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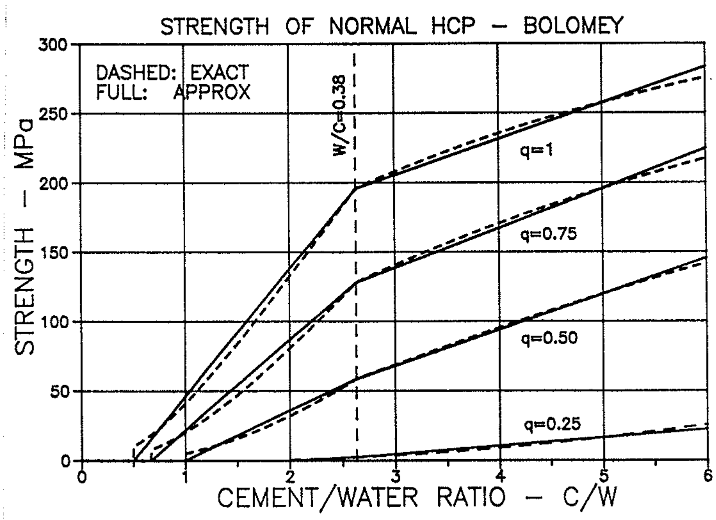

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ABSTRACT

A number of empirical expressions are frequently used to describe or predict strength of normal hardened cement paste. The more well-known expressions by Balshin, Hasselmann, and Ryshkewitch relate strength and porosity. The Bolomey formula relates strength and water-cement ratio. All these expressions are shown to be theoretically well founded. They are pore specific versions of a more general expression presented in the paper. The Balshin expression is suggested to be in general the better strength-porosity relation. Bolomeys formula is shown to be a logical numerical consequence of this statement. Maturity dependent parameters are given for both these relations. The Ryshkewitch expression applies strictly only at vanishing porosity. Low porosity strengths are overestimated by the Ryshkewitch expression when calibrated (fitted) to experimental data at finite porosities.

Keywords: Hardened Cement Paste (HCP), Porous materials, Strength, Prediction, Balshin, Hasselmann, Bolomey, Ryshkewitch.

I. INTRODUCTION

Strength data from experiments on normal hardened cement paste are frequently reported in the literature to be well fitted by a number of empirical expressions. A review on this subject is given in (1). The more well-known relations by Balshin (2), Hasselmann (3), and Ryshkewitch (4,5) express strength as related to porosity. Bolomey's formula (6) relates strength to water-cement ratio. The scope of this paper is to evaluate these relations by comparing them with a more general expression theoretically developed in previous studies by the present author in (7,8,9) on the influence of pore geometry on strength and stiffness of porous materials. The hardened cement pastes (HCP) considered throughout the paper are "normal", meaning that they have not been subjected to special high-pressure compaction changing the virgin pore structure developed during hydration.

II. MATERIALS MODEL

We adopt from Powers (10) and Powers and Brownyard (11): Normal hardened cement paste is a mixture of cement, cement gel (reaction products), and capillary pores. Cement gel is in itself a porous material consisting of approximately 72 vol-% gel particles and 28 vol-% gel pores. Hydration stops when all cement has been hydrated - or when no further capillary pore space is available. Based on this concept and further results in (11) on volume transitions the normal HCPs considered in this paper are defined as follows:

Porosity: *Total porosity,* c = (capillary pores + gel pores)/total cement paste volume, *capillary porosity,* c_{CAP} = capillary pores/total cement paste volume, and *second capillary porosity,* c'_{CAP} = capillary pores/(gel + capillary pores, can be calculated as follows

$$c = \begin{cases} \dfrac{W/C - 0.18q}{W/C + 0.32} \\ \dfrac{W/C(1 - 0.47q)}{W/C + 0.32} \end{cases} \quad c_{CAP} = \begin{cases} \dfrac{W/C - 0.38q}{W/C + 0.32} \\ \dfrac{W/C(1 - q)}{W/C + 0.32} \end{cases} \quad c'_{CAP} = \begin{cases} \dfrac{W/C - 0.38q}{W/C + 0.32q} & [W/C > 0.38] \\ \dfrac{1 - q}{1 + 0.84q} & [W/C \le 0.38] \end{cases} \qquad [1]$$

where W/C is *water/cement ratio* by weight and q is *relative maturity* defined as amount of cement hydrated relative to the amount of cement which can be hydrated (in capillary space available). The more well-known (absolute) *maturity, m,* is defined as fraction of total amount of cement which has become hydrated. The two maturities are related as follows

$$m = \begin{cases} q & [W/C > 0.38] \\ q(W/C)/0.38 & [W/C \le 0.38] \end{cases} \qquad [2]$$

Unless otherwise indicated the term, maturity, is used subsequently in the meaning, relative maturity, q. A graphical representation of total porosity versus water-cement ratio and maturity is shown in Figure 1.

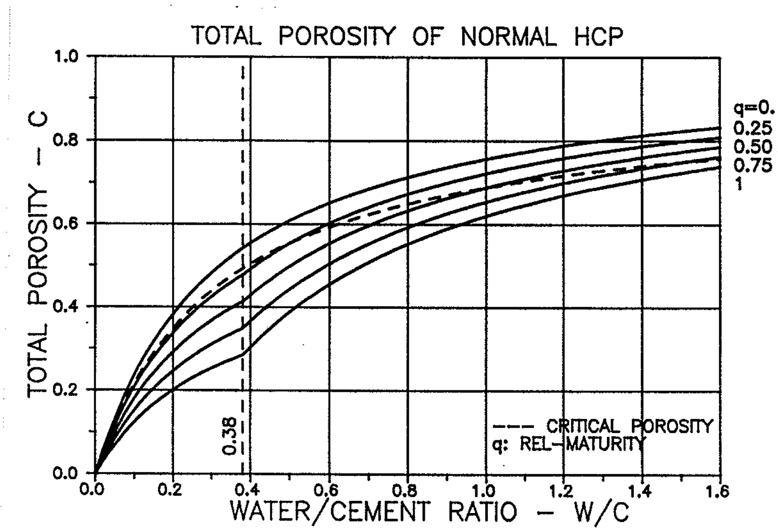

Figure 1. Total porosity in normal hardened cement paste as related to water cement-ratio, W/C, and maturity, q, as defined in Equation 2. Critical porosity from Equation 5.

In order to calculate porosity of a given HCP we need to know its maturity. Unfortunately, however, many important data from strength experiments reported in the literature do not include this information (1) which then has to be estimated from other experiments where maturity is related to curing conditions and age (t) of HCP (e.g. 12,13). The following maturity relation is a modified version of a more complex expression given by the present author in (14). It applies for non-drying ordinary Portland cements hydrated at normal room temperature which are the approximate conditions for any experiment considered numerically in this paper.

$$q \approx 1 - 0.5\left(\frac{t_R}{t}\right)^{0.2} \qquad [t_R \approx 3 \text{ days, } t \text{ in days, } q > 0.15] \qquad [3]$$

With an average *relaxation time* of $t_R \approx 3$ days as suggested in (14) maturities of q = 0.58, 0.68, 0.75, and 1 are predicted at $t \approx 7$ days, 28 days, 100 days, and several years respectively. The average nature, however, of Equation 3 should be kept in mind. Some deviation corresponding to $\log_{10}(t_R/3) \approx 0 \pm 0.25$ may occur due to varying cement quality. Equations 3 and 2 consider in a simplified way the well-known fact that absolute maturity (m) decreases with decreasing water-cement ratio.

Geometry: The geometry of the gel pore phase is similar to the pore phase in a pile of needles and plates. Capillary pores have a more coarse geometry like interconnected pockets which become less interconnected as hydration proceeds. Increasing porosity is thought of as a result of changing the water-cement ratio at constant maturity (q). The pores are "crack-pores" as defined in (9). This means that pores are modelled by tunnels or voids crossed by concentric flat cracks. At increasing maturity these cracks become smaller at the same time as the capillary pore volume decreases and becomes less continuous.

The thicknesses of gel pores and capillary pores have the rough orders of magnitudes 2 nm and 50 nm respectively (15). A rigorous size distinction, however, between the two pore types should not be made. Measurements on pore sizes have often shown a continuous distribution.

Strength: We assume that cement and gel particles have similar strengths. It is noticed from Equations 1 and 2 that 0 porosity is approached at W/C (and m at any q) -> 0. This means that "solid" phase at vanishing porosity is thought of as a structure of well graded cement grains "glued" together by an extremely thin layer of cement gel. The glue lines are considered to contain a small number of inherent cracks which reduces strength to be lower than strength of cement and gel particles.

A stiff substance (gel + capillary pores) between neighbouring cement grains is required to ensure stiffness and strength of the total HCP structure. This means that the second capillary porosity, c'_{CAP}, must be finite. We estimate $c'_{CAP} < 0.7$ from (7) which by the latter expression in Equation 1 produces the following coherence criterion

$$q > \begin{cases} 0.5W/C & [W/C > 0.38] \\ 0.19 & [W/C \le 0.38] \end{cases} \qquad [4]$$

The first term of Equation 4 is close to the Powers and Brownyard coherence criterion, $m > 0.46W/C$ presented in (11). When the information in Equation 4 is introduced into the first expression of Equation 1 we get the following *critical porosity*, c_{CR}, above which no further structural coherence is present.

$$c_{CR} \approx \frac{0.91W/C}{W/C + 0.32} \qquad [\text{any } W/C] \qquad [5]$$

or by Equation 4,

$$c_{CR} \approx \frac{1.82q}{2q + 0.32} \qquad [q > 0.19] \qquad [6]$$

where $q = 0.19^{+}$ is the lower limit maturity at which structural coherence can just be established (with $c_{CR} \approx 0.5$). It is obvious that reliable experimental HCP strength results are very difficult to obtain when the porosity area of $c \approx c_{CR}$ (where $W/C \approx 2q$) is approached.

Compaction: The pore system of HCPs produced by special *high-pressure* techniques of compaction may deviate substantially from the pore system just described - especially at low porosities where the solid phase (dependent on production technique) is a mixture of arbitrary amounts of compacted cement and solid gel particles. Theoretically the extreme case is not excluded where the 0-porosity solid phase is pure hydrated cement substance obtained by total compaction of plain cement gel.

A successful compaction leaves a 0-porosity solid with fewer and smaller cracks than in normal HCP. Strength is correspondingly higher. As the effect of compaction decreases with increasing porosity it is obvious that low porosity crack length variation (with porosity) is larger in successfully compacted HCP than in normal HCP. We may state that low porosity crack length variation increases with increasing quality of compaction. In an extreme example crack length jumps from 0 at $c = 0$ to some finite length at $c = 0^+$ which at the same time causes a sudden strength reduction from strength of plain cement and gel particles to a much lower strength.

The question of crack length variation is very important in the strength analysis of porous bodies. Two groups of porous materials are identified in (9) with respect to crack length variation at $c = 0$ relative to the variation at $c = c_{CR}$. A factor $0 \le Q \le 1$ is used to define porous materials with *"low to moderate"* low porosity (relative) crack length variation. Porous materials with *"moderate to high"* low porosity crack length variation are defined by $Q \ge 1$. The authors estimate is that normal HCP is a $Q = 0$ material while well compacted HCP's are $Q > 1$ materials like the fine structured ceramic pore systems, aluminum oxide and silicon nitride, analyzed in (9) with $Q \approx 5 - 7$. The subsequent text will justify the estimate of $Q = 0$ for normal HCP.

III. STRENGTH

The strength of porous materials with low (relative) crack length variations ($Q = 0$) at small porosities are predicted by the following expression presented in (9)

$$s^* = S/S_o = e^{[\Gamma - 1/\Gamma + P^* \log_E(\Gamma)]/2} \qquad [7]$$

where S and S_o are strength at porosity, c, and at zero porosity respectively. Relative strength is denoted by s^*. The parameter,

$$\Gamma = 1 - c/c_{CR} \qquad (\equiv 0 \text{ at } c \ge c_{CR}) \qquad [8]$$

is a so-called shape function reflecting the influence of pore shape and the variation of pore interaction on strength (and stiffness). c_{CR} is critical porosity as previously defined. The *crack length variation parameter*, $P \ge 0$, reflects crack length variation with porosity according to

$$l/l_o = \Gamma^{-P} \qquad (\equiv \infty \text{ at } c \ge c_{CR}) \qquad [9]$$

where l and l_o are crack lengths at porosity, c, and $c = 0$ respectively. Crack length is constant with $P = 0$. An increasing variation of crack lengths is described by an increasing crack length variation parameter.

Equations 7 - 9 differ slightly from their counterparts in (9). A factor M appearing in this reference has been introduced by $M = 1$. This simplification has recently been justified in (16).

At *small porosities* Equation 7 reduces as follows

$$s^* = e^{-Dc/c_{CR}} \qquad [c \approx 0] \qquad [10]$$

with a power factor of

$$D = 1 + P/2 \qquad [11$$

At any porosity we may approximate Equation 7 introducing $(\Gamma-1/\Gamma)/2 \approx \log_E(\Gamma)$. We get

$$s^* \approx \Gamma^D = (1 - c/c_{CR})^D \qquad [12]$$

with $s^* \equiv 0$ at $c \geq c_{CR}$ showing that strength decreases with increasing crack length variation (P). Pore geometries with nearly constant crack lengths ($P \approx 0$) produce simple *straight line relations*, $s^* = 1 - c/c_{CR}$, between strength and porosity.

The following strength-porosity expressions known from the literature on the mechanical behavior of normal HCP (and some other porous materials) are immediately recognized as pore specific versions of Equation 7 with material constants, A, B, and c_{CR}:

$$s^* = EXP(-Ac) \qquad \textit{Ryshkewitch (4,5)} \qquad [13]$$

$$s^* = (1 - c)^B \qquad \textit{Balshin (2)} \qquad [14]$$

$$s^* = 1 - c/c_{CR} \qquad \textit{Hasselmann (3)} \qquad [15]$$

IV. BALSHIN'S EXPRESSION

For reasons explained in a subsequent section we rule out the general applicability of the Ryshkewitch expression to predict strength of normal HCP. Only the Balshin and Hasselmann relations (and Equation 7) poses the qualities to describe strength as a function of porosity in general. Due to the difficulties previously explained to produce high porosity HCPs experimental data are often seen to be fitted equally well by these expressions (e.g. 1,17,18).

However, looking at the data of Alexander et al. (19) it seems that a truncated Balshin relation is the better expression. "Truncated" means that Balshins expression does not apply at porosities approaching the area of no proper structural coherence previously referred to. The tests referred to in (19) were made at an age of 7 days on HCPs with W/C = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9. The results are well described with $S_o \approx 450$ MPa and B(7 days) ≈ 3.5. Porosities are calculated by Equation 1 with maturity ($q = 0.58$) estimated from Equation 3 with $t_R = 3$ days.

Bergström (20) observed that strengths of 2 and 7 days old HCPs with $W/C \approx 0.5$ are approximately 34 % and 62 % respectively of the strength at 28 days. This information, Equations 1 and 14 together with q as estimated from Equation 3 ($t_R = 3$ days) are used to derive B(2 days) ≈ 4.1 and B(28 days) ≈ 2.9. It is now suggested that strength of normal HCP can be estimated by the following Balshin relation

$$S = S_o(1 - c)^B \qquad [c < c_{CR},\ S_o \approx 450\ MPa,\ B \approx 2.25/(q - 0.19)^{0.45}] \qquad [16]$$

with a maturity dependent power factor determined by extrapolation (in round figures) from the B-quantities mentioned above, and from considering that structural coherence is possible only at $q > 0.19$. The critical porosity is given by Equation 6. The hypothetical nature of Equation 16 at low maturities ($0.19 < q < 0.35$ with $W/C < 2q$) is recognized. More systematic experimental evidence is needed in this area.

Some results of Equation 16 are shown in Figure 2. A gel strength of $S_{GEL} \approx$ 195 MPa is predicted with c = 0.286 and maturity, q = 1. This order of magnitude is generally accepted in the literature (e.g. 1,21) on the mechanical behavior of hardened cement paste. A value of S_o = 210 MPa was first calculated empirically in (11). Data presented by Fagerlund in (1, Fig. 93) support the general trend of Equation 16.

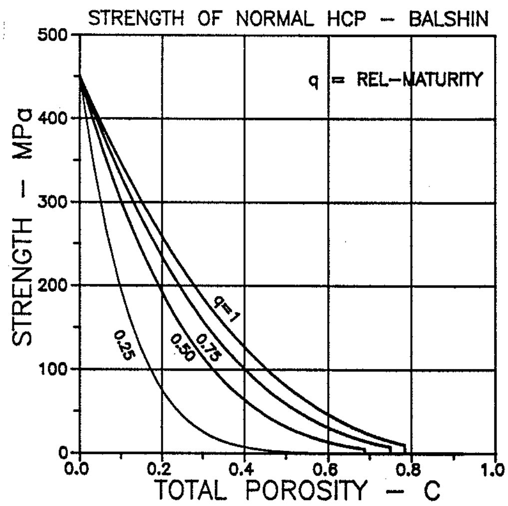

Figure 2. Strength of normal hardened cement paste as related to total porosity. Equation 16. Relative maturity, q, is defined in Equation 2.

Comments: A sensitivity study on the influence of maturity on the Alexander S_o and B quantities obtained above demonstrates a coefficient of variation of c.v. ≈ ± 6% and c.v. ≈ ± 0.4 % respectively considering the variations in cement qualities explained in Section II. Practically this means that $S_o \approx$ 450 MPa and $S_{GEL} \approx$ 195 MPa in the following mean $S_o \approx$ 420 - 480 MPa and $S_{GEL} \approx$ 180 - 210 MPa. The B quantities do not change.

The considerations made in this section justify the estimate previously made that normal HCP behaves as a porous material with a low crack length variation at small porosities (Q = 0). The 0-porosity strength, $S_o \approx$ 450 MPa, can be considered as a lower S_o-quantity for successfully compacted HCPs. This statement is justified looking at the results $S_o \approx$ 500 MPa and S_o > 700 MPa which can be extrapolated from test results by Bajza (22) and Roy and Gouda (23) respectively on HCP compacts with low W/C.

V. BOLOMEY'S FORMULA

From a practical point of view it is appropriate to evaluate strength of normal HCP directly on the basis of water-cement ratio and maturity (or age, see Eq. 3). Expressions for this purpose are easily obtained from Equation 16 with porosity from Equations 1. We get

$$s^* = \begin{cases} \left(\frac{0.32 + 0.18q}{0.32 + W/C}\right)^B & [W/C > 0.38,\ q > 0.5W/C] \\ \left(\frac{0.32 + 0.474q(W/C)}{0.32 + W/C}\right)^B & [W/C \le 0.38\ ,\ q > 0.19] \end{cases} \qquad [17]$$

shown graphically in Figure 3. Also shown in this figure are linear approximations obtained by

$$s^* \approx \alpha^*(C/W - \beta) \qquad [W/C > 0.16] \qquad [18]$$

with the parameters, α and β, chosen such that "true" and approximate quantities coincide at W/C = 0.38 (s^*_1), and W/C = 0.20 (s^*_2), and S becomes 0 where structural coherence is lost according to Equation 4. We get

$$\alpha = \begin{cases} s^*_1/(2.63 - 0.5/q) & (W/C > 0.38) \\ (s^*_2 - s^*_1)/2.37 & (0.38 \geq W/C > 0.16) \end{cases} \qquad [19]$$

$$\beta = \begin{cases} 0.5/q & (W/C > 0.38) \\ 2.63 - 2.37s^*_1/(s^*_2 - s^*_1) & (0.38 \geq W/C > 0.16) \end{cases} \qquad [20]$$

Formally Equation 18 is identical to the following well-known *Bolomey expression* (6) frequently used to estimate strength of concrete materials,

$$S \approx k_1^*(C/W - k_2) \qquad [21]$$

where k_1 and k_2 for concrete have been suggested as a maturity dependent factor and a constant (≈ 0.5) respectively. In the present HCP-context we have

$$k_1 = S_o^*\alpha \approx 450^*\alpha \text{ MPa} \qquad k_2 = \beta \qquad [22]$$

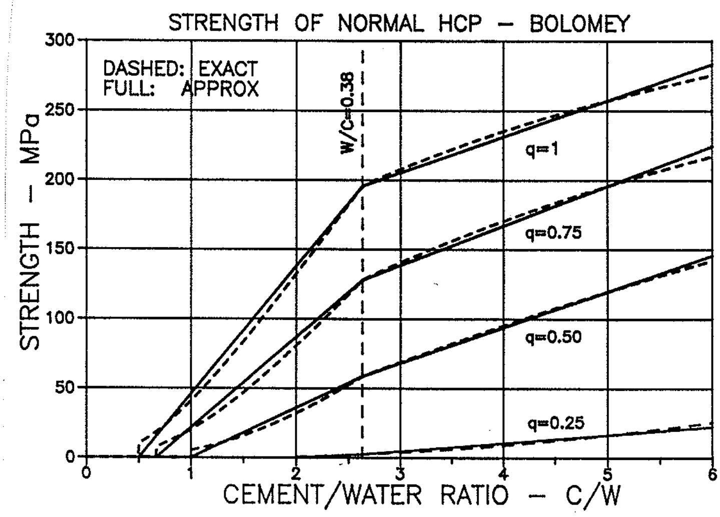

Figure 3. Strength of normal hardened cement paste as related to inverse water cement-ratio. Equations 18 - 22. Relative maturity, q, is defined in Equation 2.

Bolomey's formula has also been explained theoretically by Hansen (24) for 1 > W/C > 0.4. Hansens observations, however, concerning α and β are different from the ones made in this paper. 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 (9). Hansen's point of departure is the capillary pore system which he modelled by cubically arranged spherical pores of equal sizes. Strength is then assumed to be proportional to the smallest cross-sectional area between pores. A similar model was suggested in (25).

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 it is more likely (9) that Hansen's model is closer to describe strength of materials with fine structured pores - with steeply increasing crack lengths at c = 0 like the compacted hardened cement pastes for example (e.g. 22,23) not considered in this paper. It is interesting, however, to notice that although the two conclusions are different in details (α and β) they agree on the main conclusion indicating that Bolomey type of expressions might also be established to predict strength of some compacted HCPs.

Curiosum: Hansens model predicts $ds^*/dc = -\infty$ at $c = 0$ just as the Schiller expression (26) does. This expression, given by

$$S = S_o' \log_E(c_{CR}/c) \qquad [S_o' \text{ is a constant}] \qquad [23]$$

has been shown in (15,23) to describe compacted HCP results quite well when $c > 3$ %. (At vanishing porosity Schiller's relation predicts a strength of $S \rightarrow \infty$).

VI. RYSHKEWITCH'S EXPRESSION

The Ryshkewitch strength expression (4,5) was originally suggested as a fit method which describes very well strength data obtained from experiments on porous materials at moderate porosities ($c \approx 0.1 - 0.5$).

This feature is very often forgotten in practice where the expression is widely used to predict solid phase strength of porous materials by extrapolation of strength data at finite porosities. The author has shown in (9) that strength prediction by the Ryshkewitch's expression is not in general justifiable at low and high porosities. In the present context of normal HCP an overestimated low porosity strength is a consequence of regression by 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 $c = 1$. The approximate nature of the Ryshkewitch expression is explained in further details in (9).

An estimate of the overestimation of reference strength (S_o) is obtained by comparing Equation 14 ("true strength") with regression results obtained by the Ryshkewitch expression in Equation 13 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

$$A = \frac{\log_E[(1-c_L)/1-c_U)]}{c_U - c_L} B \quad ; \quad \frac{"S_o"}{S_o} = \left[\frac{(1 - c_L)^{c_U/(c_U - c_L)}}{(1 - c_U)^{c_L/(c_U - c_L)}} \right]^B \qquad [24]$$

Examples: When $B = 2.7$ ($q \approx 0.9$ from Eq. 16), $c_L = 0.2$ 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 14. This means that the constant power factor, A, should be modified as $A = -\log_E(s^*)/c$. We get the following factor which is a monotonically increasing function of porosity and certainly not a constant as normally assumed.

$$A \approx - \frac{\log_E(1 - c)}{c} B \qquad [25]$$

VII. CONCLUSIONS AND FINAL REMARKS

The well-known expressions by Balshin, Hasselmann, and Ryshkewitch, relating strength and porosity, and by Bolomey relating strength and water-cement ratio are shown in the paper to be theoretically well founded to predict strength of normal hardened cement paste. They are all pore specific versions of the more general expression presented in Equation 7 which considers porous materials with low crack length variations at small porosities ($Q = 0$).

It is suggested that the better strength-porosity expression is the Balshin relation. The power factor is dependent on crack pores geometry. A minimum factor of $B \approx 2.5$ applies at maximum maturity where cracks are relatively small. Increasing power factors are associated with increasing crack length variation (P) of the pore system which again is associated with a decreasing maturity of the cement paste considered. The strength at vanishing porosity and the maximum strength at $c = 28$ % (plain cement gel) are $S_o \approx 450$ MPa and $S_{GEL} \approx 200$ MPa respectively.

The Bolomey's expression relating strength of concrete to water/cement ratio is shown to apply also when normal hardened cement paste are considered with $W/C > 0.16$. This is a logical numerical consequence of the applicability of the Balshin expression just referred to. It is found that both Bolomey parameters are maturity dependent. Two sets of Bolomey's expressions apply separated by $W/C = 0.4$. For very mature HCPs with $W/C \geq 0.4$ the first and second Bolomey's parameters are given by $k_1 \approx 90$ MPa and $k_2 \approx 0.5$ respectively.

The Ryshkewitch expression is shown to apply strictly only at vanishing porosity. As a fit method it must be used with much caution - and only when limited porosity intervals are considered. In general an overestimated strength at vanishing porosity is a consequence of data fitting on normal HCP by the Ryshkewitch expression.

Finally it is suggested that the strength behavior of compacted HCP can be analyzed by the authors more general theory in (9) with high crack length variations ($Q > 1$) at small porosities as in fine structured ceramic materials. A lower limit solid strength of $S_o \approx 450$ MPa is expected when successfully compacted HCPs are considered.

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