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On the Relevance of Bolomey and Ryshkewitch Descriptions

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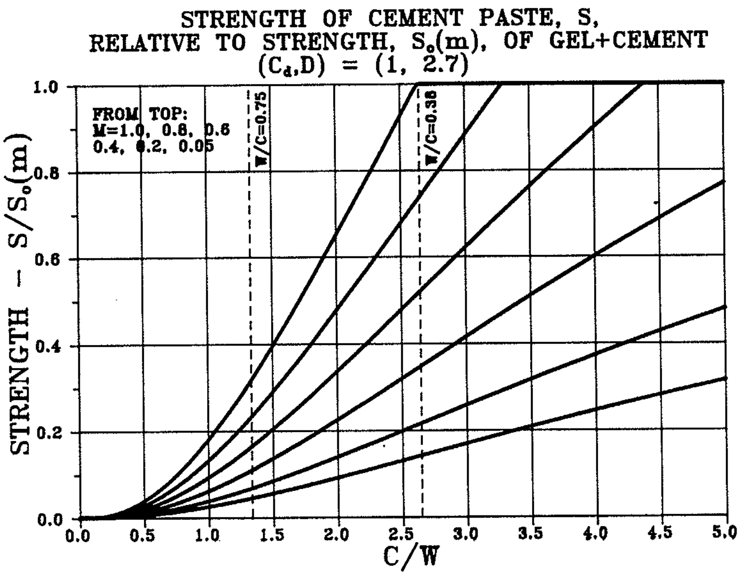

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Strength of Cement Paste

On the Relevance of Bolomey and Ryshkewitch Descriptions

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Abstract: The stiffness and strength properties of porous materials have previously been analyzed by the present author on the basis of materials mechanics. The strength results obtained with respect to porous materials with a relatively coarse pore structure are summarized in this paper - and used 1) to show that Bolomey's empirical expression frequently used to predict strength of concrete by its water/cement ratio is theoretically well founded when applied to hardened cement paste - and 2) to evaluate the well-known Ryshkewitch's expression relating strength of HCP to capillary porosity. It is found that the quality of the Bolomey's expression is superior to the latter relationship. The validity range of the Ryshkewitch's expression is rather limited. The constants of Bolomey's expression are quantified and a modified version of the Ryshkewitch's expression is presented.
Keywords: Hardened Cement Paste (HCP), Porous materials, Strength, Prediction, Bolomey, Ryshkewitch.

I. INTRODUCTION

The stiffness and strength properties of porous materials have been analyzed by the present author in (1,2,3) on the basis of materials mechanics. The strength results obtained with respect to materials with a relatively coarse pore geometry are summarized in this paper - and used 1) to show that the Bolomey's empirical expression frequently used to predict strength of concrete is theoretically well founded when applied to hardened cement paste - and 2) to evaluate the well-known Ryshkewitch's expression often applied to relate strength and porosity of hardened cement paste.

The hardened cement pastes (HCP) considered throughout the paper are "normal", meaning that they have not been subjected to special high-pressure compaction. Abbreviations commonly used have the following meanings:

- c Porosity = volume of pores relative to total volume of material. (HCP: Capillary pores).
- c_{cr} Critical porosity = porosity at which the material considered has no coherence.
- S Strength at porosity, c.

S_o Strength at vanishing porosity = strength of matrix = reference strength.

s^* $= S/S_o$, Relative strength

W/C Water/cement ratio (by weight) of HCP.

m Maturity of HCP (degree of hydration). Fraction of total amount of cement which has become hydrated.

The two empirical strength relationships previously referred to are: The Bolomey's formula (4) relating strength of concrete to water/cement ratio,

$$S = k*(C/W - \beta) \tag{1}$$

where β is a constant while k is a maturity dependent factor - and the Ryshkewitch expression relating strength of HCP to capillary porosity,

$$s^* = \mathrm{Exp}(-A*c) \tag{2}$$

with a constant power factor, A. Equation 2 was originally suggested by Ryshkewitch (5,6) to describe strength of real ceramic materials like porous sintered Alumina and Zerconia for example.

II. STRENGTH OF COARSE-POROUS MATERIAL

The relative strength of a porous material can be written as follows (3) when relatively coarsely structured pore systems are considered,

$$s^* = e^{[\Gamma - 1/\Gamma + (P/M)*\log_e(\Gamma)]/2} \tag{3}$$

The parameter,

$$\Gamma = (1 - c/c_d)^M \qquad (\equiv 0 \text{ at } c \geq c_d) \tag{4}$$

is a so-called interaction function reflecting the influence of pore shape and the variation of pore interaction on strength (and stiffness). An increasing variation of interaction between pores is described by an increasing interaction power, $M \geq 0$. At $M \approx 0$ there is no variation before interaction becomes "complete" at $c = c_d$.

The crack length variation power, $P \geq 0$, reflects the crack length variation with porosity according to

$$\ell/\ell_o = (1 - c/c_d)^{-P} \qquad (\equiv \infty \text{ at } c \geq c_d) \tag{5}$$

where ℓ and ℓ_o is crack length at porosity, c, and c_d respectively. With P = 0 crack length is constant. An increasing variation of crack diameters is described by an increasing crack length variation power.

We may approximate Equation 3 for any practical purpose introducing $(\Gamma - 1/\Gamma)/2 \approx \log_e(\Gamma)$. We get

$$s^* \approx \Gamma^D = (1 - c/c_d)^D \qquad ; \ (D = M + P/2) \qquad (6)$$

with $s^* \equiv 0$ at $c \geq c_d$, showing that strength decreases with increasing complexity of pore geometry (increasing M and P).

III. HARDENED CEMENT PASTE

Normal HCP can be considered as a porous material where a composite solid phase consisting of cement and cement gel (fully hydrated cement) is made porous by capillary pores. The volume concentration, c, of these pores (relative to total volume of HCP) can be calculated applying the volume and phase transition model for cement paste developed by Powers (7). We get

$$c = \frac{W/C - 0.38*m}{W/C + 0.32} \qquad (7)$$

where W/C and m are water/cement ratio and maturity respectively as defined in Section I.

The composite solid phase is cement gel being reinforced by not yet hydrated cement particles the volume concentration, c_c, of which (relative to volume of cement+gel), can also be calculated by (7). We get

$$c_c = \frac{1 - m}{1 + 1.2m} \qquad (8)$$

The solid phase mechanical properties are functions of c_c, meaning f.ex. that strength of HCP is a maturity dependent quantity, $S_o = S_o(m)$. Strength of plain cement gel is given by $S_o = S_o(1)$.

It is generally accepted that capillary pores in normal HCP have a relatively coarse geometry. Thus, strength may be predicted by the theory presented in Section II introducing porosity, c, as capillary porosity and reference strength, $S_o = S_o(m)$. The following orders of magnitudes for the pore geometrical parameters needed for strength prediction may be estimated from (2,3). We get

$$c_d \approx 1; \quad (M,P) \approx (1,\ 3-4) \quad \Rightarrow D \approx 2.5 - 3 \qquad (9)$$

by which Equation 6 turns into an expression frequently reported in the literature (e.g. 8,9) with D ≈ 2.5 - 3.3 to fit very well the results of strength versus porosity experiments on normal HCP. That is,

$$s^* \approx (1 - c)^D \qquad (10)$$

Bolomey's formula

The relative strength of normal HCP can be related to water/cement ratio and maturity combining Equations 10 and 7. As reference strength, $S_o = S_o(m)$, has just been shown to be W/C-independent it is obvious that an appropriate representation of strength versus water/cement ratio is one where m is maintained a constant. Additionally, as we are going to examine the ability of the Bolomey's expression (Eq. 1) also to predict strength of HCP we will use the inverse water/cement ratio as the independent variable in a numerical analysis.

It is noticed from Equation 7 that capillary porosity becomes 0 at m = (W/C)/0.38 when W/C < 0.38. This means that a relative strength, s* = 1, is here obtained at C/W = 1/(m*0.38).

An example is shown in Figure 1 with a power factor of D = 2.7 as suggested by Wischer (8) The figure demonstrates clearly that strength is practically a linear function of C/W in some area, C/V > 0.75, - meaning that the applicability of Bolomey's expression in this area is a logical consequence of the theory developed in (3).

To examine the generality of this statement considering the values of D observed in the literature on strength of HCP a computer analysis has been made with 2 ≤ D ≤ 3.5 and 0.38 ≤ W/C ≤ 0.75. The result is positive. With a high quality of regression we may express strength according to

$$s^* \approx \alpha*(C/W - \beta) \qquad (11)$$

with α and β presented graphically in Figures 2 and 3. The β-parameter is fitted very well by the following Equation 12a from which α can be estimated roughly by Equation 12b.

$$\beta \approx -1.64 + 1.32*D - 0.16*D^2 \qquad (12a)$$

$$\alpha_{MAX} \approx 1/(2.63 - \beta)$$
$$\alpha/\alpha_{MAX} \approx e^{m-1} * m^{(D/4)^2} \qquad (12b)$$

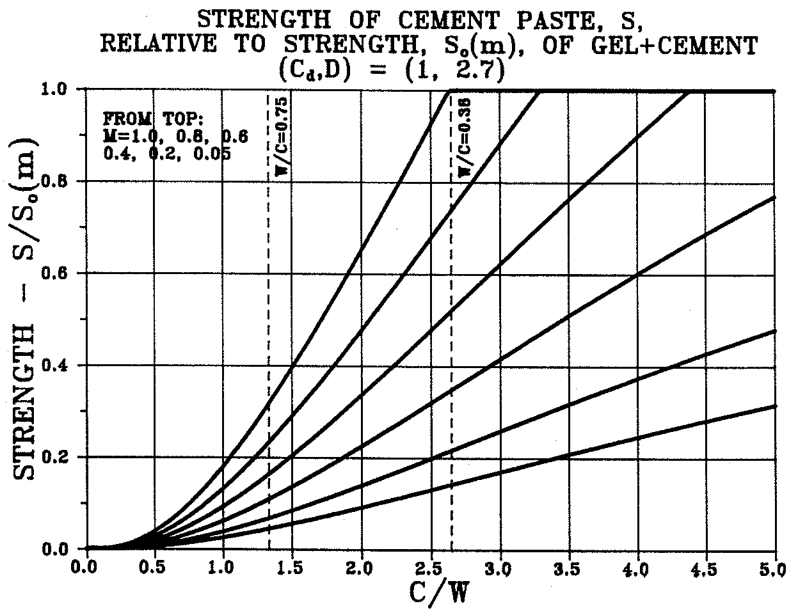

Figure 1. Strength of normal HCP as predicted by Equation 10 with D = 2.7 and porosity from Eq. 7.

It is noticed that the second constant, β, in Bolomey's expression is dependent on D only - and such that β increases with increasing D. This means, according to Section II, that β increases with increasing geometrical complexity of capillary pores - which at the same time decreases the water/cement ratio (W/C = $1/\beta$) at which the HCP considered is practically without strength at any maturity.

The first "constant" in Bolomey's expression, $k = S_o(m)*\alpha(D,m)$ is a function of both pore geometry and maturity. With a given complexity of pore geometry, D, this means that β is a constant while k is a time dependent factor - a conclusion which agrees well with the assumptions applying to the original Bolomey's expression.

It is emphasized that the applicability observed of the Bolomey's expression on normal HCP is a logical consequence of the strength analysis made in (3) which, in the present context, means that Equation 10 and Equation 11 (with α and β from Eq. 12) express the same results. Only the "language" is different.

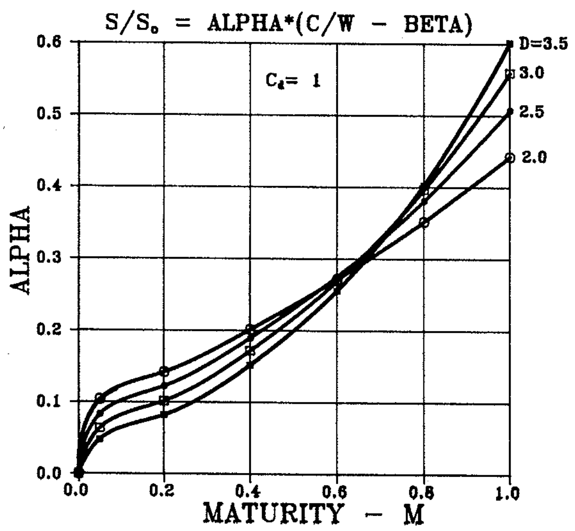

Figure 2. Influence of maturity, m, and complexity, D, of pore geometry on the α-parameter in Equation 11. Dots are calculated values. Heavy line is qubic spline connecting line.

The lower limit of W/C = 0.38 chosen for the computer analysis referred to above is rather casual. Figure 1 indicates that the conclusions made are practically valid at lower water/cement ratios.

Hansen (10) has also shown that Equation 11 applies to HCP. He's observations, however, concerning α and β are different from the ones made in this paper. A.o. Hansen concluded that β is strongly dependent on maturity.

The discrepancies between the present conclusions and Hansens are due to the strength model used by Hansen which is completely different from the crack mechanics model used by the present author in (3). Hansen assumed strength to be proportional to the smallest cross-sectional area between cubically arranged spherical pores of equal sizes simulating capillary pores.

The strength results obtained by Hansens model are, in the present authors opinion, not representative for strength of normal HCP. Predicting a more steep low porosity strength variation (and a critical porosity of c_d = 0.74) it is more likely (3) that Hansen's model is closer to describe strength of pressed materials with fine structured pores - like the compacted hardened cement pastes for example (11,12) not considered in this paper.

It is interesting to notice that although the two conclusions are different in details (α and β) they agree on the main conclusion, meaning that the applicability of strength relations similar to Bolomey's expression is probably not limited to the normal types of HCP presently examined.

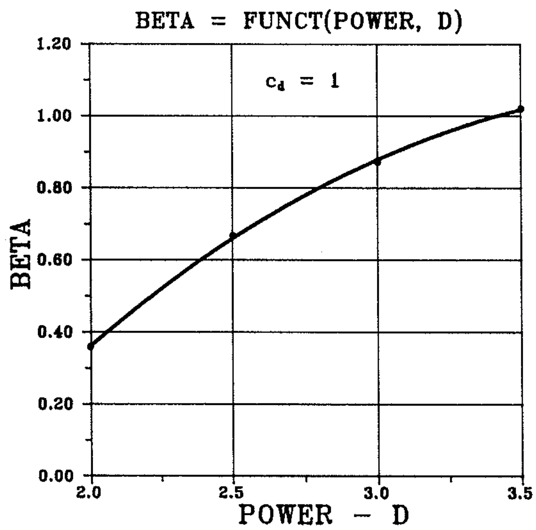

Figure 3. Influence of complexity of pore geometry on β-parameter in Equation 11. Dots are calculated values. Heavy line is fit according to Equation 12a.

Ryshkewitch's expression

The Ryshkewitch's expression given by Equation 2 is widely used to predict strength of porous materials. It is hereby often forgotten that the expression was originally suggested by Ryshkewitch to describe very well strength data obtained from experiments on porous materials at moderate porosities ($c \approx 0.1 - 0.5$).

The present author has shown in (3) that strength prediction by the Ryshkewitch's expression is not in general justifiable at low and high porosities. In the present context (coarse structured pores) an overestimated low porosity strength is a consequence of regression applying the Ryshkewitch expression. At the other end of the porosity scale it is obvious that Ryshkewitch's expression is disqualified. No material has a finite strength at $c = 1$. It is concluded in (3) that the descriptive quality of the Ryshkewitch expression and of the theory presented comply only approximately - and only when limited porosity intervals are considered.

An estimate of the overestimation of reference strength is obtained by comparing Equation 10 (true strength) with regression results obtained by the Ryshkewitch expression (with constant A) considering two "experimentally" determined (true) strength values at $c = c_L$ and $c = c_U$ respectively. "S_o" is reference strength obtained by regression - and S_o is true reference strength. We get

$$A/D = \frac{\log_e[(1-c_L)/1-c_U)]}{c_U - c_L} \tag{14}$$

$$(\text{"}S_o\text{"}/S_o)^{1/D} = \frac{(1-c_L)^{c_U/(c_U - c_L)}}{(1-c_U)^{c_L/(c_U - c_L)}} \tag{15}$$

Examples: When $D = 2.7$, $c_L = 0.2$ and $c_U = 0.5$ we get a power factor, $A = 4.23$, and "S_o"/S_o = 1.28, meaning that reference strength is overestimated by 28 %. When c_L in the same example is lowered to 0.1 we get $A = 3.97$. At the same time overestimation of the reference strength is reduced to 12 %.

A modified Ryskewitch expression applying to normal HCP must predict the same results as given by Equations 3 or 6 with pore geometrical parameters from Equation 9. This means that the constant power factor, A, should be modified by the following expression which is a monotonically increasing function of porosity.

$$A = -[\Gamma - 1/\Gamma + (P/M)*\log_e(\Gamma)]/(2c)$$
$$A \approx -(D/c)*\log_e(1 - c) \quad ; \; (D = M + P/2) \tag{16}$$

The approximation which applies for any practical purpose (as in Equation 6) is shown graphically in Figure 4. The Y-readings of the figure are normalized, meaning

$$A/D \approx -\frac{\log_e(1 - c)}{c} \tag{17}$$

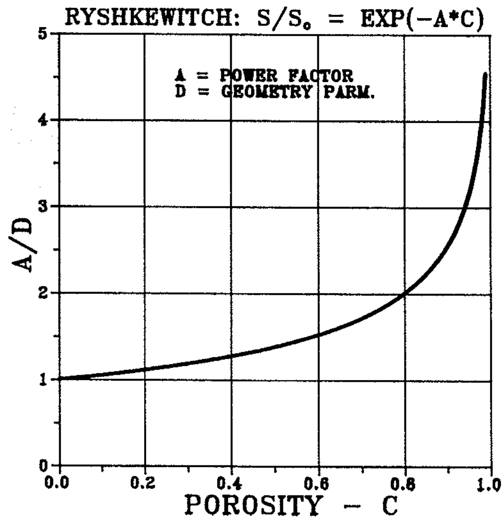

Figure 4. Corrected power factor in Ryshkewitch's expression when applied to normal hardened cement paste.

We recall from the preceding section that reference strength is a function of maturity, $S_o = S_o(m)$, which must be kept in mind also when the Ryshkewitch's expression is applied to explain strength variation of HCP.

IV. CONCLUSIONS AND FINAL REMARKS

It has been shown in this paper that the concept of hardened cement paste being a porous material where pores are capillary pores leads to the conclusion that the empirical Bolomey's expression relating strength of concrete to water/cement ratio is theoretically well founded when applied to normal (not high-pressure compacted) hardened cement paste with $0.4 < W/C < 0.8$. The regression results obtained (see Figure 1) indicate that the practical applicability of Bolomey's expression can be extended to even lower water/cement ratios than W/C = 0.4.

It is hereby found that the second Bolomey parameter, β (defining the water/cement ratio, $1/\beta$, at which strength is practically 0 at any maturity) is only dependent on pore geometry. The β-parameter increases with increasing complexity of pore geometry involving higher specific pore surface. The first Bolomey parameter , k, is dependent on both maturity and pore geometry.

The applicability of Ryshkewitch's expression on normal HCP relating strength to capillary porosity has also been evaluated in this paper. It is concluded that the expression must be used with much caution - and only to fit data when a limited porosity range is considered. Overestimated strengths at low porosities is a consequence of applying Ryshkewitch's expression as a prediction formula.

It is illustrated how the Ryshkewitch's expression can be modified in order to qualify for prediction purposes: The constant power factor in Ryshkewitch's formula then becomes a porosity dependent factor reflecting more realistically pore geometry and interaction between pores. The modification implies that the Ryshkewitch's expression becomes identical to the simpler and more easy power expression, $s^* = (1 - c)^D$, where increasing pore geometrical complexity is reflected by an increasing power constant, D.

Hardened cement pastes subjected to high-pressure compaction and with extremely low water/cement ratios have not been considered in this paper. The conclusions made concerning normal HCP cannot in general be transferred directly to such materials. A special analysis is here required which involves the more general theory developed by the present author (3) on strength and stiffness of porous materials including materials with fine structured pore systems as in ceramic materials - and in the gel structure of HCP.

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