Simple hydration equation as a method for estimating water-cement ratio in old concrete

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ABSTRACT: Hydration studies done several years ago by R.H. Mills, built on the work of T.C. Powers and other researchers to derive a relationship between the ultimate degree of hydration and water-cement ratio (w/c). This paper reviews the α_{ult}-w/c hydration equation for possible application to w/c estimation in hardened concrete. Unlike current methods, the empirical method based on hydration equation has the merit of simplicity but its accuracy has not been tested and proved. A χ^2-test statistic showed a good agreement between values of original w/c and estimated w/c for pastes hydrated for 448 days. Accuracy seemed particularly good for mixtures of portland cement only. The method is sensitive to the C_3A content while use of extenders in mixtures appears to reduce accuracy. These and other shortcomings are discussed including the effects of advances in cementitious material systems. The need for modifications and development towards an improved method is highlighted.

1 INTRODUCTION

It is usually essential to determine the actual w/c in already hardened concrete regardless of prior knowledge of its original mix design. W/C is a key parameter of influence in mix design of concrete and subsequently, its long-term durability. Determination of w/c for new concretes may be needed to verify adherence to specifications during concreting or to examine effects of adverse environmental conditions encountered during casting such as rainy conditions. In certain situations, knowledge of w/c is required to settle disputes.

For old concretes, determination of w/c can be important in preparation for repairs. Old concrete structures often have no available records, the structure perhaps having outlived the project team responsible for its construction, or records lost in some way or were simply not kept to begin with. Prior to conduct of repairs, analysis of the aged structure is usually done to establish the source(s) or cause(s) of distress. The quality of concrete is thus brought to focus. Although mechanical properties are commonly used in quality assessment, they only provide partial indication of durability and performance characteristics. W/C is a parameter possessing plenty of information associated with durability. Accurate measurement of w/c in hardened concrete is however elusive and the current methods available have several limitations.

2 STANDARD METHODS FOR ESTIMATION OF W/C IN HARDENED CONCRETES

Current methods for w/c determination in hardened concrete are based on chemical analyses or microscopy techniques. Problems common to the methods are *poor accuracy*, *expense*, and *practical limitations*. Chemical methods require analysis for cement content and water content followed by calculation of w/c ratio. It is worth noting that the standardized method BS 1881: Part 124 is not considered suitable for analysis of old concretes of age more than 5 years but even more importantly, the method does not apply to poor concretes, distressed concretes or concretes containing extenders. Yet some of these issues may be the very reason(s) for requiring determination of w/c value. Accuracy of the method is suspected to be as poor as ± 0.1. Another method requiring cement content and capillary porosity measurement is found in Axon, 1962. The same limitations as for BS 1881 method apply here too considering that presence of distress and different forms of pore filling deposits in aged concrete is likely to alter the capillary porosity which is a key factor used in the expression to calculate w/c.

ASTM C 457, a standard technique utilizing optical microscopy by manual inspection, to examine the volume proportion of constituents (by linear transverse or modified point count methods), has considerable errors of around 10% for cement content and even greater errors for water content. Accuracy of w/c ± 0.05 has been found possible (Neville, 2003). Other techniques utilizing microscopy have been attempted including image analysis by scanning electron microscopy and optical fluorescence microscopy but their efficacy has not been proved to be any better than other existing methods. Critical review of a recent method NTBUILD 361, a technique based on use of optical fluorescence microscopy for w/c determination, showed the claimed high accuracy of ± 0.02 to be flawed (Neville, 2003). These techniques also involve a fair expense derived from test procedures such as chemical analyses or equipment itself. The empirical method discussed in this paper requires simple equipment and a quick test procedure, but its problems and limitations call for modifications towards development of the technique.

3 A DIFFERENT APPROACH TO W/C ESTIMATION

3.1 Early hydration studies

Studies on hydration conducted by Powers and other researchers around 1930's to 1960's divulged incredible understanding of micro-mechanics and characteristics emanating from cement hydration. Research done in later years on engineering properties viz:- creep, shrinkage, permeability have benefited from basic understanding of the hydration process, its mechanics and influential factors. It can be appreciated that w/c plays a significant role in the important properties of concrete.

If for arguments sake, all water mixed with cement paste reacted to full hydration (which is known to be unlikely), the quantity of products of hydration would provide a direct account of the cement and water contents used. Complexity is introduced when in reality, water takes different forms during hydration and a fair amount of it is not at all involved in chemical reaction. Another difficulty encountered is the lack of accurate means of quantifying hydration products. The hydration product calcium silicate hydrate (CSH or tobermorite) gel is amorphous while $Ca(OH)_2$ may be semi-crystalline. The use of x-ray diffraction is unable to provide adequate quantification of both products present in the system.

To get around the fore-mentioned difficulties, it suffices to assume that the extent of hydration attainable in a closed hydrating systems of cement paste (containing sufficient water for full hydration), can be monitored through the degree of hydration ultimately achieved or achievable. The ultimate degree of hydration in a closed system must therefore correlate to the quantities of hydration products, and in turn relate to the original cement and water contents used in the mix, that is the original w/c. It is this relationship that Mills, 1965 found to exist when studying cement pastes cured at normal temperatures in his work conducted at University of the Witwatersrand. He concluded that ultimate degree of hydration, α_{ult} in cement pastes can be related empirically to w/c by the equation:-

$$\alpha_{ult} = \frac{1.031.w_o}{0.194 + w_o}$$

Where w_o represents the original water-cement ratio of the paste mixes.

The ultimate degree of hydration was obtained at 448 days (taken as the terminal age) by determining the non-evaporable water content, being the mass of water retained at 110°C but lost at 1000°C. The equation does imply that if the ultimate degree of hydration attained in hardened paste could be determined accurately, then the original w/c can be calculated directly from the equation.

3.2 Accuracy

The equation was derived using mathematical and geometric relationships based on simplified model assumptions. The credibility of this relationship is founded on strong correlations between experimental results and predictions tested on data by different authors referenced in Mills, 1965 (Powers, 1947; Verbeck & Foster, 1950; Cernin, 1960), and his own data. These have been plotted for a selected practical range of w/c's = 0.25 to 0.85 as seen in figure 1. Knowing that slight changes to w/c do represent major swing effects on concrete properties, the important question then relates to the level of accuracy needed in estimation of w/c. Neville, 2003 concluded that an accuracy of ±0.1 is not useful, ±0.05 is achievable by some existing methods but better accuracy is required for practical purposes.

A chi-square test was done on the empirical method to get an indication of accuracy. A chi-square statistic giving $\chi^2=0$ indicates zero differences between actual and estimated values for perfect agreement between the two values, while χ^2 of nearly zero represents a close agreement between the values. Table 1 shows results of chi-square test done on the data. Mills, 1965 data for portland cements (pc) with and without ground granulated blast-furnace slag (ggbs) gives χ^2 = 0.29. The χ^2 value is virtually zero for mixtures of pc only, suggesting nearly perfect estimation of w/c. It can be seen that applying the method to mixes of both pc only and mixes of pc/ggbs, increases the error margin in the w/c estimate relative to respective χ^2 values at a given significance level (see Table 1). When independent data from other authors was included in the analysis, the error is further increased. Generally, the χ^2-test results for the method give a good indication that the original w/c's and estimated w/c's are in close agreement.

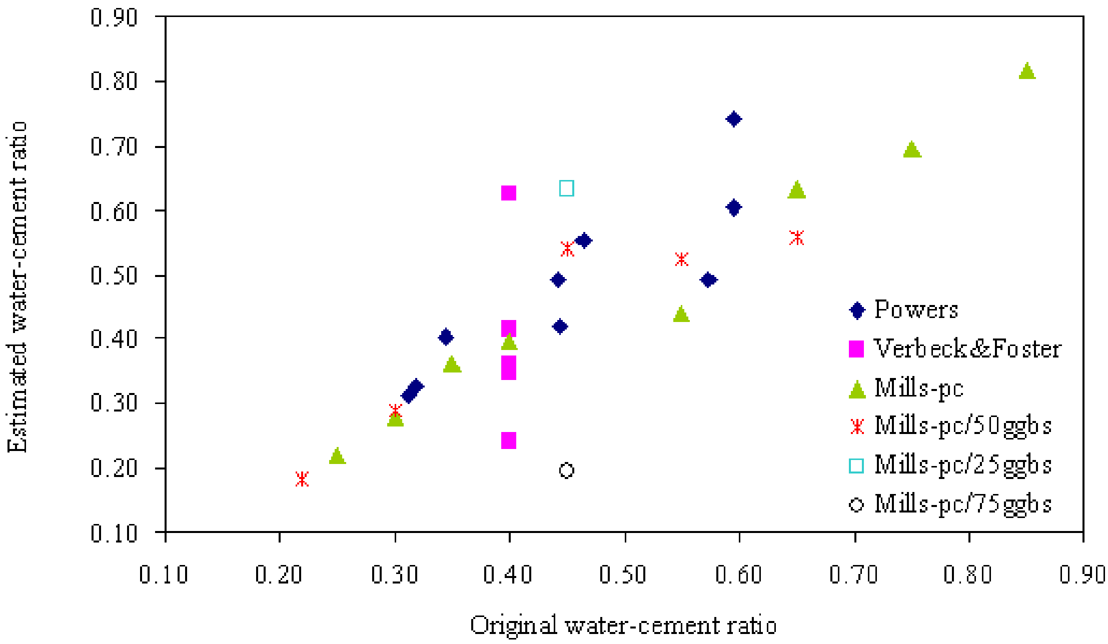

Figure 1. Correlation between original and estimated w/c values (produced with data from Mills, 1965)

Table 1. Chi-square test of w/c estimation (produced with data from Mills, 1965)

	All data (Powers, Verbeck & Foster, Mills)	Mills (pc only)	Mills (pc+ggbs)
Data points (No.)	29	8	15
Age (days)	Various	448	448
w/c	Various	0.25 to 0.85	0.22 to 0.45
$\alpha_{ult\ (\%)}$	Various	54.9 to 83.3	50.1 to 51.8
χ^2	0.57	0.03	0.29
$\chi^2_{.05}$	41.34	14.07	23.68
$\chi^2_{.99}$	13.56	1.24	4.66

3.3 Advantages of the α_{ult} - w/c empirical approach

Considering the empirical α_{ult}-w/c equation as a different approach that could be developed for possible w/c estimation in hardened concretes, the method does have the merit of simplicity and is much cheaper compared to established methods discussed in 2.0. Chemical methods require analysis for calcium oxide or silicon dioxide in the paste and aggregates, and water content. In the case of microscopy methods, the cost associated with the equipment is a very limiting factor and only few specialized laboratories may be so equipped. Microscopy methods also involve a lengthy and detailed analytical procedure. Neither of these limitations are of concern with the empirical hydration method. Problems with the empirical method arise when it comes to applicability and accuracy of the technique. Matters on accuracy were discussed in Section 3.0 and applicability of the method is examined in the next section.

4 PROBLEMS OF ESTIMATING W/C WITH THE α_{ult}-W/C EQUATION

4.1 Cement types and extenders

Portland cement and ggbs were cementitious materials used to generate experimental data resulting in derivation of the hydration equation. It can be considered that the relationship applies to other extenders, such as fly ash that generally exhibit similar hydration characteristics as slag. Analysis by Mills, 1965 showed that the degree of hydration between paste mixes of pc only and those mixes containing pc/ggbs blend was different until the age of 224 days. Beyond this age, the degree of hydration were practically the same. These results suggest that in the long-term, extenders affect the hydration relationship in as much as it concerns the age required to attain the ultimate degree of hydration under normal curing conditions. This is consistent with general understanding that extenders are characteristically slow hydrating, as the pozzolanic reaction awaits $Ca(OH)_2$ formation from cement hydration, then reacting with it resulting in secondary formation of CSH gel. Thus ultimate degree of hydration will take longer to achieve in cementitious systems containing extenders compared to systems with portland cement only.

There are, however, highly reactive extenders intended to enhance early strength and perhaps hydration properties also. Condensed silica fume and ultra-fine fly ash fall in this category. Usually, fineness of these extenders is much higher than that of cement, allowing a pore filling effect in addition to increased reactivity. Applicability of the α_{ult}-w/c equation to these extenders is a matter requiring further study.

Also, it has not been determined if the α_{ult}-w/c relationship does hold for cements other than pc or pc/extender blend. These include expansive cements and alumina cements. For example, alumina cement is used in small repair applications for its quick setting and high early strength. The rapid hydration of the alumina cement may result in relatively early attainment of ultimate degree of hydration timewise but the numerical value of degree of hydration reached may be lower than for normal pc. In such cases, it may be considered that the general expression could still apply though the constants required to approximate the α_{ult}-w/c relations might actually change. This may as well apply to the different types of portland cements in use.

Although Mills, 1965 concluded that the α_{ult}-w/c equation was found satisfactory for pc and pc/ggbs cements, one particular result for high volume slag content of 75% which is reported in Table X of the article was clearly unacceptable, estimating a value of w/c = 0.20 for original w/c = 0.45. Considering that, the other result for the same cement blend reported for 4.65 w/c was quite close and that a result of even a higher proportion of 90% ggbs for 4.61 w/c was good as well, it is not clear whether accuracy of the hydration equation is affected by the numerical value of w/c in relation to use with high extender volumes.

4.2 C_3A content

The article (Mills, 1965) clearly mentions that the α_{ult}-w/c equation is sensitive to the C_3A content of cements and regards the equation to be applicable to cements of low C_3A contents but very little discussion was presented on it. The borderline C_3A content for use with the equation was not defined but regarded relatively according to cements used in the experiments. However, it is clear in fig. 4 of Mills, 1965 that cements of 14% C_3A used by Powers plotted on a straight line that was completely separate from that of cements with $C_3A \leq 9.7\%$. Besides, Mills' own experiments were conducted with cements of 10.6% C_3A and used to derive the α_{ult}-w/c equation. According to experimental data therefore, the high C_3A would refer to cement of 14% C_3A used by Powers.

Most modern portland cements in use contain low C_3A contents with ordinary portland cement, rapid hardening portland cement and white cement having C_3A not exceeding 10%. Portland cements of higher C_3A are for special use in marine environment for their chloride binding effect. In other words, the hydration equation is widely applicable to different portland cement types but it is the underlying process exhibited by C_3A effect on heat of hydration which may perhaps be more important. C_3A in cements generates heat of hydration and its presence in high proportions increases the rate of hydration due to temperature rise. Studies (Detwiler et al. 1991; Kjellsen et al., 1991) have shown that rapid hydration, whether from hydration heat or externally applied heat, results in a reduced degree of hydration and lesser formation of hydration products. A close inspection of Table VII in Mills, 1965, indeed confirms that the value of A_c, a quantity representing the surface area of unhydrated cement which is in contact with water was relatively lower in all cements of high C_3A. This is consistent with the explanation often fronted that rapid hydration leads to deposition of the highly dense hydrates within the vicinity of unhydrated cement grains, preventing penetration of water required for further hydration. The explanation was reported in the article to be true as a contributing factor but not a decisive one since results showed that there was no limiting value for A_c that existed for all w/c ratios.

The influence of heat of hydration becomes paramount when concerned with heat cured precast concretes subjected to different temperatures. It may also apply to insitu cast concretes associated with large pours of high cement contents or coincidentally abnormally high ambient temperatures such as may be experienced in tropical climates. Simulation studies (Hobbs, 1999) have shown that concrete temperatures as high as 85°C can be attained without external application of heat. Accurate application of the α_{ult}-w/c equation to such concretes will likely require modification of the constants applied.

4.3 Maturity

The α_{ult}-w/c equation is based on ultimate rather than the present degree of hydration attained at any given time. In reality, it takes several years under normal exposure conditions, to attain the ultimate degree of hydration making the hydration equation mostly relevant for old concrete structures. Experimental results used to derive the hydration equation were based on 448 days as terminal age although Mills, 1965 acknowledges that the cementitious systems incorporating extenders would be expected to hydrate further for several years. The defining point then becomes the age where any further hydration makes no significant change to the present degree of hydration and this may vary with the type, grade, quality and complexity of the cementitious system.

For any given curing conditions, age and temperature are critical maturity factors of influence to the degree of hydration. The hydration equation is not capable of accounting for the effects of different curing temperatures and time in their present form. The method is also not of much use for new concretes. For example, it cannot be used to verify whether newly placed concrete satisfies mix design specifications submitted to the ready-mix concrete supplier. In light of practical application, the method lacks robustness and modifications may be necessary to incorporate essential applicability.

4.4 Effect of carbonation

Chemically combined water, the basis for assessment of the degree of hydration by mass loss on heating of samples to 1000°C, is bound within the hydration products $Ca(OH)_2$ and CSH gel. Carbonation of concrete is likely to introduce errors to the measurement. Firstly, bound water in $Ca(OH)_2$ is released upon carbonation of concrete, forming $CaCO_3$ compound. The 'lost' water can no longer be in the account of mass loss during ignition. Further still, the $CaCO_3$ having a different molecular weight from $Ca(OH)_2$, results in erroneous mass loss from release of CO_2 at about 800°C rather than removal of water at 500°C.

Fortunately, the influence of carbonation on results is avoidable through proper sampling. Since carbonation is mainly found within cover concrete, carbonation testing can be done rapidly and then samples for measuring the degree of hydration may be taken at uncarbonated depths.

4.5 Advances in cement chemistry and material characteristics

The chemistry of cement changed considerably over the last century, from C_2S content being higher than C_3S content prior to the 1950's to complete reversal of trend in the second half of the century. This can be attributed to industry's demand for high early strength and as concrete became the preferred material of construction, the quest for "fast track" concreting also became unavoidable. The cement industry modified cement properties accordingly. There were also significant changes in cement manufacturing from largely wet process prior to the 1950's to dry and semi-dry processes following the energy crisis of 1970's. C_3S content and cement fineness are responsible for early strength development through reactivity and hydration heat generation. C_3S has increased to a range of about 55 to 65% in modern cements while C_2S, the compound responsible for late strength gain has reduced to about 15 to 25%. An inspection of cement compositions used by Powers, Verbeck and Foster, and Mills (Mills, 1965 Tables I &VI) in their hydration studies confirms that most cements had relatively low C_3S contents, all below 50% except one ASTM type III cement which had 59% C_3S. Correspondingly, nearly all the cements had C_2S contents which were fairly high, exceeding 25%. Supported by improved cement manufacturing technology, cement fineness has also increased remarkably to about 300 to 600 m^2/kg compared to much lower fineness prior to the 1960's. Portland cement of 274 m^2/kg was used in the Mills, 1965 experiments.

As a result of these changes, modern cements can be expected to generate relatively high heat of hydration, relatively high early strength but reduced degree of hydration in a manner similar to the effect of high C_3A content discussed in Section 4.2. As a consequence, the constants used in the original α_{ult}-w/c equation could now be different for modern cements. Other implications of the changes in cement manufacture are evident in material constants. Portland cements prior to 1960's, had a different specific gravity. Modern cements have a specific gravity of 3.14. Mills used specific gravity of 3.22 for the α_{ult}-w/c relationship.

Clearly, modern material characteristics of cement are remarkably different to cement used in experiments leading to derivation of α_{ult}-w/c equation. While the principle remains unchanged, the need for different constants that properly characterize the behaviour of modern complex cementitious material systems is apparent.

5 WHAT IS NEEDED

From foregone discussions, it is quite clear that the material characteristics of modern cementitious systems have changed from those that were used to derive the hydration equation. It is possible that the α_{ult}-w/c equation may no longer be reliable for use in their original form. While the original mathematical concept remains intact and should be hailed, employment of the method requires improvements to the original equation to:- (1) suit modern material characteristics of cementitious systems, and (2) incorporate robustness for applicability to hardened concretes.

Modifying the original hydration equation so as to properly characterize modern cement characteristics is quite straightforward. This can be achieved by utilizing modern cements of known characteristics in similar hydration experimental studies to generate new constants for the equation. Introducing robustness into the hydration equation is more complex. Rather than rely on the *ultimate* degree of hydration for estimation of w/c ratio of concretes, mathematical equation may need to take a different form of a model expressing the degree of hydration as a continuous function of temperature and time, and relating it to w/c ratio. With reasonable assumptions, the w/c ratios of both new and old concretes, subjected to different levels of maturity can then be reliably estimated using such a model.

6 CONCLUSION

The aim of this paper was to examine the α_{ult}-w/c hydration equation as an approach for estimation of w/c in hardened concretes. Accuracy and precision of the method hasn't been tested nor proved although good w/c estimations were determined within the confines of experimental data used. While the method does have useful advantages over current techniques, constants used in the original expression appear to be rather inappropriate for modern cementitious materials whose characteristics and chemistry changed remarkably over the past century. The effect of these changes can best be proved and /or corrected in the equation through experimental work.

The hydration equation applies to portland cements and its blends with conventional extenders. The method is quite sensitive to the C_3A content of portland cement presumably due to increased hydration heat affecting the degree of hydration attained. Similar arguments can be made for heat treated concretes. This can be overcome by expressing the degree of hydration as a continuous function of maturity. With modifications for robustness and appropriate material constants, it is believed that the core mathematical and experimental approach employed holds promise to an effective approach for w/c estimation in hardened concretes.

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