

## A WEIGHING METHOD FOR CEMENT HYDRATION

P Paulini

*Institut für Baustofflehre und Materialprüfung  
Universität Innsbruck, AUSTRIA*

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### SUMMARY

Traditionally cement reactions are recorded by calorimetric methods. A simple and accurate kinetic record of hydraulic reactions can be performed with a dipping and weighing method. Changes in sample volume, respectively in their density, are measured continuously during the reaction with a balance. In this contribution the basics of the method will be explained and some examples are given in order to prove the suitability for cement hydration. In the early phase of cement hydration either chemical shrinkage processes or swelling processes can occur. The induction period is defined by a swelling process while the hardening phase is characterized by the appearance of chemical shrinkage. A rough calculation of bond energies leads to values normal for concrete materials.

### ZUSAMMENFASSUNG

Zementreaktionen werden traditionell mittels kalorimetrischer Methoden aufgenommen. Eine einfache und genaue kinetische Aufnahme hydraulischer Reaktionen kann auch mittels dem Tauchwägewerfahren durchgeführt werden. Dabei werden die Änderungen des Probenvolumens, respektive deren Dichteänderungen, kontinuierlich während der Reaktion mittels einer Waage gemessen. In diesem Beitrag werden die Grundlagen des Verfahrens erklärt und anhand einiger Beispiele die Anwendbarkeit der Methode auf die Zementhydratation gezeigt. In der Anfangsphase der Zementhydratation können sowohl Schrumpfvorgänge wie auch Quellvorgänge vorliegen. Die Ruheperiode wird durch die Dauer der Quellperiode bestimmt während die Erhärtungsphase durch das Auftreten von Schrumpfvolumen charakterisiert ist. Eine Abschätzung der Bindungsenergie ergibt für Betonmaterialien gängige Werte.

## INTRODUCTION

The determination of the kinetic behaviour of cement reactions can be classified into direct and indirect methods. Direct methods like calorimetry or volumetry are carried out continuously during the reaction and their analog output can be transformed to any desired resolution. Direct methods have also a direct relation to energy changes in the reacting sample. Indirect methods require to stop the reaction and need mostly a sample preparation, which leads to discrete measurements. Such methods are quantitative X-ray analysis (QXRA), nuclear magnetic resonance (NMR), differential thermal analysis (DTA), determination of evaporable water and chemical and optical methods. A comparison of some of these methods is given in [1].

## ENERGY PRINCIPLES OF CHEMICAL REACTIONS

Energy changes of chemical reactions are described by the 1st and 2nd law of thermodynamic. The inner energy  $U$  of a system can be expressed with a heat energy term  $Q$  and a volume work  $W$

$$U = Q + W \quad (1)$$

From conservation law of energy it is required that the inner energy of a closed system remains unchanged. This can be expressed as

$$dU = dQ + dW = 0 \quad (2)$$

Thus we receive for a chemical reaction opposite directed energy terms of the same absolute amount for changes in heat energy and volume work

$$dQ = -dW \quad (3)$$

The direction of the chemical reaction can be determined with the 2nd law of thermodynamic. We divide the entropy  $S$  in an inner term  $dS_i$  remaining in the system and in a dissipative flux term  $dS_e$  released from the system

$$S = S_i + S_e \quad (4)$$

The 2nd law can be written claiming an increase of the inner entropy term  $dS_i$  [2]

$$0 \leq dS_i \quad (5)$$

For irreversible chemical reactions it can be shown that energies remaining in the system and dissipative flux energies underlie the following relations [3]

$$\begin{array}{l} T \cdot dS_e < 0 < T \cdot dS_i \\ \text{exothermic reactions .....} \quad dQ_R < 0 < dW_{irr} \\ \text{endothermic reactions .....} \quad dW_{irr} < 0 < dQ_R \end{array} \quad (6)$$

In an exothermic reaction the heat of reaction  $dQ_R$  is an energy loss term, which is released from the system and transferred to the surrounding. Coincidentally a positive volume work  $dW_{irr}$  is transferred to the system, resulting in a hardening process. An endothermic reaction is characterized by a supply of heat energy to the system with a simultaneous negative volume work (solution process). Hardening processes are therefore exothermic whereas solution processes are of endothermic nature. These relations hold not just for nonequilibrium chemical processes (hydraulic hardening, 2-component resin reactions), they are also valid for equilibrium crystallization like ice formation or stiffening of meltings of metals and polymers.

Chemical reactions can therefore be recorded either by measuring the heat of reaction  $\Delta Q_R$  or by measuring the volume work  $\Delta W_{irr}$ . In classical thermodynamics volume work has mostly been neglected because the pressure is regarded as working from outside "on the system". This is valid especially for gas reactions. For liquid and solid reactions the pressure is regarded here as an inner bond pressure  $p_B$  working "in the system between particles" !

Figure 1 shows a p-V diagram of a chemical reaction starting at state 0 and ending at state 1. An irreversible process from state 0 to state 1 occurs along the adiabatic path 0 - 2 - 1 and performs a total work according equation (7). We assume that the system allows a reversible process along the path 0-1 with a reversible work according equation (8). This reversible work must also be overcome during the irreversible process and is directed against the total work. The remaining irreversible volume work responsible for material structure changes like hardening can be expressed as difference of these two opposite energies.

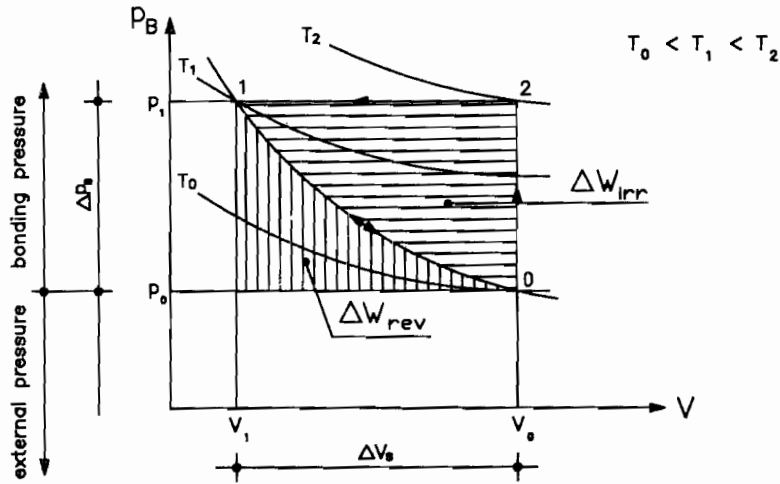


Fig. 1, p - V - Diagram

The total produced volume work  $\Delta W$  during the irreversible process can be written as

$$\Delta W = -\Delta p_B \cdot \Delta V_s \quad (7)$$

Against this bonding work effects the reversible volume work  $\Delta W_{rev}$

$$\Delta W_{rev} = -\int_{V_0}^{V_1} p_B \cdot dV \quad (8)$$

The irreversible bonding work  $\Delta W_{irr}$  remaining in the system and responsible for material hardening can be stated as

$$\Delta W_{irr} = \Delta W - \Delta W_{rev} \quad (9)$$

We express the bond pressure  $p_B$  in terms of volume changes and bulk modulus  $K$

$$dp_B = -K \cdot \frac{dV}{V_0} \quad (10)$$

Under the simplified assumption of a constant bulk modulus  $K$  we receive the bond energy produced by a chemical reaction as a true function of the shrinkage volume  $V_s$  [4].

$$\Delta W_B = \Delta W_{irr} = \frac{-K}{V_0} ((\Delta V_s)^2 - \iint d^2V) = \frac{-K}{2 \cdot V_0} \cdot (\Delta V_s)^2 \quad (11)$$

If we express equation (11) in terms of relative volume changes  $e$

$$d\theta = \frac{dV_s}{V_0} \quad (12)$$

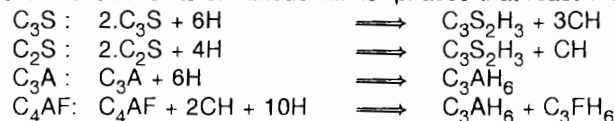
we receive the bond energy as

$$\Delta W_B = -\frac{K}{2} \cdot (\Delta\theta)^2 \cdot V_0 = \sigma_t \cdot V_0 \quad (13)$$

$\sigma_t$  is the uniform directed bond strength of the material and can be regarded as a uniform tension strength. Thus, the square of the shrinkage volume  $\Delta V_s$  is a direct unit for the hardening process.

## VOLUME CHANGES OF CEMENT PHASE REACTIONS

Portland cement consists of various clinker phases that react with water according to the following symbolic equations:



All these phase reactions are exothermic processes accompanied by a decrease of volume (chemical shrinkage). Table 1 show for  $C_3S$  a comparison of volumes of basic and reaction products. The shrinkage volume  $V_s$  as difference between volume of reaction and basic products becomes negative.

$C_3S$ - Reaction	Mol.Wt. g/mol	Density g/cm <sup>3</sup>	Mol.Vol. cm <sup>3</sup> /mol
2.(3CaO . SiO <sub>2</sub> )	456,6460	3,1300	145,8933
6 H <sub>2</sub> O	108,0918	0,9982	108,2867
Basic Products	564,7378	2,2218	254,1800 = $V_b$
3CaO.2SiO <sub>2</sub> .3H <sub>2</sub> O	342,4538	2,6300	130,2106
3.(Ca(OH) <sub>2</sub> )	222,2841	2,2300	99,6790
Reaction Products	564,7379	2,4566	229,8895 = $V_r$
			-24,2905 = $V_s$

Tab. 1,  $C_3S$  - Reaction

Relating the shrinkage volume to the solid mass of the basic product we get for  $C_3S$

$$V_{ca} = \frac{V_s}{M} = \frac{-24,2905}{456,646} = -0,0532 \text{ cm}^3/\text{g}$$

Negative shrinkage volumes were found with analogue calculations for all other clinker phase reactions too. The mass related shrinkage volume  $V_{cs,u}$  of a full hydrated portland cement can be calculated with the phase constituents according

$$V_{ca,u} = -0,0532.[C_3S] - 0,0400.[C_2S] - 0,1785.[C_3A] - 0,1113.[C_4AF] \quad (14)$$

A similar characteristic cement parameter is the volumetric water demand factor  $F_{wv}$ . For  $C_3S$  it becomes

$$F_{wv} = \frac{V_w}{V_r} = \frac{108,2867}{145,8933} = 0,7422$$

and for portland cement

$$F_{wv,u} = 0,7422.[C_3S] + 0,6874.[C_2S] + 1,2023.[C_3A] + 1,3754.[C_4AF] \quad (15)$$

ASTM	$C_3S$ [%]	$C_2S$ [%]	$C_3A$ [%]	$C_4AF$ [%]	Total [%]	$V_{cs,u}$ [cm <sup>3</sup> /g]	$F_{wv,u}$
Type I	49	25	12	8	94	-0.0605	0.825
Type II	46	29	6	12	93	-0.0608	0.819
Type III	56	15	12	8	91	-0.0669	0.827
Type IV	30	46	5	13	94	-0.0577	0.812
Type V	43	36	4	12	95	-0.0578	0.808

Tab. 2, Cement Parameters for ASTM - Type Cements

Table 2 shows these cement parameters for ASTM-type cements. In these calculations the remaining mass fraction to 100% was considered with a 30% lower reactivity. Similar values for cement have been reported by other authors too. Using a mean chemical shrinkage volume for cement of 60 cm<sup>3</sup>/kg with a mix of 300 kg cement/m<sup>3</sup> and a bulk modulus of 20 GPa we receive with equation (13) a tension strength of 3,24 MPa, well in the range of concrete materials.

The degree of hydration  $\alpha(t)$  can be expressed as relation of time dependent shrinkage volume  $V_{cs}(t)$  to the ultimate shrinkage volume  $V_{cs,u}$

$$\alpha(t) = \frac{V_{cs}(t)}{V_{cs,u}} \quad (16)$$

and can be determined through a continuously weighing of shrinkage volume  $V_{cs}(t)$ .

## WEIGHING METHOD

A simple method to measure volume changes of hydraulic reactions is the use of a dipping and weighing method. This has been applied for cement reactions already in [5,6]. The equipment is very simple and a system plot is shown in Fig. 2. The required components are a self levelling water bath with a thermostat, a digital balance (0,001 g) and a data logger.

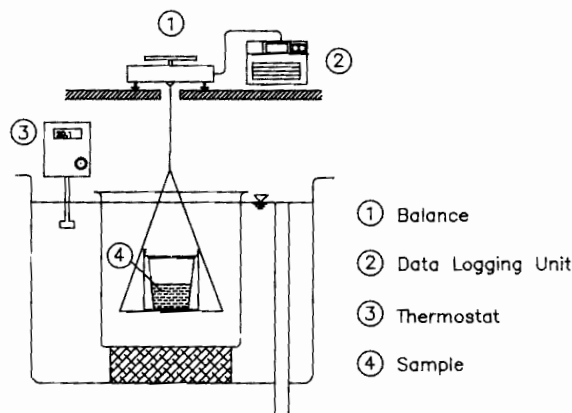


Fig. 2, Immersion Weighing Method

The immersion weighing vessels are divided into a temperature controlled outer water bath and a stabilized inner water bath. The two baths intercommunicate via an aperture of small area or a siphon. The common water level is kept constant. The sample is placed in a plastic case that, in turn, is placed in a vessel to separate it from the inner water bath. An elastic sheet is used to separate the sample from the water bath. The purpose is to avoid density changes by diffusion of dissolved ions to the free water bath. Placing of the sample and covering of the sample holder must be done under water.

The immersion weighing method can be applied to pure cement samples as well as to mortar or concrete samples. Measurements can be taken from the earliest time on, just after placing the sample and calming down of the water level after 1-2 min. The method is suitable for long term runs too, because control procedures like in calorimetry are not necessary. Interpretations of datas from immersion weighing recordings are simple. The shrinkage volume for isothermal storage can be calculated just from mass changes  $\Delta G(t)$  and the density of water  $\rho_w$

$$V_s(t) = \frac{G(t) - G_0}{\rho_w} = \frac{\Delta G(t)}{\rho_w} \quad (17)$$

and related to cement mass  $Z$

$$V_{cs}(t) = \frac{\Delta G(t)}{Z \rho_w} \quad (18)$$

In order to get conventional graphs of cement reactions, the original negative shrinkage volume is introduced here with a positive sign. An increase in the reading of an immersion weighing means a volume shrinkage resp. an increase in density.

## EXPERIMENTS

The following plots represent typical cement reactions. The plots show  $V_{CS}$  - time - diagrams in which positive values mean a volume shrinkage and negative ones a swelling of volume. The reactions were carried out at constant temperatures of 20 °C and with w/c-ratios of 0,40.

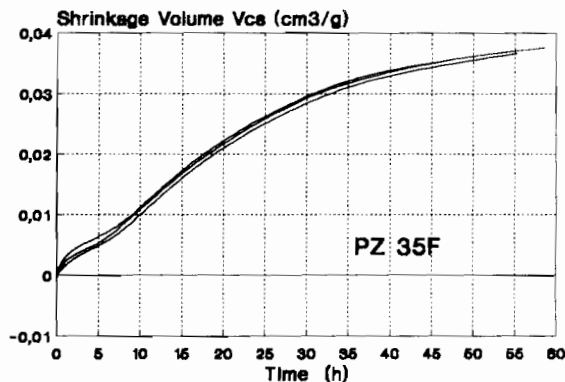


Fig. 3, Repeating Accuracy

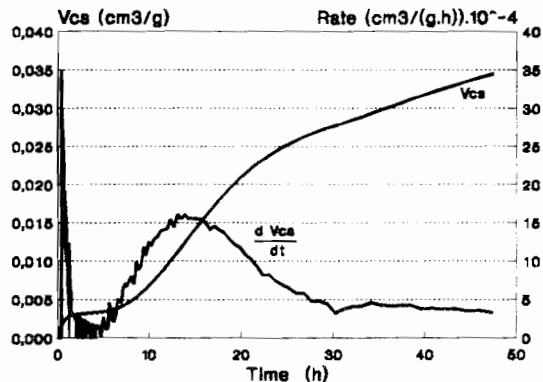


Fig. 4, Normal Cement Reaction

Fig. 3 presents the repeating accuracy of 3 repetitions of a cement reaction. The recordings show a nearly identical behaviour with small variations in the early phase. The reproducibility of the method seems to lie in a sufficient range.

In Fig.4 a reaction of a normal hardening PZ 35F is shown. Differentiation of  $V_{CS}$  values against time leads to the reaction rate. These curve has a fluctuating shape because of numerical differentiation. Though, the high early reaction followed by an induction period, and from about 5 hours on the beginning of the acceleration period, can clearly be seen.

Cement reactions recorded with an immersion weighing method differ from each other especially through the type of initial reaction. Fig. 5 shows possible initial cement reactions of different cement types. Distinguishing between the mentioned reaction types leads to the following description:

- Type H: high initial reaction, with very fine ground cement types
- Type L: low initial reaction, with quicker reacting normal cement types and cements of a medium finesse
- Type N: no initial reaction, with normal cement types
- Type S: initial swelling reaction (solution-type), change to shrinkage after an induction period, mostly with SRPC and slag modified cement types and with freshly ground cement.

The last mentioned S-type cement reaction explains the hydration mechanism of cement reactions. This can be regarded as sequential reaction of a solution and a crystallization process. In both processes a phase transition is included with well known volume changes during each transition step. As long as the solution process dominates over crystallization, an overall volume swelling results from the process. From the time of supersaturation on, crystallization shrinkage dominates over solution swelling and material hardening begins. The time period of the swelling process can be defined as induction period.

Fig. 6 shows the reaction behaviour of pure  $C_3A$  with a Blaine value of 4000  $cm^2/g$ . Relating  $V_{CS}(t)$  on the ultimate shrinkage volume of 0.1785 acc. equation (14) we receive the degree of hydration with equation (16).

The influence of concrete admixtures on immersion weighing results of cement reactions has been discussed in [7]. Generally, it can be said that accelerators lead to an immediate shrinkage behaviour while retarders and superplasticizers tend to S-type reactions.

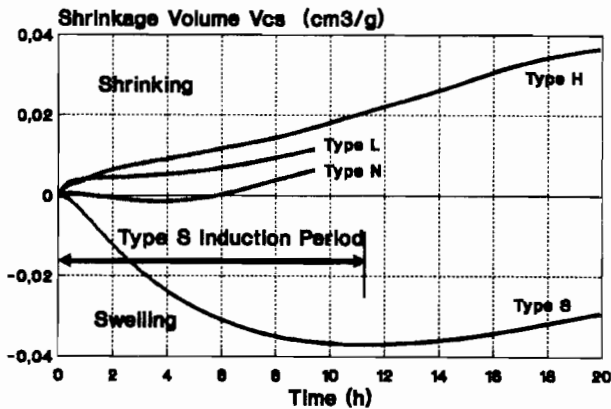


Fig. 5, Initial Reaction Types

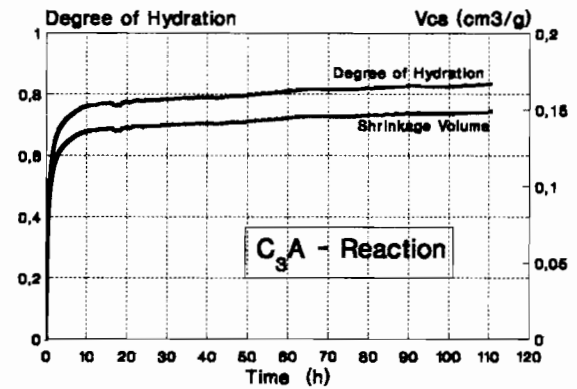


Fig. 6, C<sub>3</sub>A - Reaction

## CONCLUSION

Immersion weighing of hydraulic reactions represents a simple and accurate method to record kinetic datas of hydraulic processes. The equipment is comparatively cheap so that the method can be used not just in laboratories but also on building sites. The measured reaction curves allow an evaluation of cement types as well as the efficiency of additives or the influence of a temperature treatment. Especially for the early reaction period, the method is more sensitive than calorimetry. The induction period is characterized by the occurrence of a swelling reaction. The acceleration period, during which material strength arises, begins from the time of first occurrence of shrinkage.

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