

CHEMICAL SHRINKAGE AS INDICATOR FOR HYDRAULIC BOND STRENGTH

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ABSTRACT Hardening processes like cement hydration are exothermic and supply a bonding energy to the reacting system. Bonding forces cause a densification of the material which can be measured as chemical shrinkage. The strain work supplied to the material is described by using the bulk modulus and is applied to a strength model for hydraulic bond materials. Material tensile strength is defined with half of the strain work. The influence of porosity is considered by a linear strength reducing function.

Key-words: Chemical shrinkage, Volume change, Bound water, Porosity, Strength development

INTRODUCTION

Volume shrinkage is a natural phenomenon accompanying all hardening processes. It expresses the dominance of Coulomb attractive potentials over electrostatic repulsive potentials during the chemical reaction. The result of a hardening reaction is a material densification which can be measured as a volume loss. Therefore, volumetric measurements of cement hydration have been used for a long time together with calorimetric kinetic data to follow hydration development.

Since the early measurements of Le Chatelier (1904) many other authors have used volumetric procedures to record the kinetics of cement hydration (Czernin (1956), de Haas et al (1975), Geiker and Knudsen (1982), Raffle (1984)). Compared with calorimetric methods, volumetric measures are possible over much longer periods. Accurate results can now be obtained with strain gauges and electronic scales applying dipping and weighing methods (Paulini, 1992a).

Chemical volume changes have direct physical significance for describing material strength. A volume strain work is supplied to the material during a hydraulic hardening reaction which must be overcome by a mechanical force. Attempts to define hydraulic bond energy by means of chemical shrinkage volume are described by Paulini (1992a,b).

CHEMICAL SHRINKAGE VOLUME AND KINETICS OF CEMENT REACTIONS

Chemical shrinkage volume of cement hydration is in a range of 55-69 cm³/kg. It can be measured or can be calculated from stoichiometry of cement phase reactions. With mass fractions of cement phases the ultimate chemical shrinkage volume $V_{cs,u}$ becomes (Paulini, 1992a)

$$V_{cs,u} = - (53.2 \cdot [C_3S] + 40.0 \cdot [C_2S] + 178.5 \cdot [C_3A] + 111.3 \cdot [C_4AF]) \quad [cm^3 / kg \text{ Cement}] \quad [1]$$

In Table 1 some values are given for ASTM type cements which are reached after full hydration. They can be used to define the degree of hydration α according to Eq 2.

$$\alpha(t) = \frac{V_{cs}(t)}{V_{cs,u}} \quad [2]$$

Fig.1 shows some kinetic plots of pure cement phases where chemical shrinkage has been measured by hydrostatic weighing. Reactions occurred isothermally at 20°C and with a water/solid ratio of 0.40 (Paulini, 1988). Negative volume changes are drawn with a positive sign in order to receive

conventional kinetic plots.

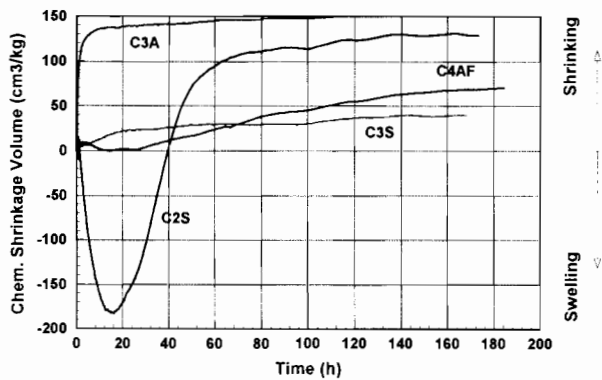


Fig. 1, Measured pure cement phase shrinkage volumes, $T=20\text{ }^{\circ}\text{C}$, $w/s=0,40$

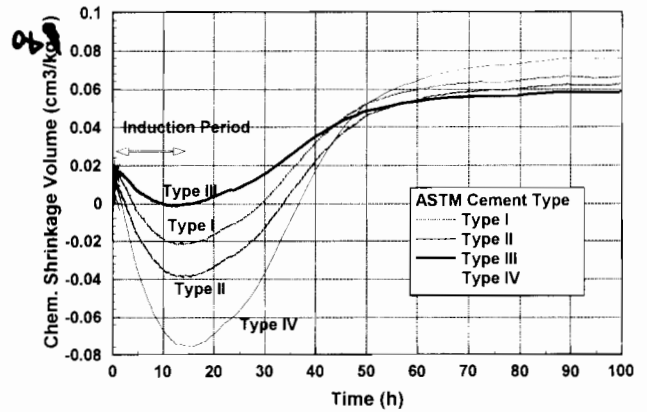


Fig. 2, Calculated shrinkage volumes for ASTM cement types

Table 1 Mean mass fractions of ASTM type cements and calculated chemical shrinkage volume and water demand factor

ASTM Cement	C ₃ S %-M	C ₂ S %-M	C ₃ A %-M	C ₄ AF %-M	Total %-M	V _{cs,u} cm ³ /kg	F _{wv,u} %-V
Type I	49	25	12	8	94	60.5	82.5
Type II	46	29	6	12	93	60.8	81.9
Type III	56	15	12	8	91	66.9	82.7
Type IV	30	46	5	13	94	57.7	81.2

Except for C₂S chemical shrinkage volumes of cement phases tend towards the ultimate values of Eq 1. In C₂S at the beginning a significant swelling occurs which changes after about 18 hours into a volume shrinkage. High Le Chatelier expansions are known for C₂S rich belite cements (Chatterjee, 1996). Fig.2 shows ASTM type cement reactions calculated as linear combinations from the kinetics of pure cement phases with the mass fractions in Table 1. Despite the fact that a linear combination of cement phase reactions may not be absolutely valid for a cement reaction and that variations of measured cement phase kinetics exist depending on burning conditions, the following conclusions can be drawn from Fig.2:

- the initial phase of cement hydration is characterised by the opposed reaction behaviour of C₃A and C₃S on the one side and C₂S on the other side
- growing fractions of C₂S lead to a dominance of early swelling in cement reaction
- the initial dormant period of setting is obviously defined by the swelling time of the cement reaction

An initial swelling behaviour has been found with blended cements (BFC, FAC), sulphate resistant cements (SRPC) and by addition of silica fumes. The use of concrete admixtures like retarders and plastizicers can also force an initial swelling (Paulini, 1990).

A stoichiometric calculation of ultimate shrinkage volume according to Eq 1 cannot be made for blended cements because the assumption of pure cement phase reactions does not hold. For such cements with an initial swelling period the ultimate chemical shrinkage $V_{cs,u}$ has to be extrapolated from long term measurements of shrinkage volume. A kinetic model based on chemical shrinkage volume has been presented by Paulini (1994).

The kinetic model assumes that volume changes occur basically during both the phase transitions of cement hydration. A first order serial reaction is taken to be



with constant reaction rates k_x and k_z . Reactant A is regarded as a solid mass of cement, the intermediate product X as solution product in pore water and the final product Z again as solid bound CSH-gel. The first phase transition solid-fluid $A \Rightarrow X$ causes a volume gain while the crystallisation step fluid-solid $X \Rightarrow Z$ leads to shrinkage. As a result of increased bond energies a shrinkage volume $V_{cs,u}$ remains in the final product Z (Eq 1). The solution of differential Eq 3 shows an interesting context for the total reaction rate (Eq 4)

$$\frac{dZ(t)}{dt} = k_z \cdot X(t) \quad [4]$$

The solution product $X(t)$ becomes the dominant quantity for the total reaction rate. The function $Z(t)$ behaves steady convergent towards 1 and is defined as the degree of hydration α . Chemical shrinkage volume $V_{cs}(t)$ is expressed by the solutions $X(t)$ and $Z(t)$ of differential Eq 3

$$V_{cs}(t) = V_{cs,u} \cdot [Z(t) - X(t)] \quad [5]$$

HYDRAULIC BOND ENERGIES AND STRAIN WORK

Chemical reaction energies set free in a system can be described with the internal energy U of the system

$$\Delta U = \Delta Q + \Delta W = \Delta(c \cdot T) + \Delta(p \cdot V) \quad [6]$$

Under the pressure term p we understand for reactions in fluids and solids the internal bonding forces p_B between particles. These forces result from changes of energy potentials and lead to volume changes. The change of internal energy dU_R of a chemical reaction becomes

$$dU_R = dQ_R + dW_B \quad [7]$$

Exothermic hardening of cement hydration supplies a positive heat of reaction dQ_R as well as a positive bonding energy dW_B to the system. According to the general understanding the total change of internal energy is positive ($dU_R > 0$).

In considering only the reacting system the exothermic heat of reaction dQ_R is regarded as an excess energy which is released from the system. This dissipative energy flux means an energy loss for the system. Instead, a positive bonding energy dW_B is supplied to the system. The first law of thermodynamics also holds true for the reacting system in the form $dU_R = 0$. Therefore, energy changes of chemical reactions are energies working in opposing directions according to Eq 8 (Paulini, 1988).

$$dW_B = -dQ_R \quad (8)$$

This opposing behaviour of chemical reactions is known as the *Le Chatelier* principle. Dissolving reactions with negative bonding energies occur endothermically while exothermic reactions are hardening or densification processes. It is obvious from Eq 8 that volumetric as well as calorimetric reaction measurements will lead to the same kinetic rates. In Fig. 3 kinetic data of differential calorimetric (Wieker, 1995) and shrinkage volume measurements are shown for a cement reaction at 20 °C. Both methods result in very similar kinetic rates.

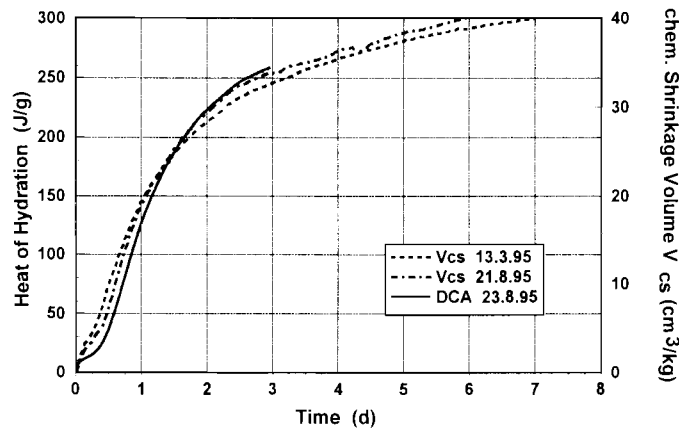


Fig.3, Cement reaction data, chemical shrinkage volume and heat of hydration, T=20 °C

Bonding forces p_B can be expressed by the bulk modulus K and relative volume changes e (Eq 9). The bonding energy W_B of the reacting material is obtained by Eq 10

$$p_B = -K \cdot \frac{\Delta V}{V} = -K \cdot e \quad [9]$$

$$W_B = p_B \cdot V = -K \cdot \Delta V = -K \cdot e \cdot V \quad [10]$$

Relative volume changes e can be calculated stoichiometrically for hydration of pure cement phases or can be measured (Paulini 1988, 1992a). It is more difficult to determine their bulk moduli K . Verbeck and Helmuth (1968) mention for cement values of $K=54.5$ GPa and $E=74.5$ GPa. Using these data, bulk moduli of CSH-gel were calculated with a composite model (Paulini and Gratl, 1995) applied to the water fraction of full hydration. Bulk moduli and bond energy of cement phases calculated with Eq 10 are shown in Table 2.

Table 2 Calculation of bond energy and strain work resulting from hydration of cement phases

Cement Phase	Heat of Hydration QR	rel. Volume Change e=Vs/Va	Density of CSH	Solid Mass Fraction	Water Content	calc. Bulk Modulus CSH-Gel	Hydration Strain Energy W _{irr}	Hydration Bond Energy WB	Ratio QR/WB
	J/g	%-V	g/cm ³	%-M	%-V	MPa	J/g	J/g	
C3S	490	-9.56%	2.457	80.86%	42.60%	23340	53.7	1123.3	0.44
C2S	222	-7.78%	2.549	82.70%	40.74%	24060	34.5	888.1	0.25
C3A	1373	-24.32%	2.520	71.43%	54.59%	19780	325.0	2672.6	0.51
C4AF	465	-17.78%	2.648	77.88%	48.86%	21620	165.7	1864.1	0.25

For all cement phases the ratio of heat of hydration to bond energy is smaller than 1 ($Q_R/W_B < 1$). It is particularly low for slow reacting phases C₂S and C₄AF for which long term calorimetric measurements are inaccurate. More precise calculations of bond energies would have to be based on measured bulk moduli.

A positive bond energy W_B corresponds with a densification work, which results in a volume loss. According to a theory given by Paulini (1988,1992a,b), only the irreversible part of strain energy is responsible for material strengthening. The total work done during the irreversible chemical reaction from initial state 0 to final state 1 along the adiabat 0-2-1 (Fig. 4) is

$$\Delta W = (p_1 - p_0) \cdot (V_1 - V_0) = \Delta p_B \cdot \Delta V \quad [11]$$

Assuming a possible reversible path between initial and final state, the irreversible strain work ΔW_{irr} remaining in the material becomes

$$\Delta W_{irr} = \Delta W - \Delta W_{rev} \quad [12]$$

The reversible strain work ΔW_{rev} is obtained by integration over the volume changes V_s (chemical shrinkage volume)

$$\Delta W_{rev} = \int_0^{V_s} p_B \cdot dV = -V \cdot \int_0^e K \cdot e \, de = -\frac{K}{2} \cdot e^2 \cdot V \quad [13]$$

With Eqs 11, 9 and 13 the irreversible strain work ΔW_{irr} is obtained with the same expression as the reversible work

$$\Delta W_{irr} = -\frac{K \cdot e^2}{2} \cdot V \quad [14]$$

Material tensile strength is considered as an all round stress, whose mechanical strain work is opposed directed to the irreversible strain work of the chemical reaction. The failure state is characterized by an equivalence of failure energy and resisting energy. Therefore, tensile strength f_t is defined by half of the supplied irreversible strain work (Eq 15).

$$f_t = -\frac{K \cdot e^2}{4} \quad [15]$$

Integration of Eq 13 assumes a constant bulk modulus during the chemical reaction. Bulk moduli of concrete change from initially 3-6 GPa to finally over 20 GPa during cement hydration. Exact values depend to a large extent on the stiffness of aggregates. Nevertheless, Eq 15 remains valid if we consider the final values for K and e and if we count the reaction from an initial state without any bond pressure. To prove this, consider the total differential of bond pressure p_B (Eq 16)

$$dp_B = - (K \cdot de + e \cdot dK) \quad [16]$$

An integration from initial state 0 to the state defined by the degree of hydration α leads to

$$p_B(\alpha) = - \int_0^\alpha (K \cdot \frac{de}{d\alpha} + e \cdot \frac{dK}{d\alpha}) d\alpha \quad [17]$$

By partial integration of Eq 17 we obtain the bond pressure p_B

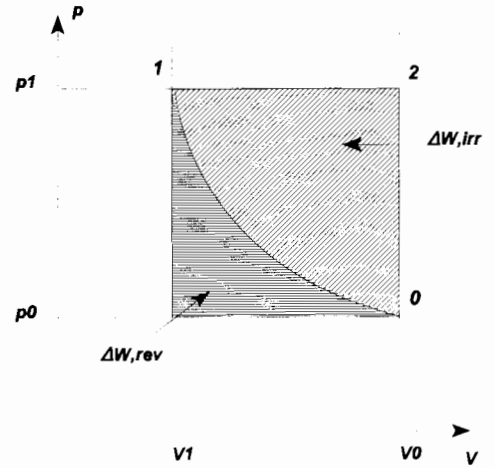


Fig.4, Strain work of an irreversible process from state 0 to 1

$$p_B(\alpha) = - [K(\alpha) \cdot e(\alpha)] + p_{B0} = - K(\alpha) \cdot e(\alpha) + p_{B0} \quad [18]$$

For engineering practice, the initial state 0 is considered to be the state when water is added to the mix, where an initial bond pressure p_{B0} can be neglected. Then, bond pressure $p_B(\alpha)$ is only dependent on bulk modulus $K(\alpha)$ and on the relative volume change $e(\alpha)$. The description of a hydration dependent tensile strength according to Eq 15 needs a formation function for the bulk modulus $K(\alpha)$. Such a stiffness model for concrete has been proposed by Paulini and Gratl (1995).

INFLUENCE OF CAPILLAR POROSITY

The dominant influence of porosity to strength properties is well known to concrete technologists through the wc-ratio. The same amount of cement C leads to the same shrinkage volume $V_s(\alpha)$

$$V_s(\alpha) = C \cdot V_{cs,u} \cdot \alpha \quad [19]$$

but will result in different concrete strength depending on the wc-ratio. The most important factor is the strength development in cement paste. In this model a strength f_0 for cement paste with zero porosity is calculated and then reduced by a function considering the capillar porosity $P(\alpha, wc)$. In the literature different theories are known to reduce a strength depending on the porosity of a material. For cement pastes the linear model of Hasselmann has been found to hold true (Rößler and Odler, 1985). Accordingly, strength $f(P)$ is reduced by porosity P (Eq 20)

$$f(P) = f_0 \cdot \left(1 - \frac{P}{P_0}\right) \quad [20]$$

Therein, P_0 is the maximum porosity where zero material strength occurs. Porosity of cement paste as a function of the degree of hydration and the wc-ratio is given in Eq 21

$$P(\alpha, wc) = \frac{v_{wc} - \alpha \cdot F_{wv}}{1 + v_{wc}} \quad [21] \quad v_{wc}(wc) = \frac{V_w}{V_c} = wc \cdot \frac{\rho_c}{\rho_w} \quad [22]$$

The constant v_{wc} represents the volume ratio of mix water to cement in the fresh mix (Eq 22). The volumetric water demand factor F_{wv} (Paulini, 1992a) is the ratio of chemical bond water V_{cw} to the binder solid volume V_s can also be calculated stoichiometrically (Eq 23) and is given for different cement types in Table 1.

$$F_{wv} = 0.7422 \cdot [C_3S] + 0.6874 \cdot [C_2S] + 1.2023 \cdot [C_3A] + 1.3754 \cdot [C_4AF] \quad [23]$$

Fig. 5 shows porosities of cement paste over wc-ratio for limiting degrees of hydration $\alpha=0$ and $\alpha=1$. Zero strength porosity P_0 of Eq 20 is taken to be $P(0, wc)$ for $\alpha=0$ according to Eq 21. The strength reducing function $(1-P/P_0)$ has a shape as shown for the degree of hydration $\alpha=1$ in Fig.5.

Hydrostatic tensile strength for zero porosity f_{f0} is calculated from Eq 15. With the cement content C_p of cement paste

$$C_p = \frac{\rho_c}{v_{wc}(wc) + 1} \quad [24]$$

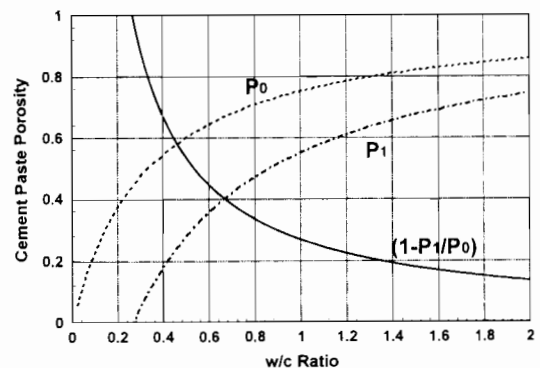


Fig.5, Limiting porosities in hydrated cement paste and strength reducing function

the relative volume change e in cement paste becomes Eq 25

$$e(\alpha, wc) = C_p \cdot V_{cs,u} \cdot \alpha \quad [25]$$

Uniform tensile strength f_{ct} of a concrete mix with a cement content C_{con} is obtained with Eq 15 to

$$f_{ct}(\alpha, wc) = - e(\alpha, wc)^2 \cdot \frac{K(\alpha)}{4} \cdot \frac{C_{con}}{C_p} \cdot \left(1 - \frac{P(\alpha, wc)}{P(0, wc)}\right) \quad [26]$$

Fig. 6 shows some model results of concrete tensile strength for different degrees of hydration calculated with Eq 26. A mix content of 300 kg/m^3 cement and an ultimate shrinkage volume of $V_{cs,u} = 60 \text{ cm}^3/\text{kg}$ have been assumed. Bulk modulus has been calculated with Eq 27 and constants of $K_0=5 \text{ GPa}$, $B=3.5$, $C=0.4$ and $D=2$ (Fig. 7)

$$K(\alpha) = K_0 \cdot (1 + B \cdot \alpha + D \cdot \alpha^C \cdot (1 - \alpha)) \quad [27]$$

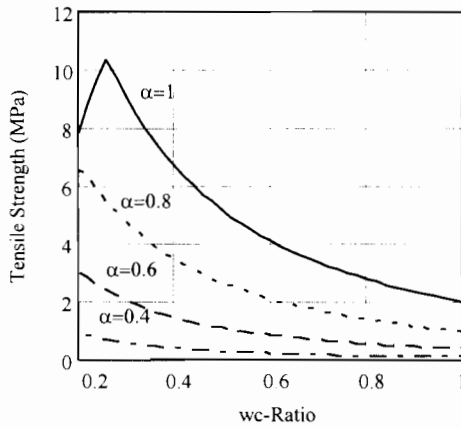


Fig. 6, Concrete tensile strength, model results, $C_{con}=300 \text{ kg/m}^3$

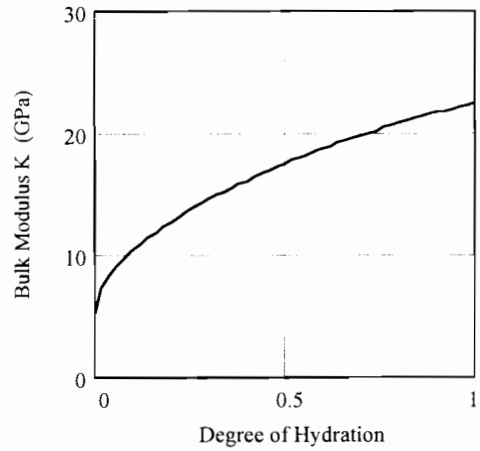


Fig. 7, Bulk modulus $K(\alpha)$

Results obtained by Eq 26 are in normal strength ranges for concrete and exhibit the known dependence on the wc-ratio. Notice also the strength limiting behaviour for low wc-ratios and high degrees of hydration, resulting from incomplete hydration. Fig. 8 shows a similar calculation for different cement contents at a degree of hydration $\alpha=0.9$.

This strength model does not describe the relationship between tensile and compressive strength. Such a model must contain a description of internal material friction and is not yet finished.

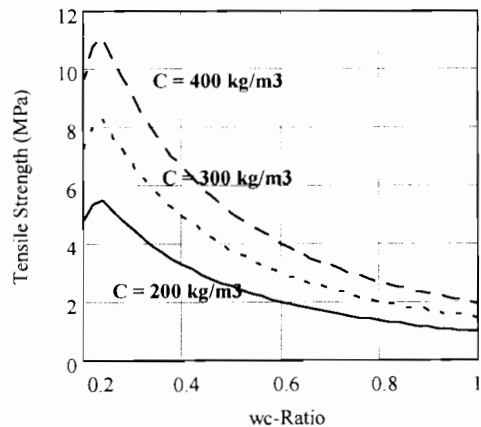


Fig. 8, Concrete tensile strength, model results, degree of hydration $\alpha=0.9$

CONCLUSION

Exothermic hydration of cement is accompanied by a chemical shrinkage. Internal volume changes of cement hydration are very much dependent on the cement type especially during the initial reaction period. During early cement hydration a swelling behaviour can dominate over volume shrinkage. The swelling period is strongly influenced by the percentage of C₂S. The induction period of setting is defined by the swelling time.

Internal volume changes during a chemical reaction are generally not considered in physics. In this article an attempt is made to express bonding forces of a chemical reaction in terms of volume changes and bulk modulus. Heat of reaction and bond energy are considered as oppositely acting energies according to the principle of *Le Chatelier*. Bonding forces lead to a material densification and supply a strain work to the material. The uniform tensile strength resulting from chemical reaction is defined with half of the supplied strain work. A strength model based on chemical shrinkage volume is introduced for cement paste. The influence of porosity has been considered according to the linear Hasselmann theory. A few results prove the model to be applicable to the tensile strength of concrete.

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