$140 \cdot 10^4$	2.56	64.9
0.60	$1.35 \cdot 10^5$	$155 \cdot 10^4$	2.46	81.9

When λ is placed in equation (10) the surface energy is found to be $F_0 = 1,370$ erg/cm^2 for w/c = 0.45 and $F_0 = 657$ erg/cm^2 for w/c = 0.6. Using the same method for hardened cement paste with w/c = 0.3 the surface energy was found to be $F_0 = 1,750$ erg/cm^2 [36]. When these values are plotted as a function of the degree of hydration the result shown in figure 5 is obtained. The surface energy of a completely hydrated cement stone can then be estimated to be about 400 erg/cm^2. Brunauer and his colleagues have determined the surface energy of tobermorite which lies in between 386 erg/cm^2 450 erg/cm^2 [26-30]. The wide scattering of results obtained by the methods described here seems to indicate that this excellent agreement is probably merely accidental. It is difficult to compare results as very few experiments on the surface energy of solids have been carried out. Schoening found the surface energy of glass to lie between 340 erg/cm^2 and 1,150 erg/cm^2 [43]. It was also found that the surface energy of Soda-Lime-Glass is 2,340 erg/cm^2 [44]. Wiederhorn found with experiments on similar glass values up to 3,000 erg/cm^2 [45]. The results described in the present paper lie within these limits. More experiments will have to be carried out before these results can be fully significant.

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