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A Through Solution Model for Volume Changes of Cement Hydration

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Abstract

Changes of volume, temperature and bonding forces accompany every chemical reaction. Cement hydration leads to volume shrinkage during CSH formation and is influenced by a twofold phase transition. Dissociation of cement into pore solution leads to volume swelling while the following crystallisation process produces volume shrinking. In the Through Solution (TS) - model presented here, the volume changes of cement reaction are described on the base of a consecutive reaction A - X - Z. The initial product A is considered as bulk volume of cement. X as a transition state product becomes the most important factor for the total reaction rate. The final product Z, as the volume of water bonded CS-phases, is regarded as the degree of hydration. The model has been shown to give adequate results for common cement reaction types.

Introduction

Crystallisation theory and colloid formation theory havealways adopted different points of view in explaining cement hardening. In colloidal theory the growth of strength is interpreted by increasing surface areas of CSH-gel and the influence of surface energies. Van der Waal's attraction forces and electrostatic double layer interactions build the primary working forces, which are also used in DLVO theory for hydration bindings [1]. In the short range region repulsive hydration forces dominate in contact with an electrolyte over long range Van der Waal's attractive forces [10].

On the other hand, crystallisation theory initially used a through solution model [2]. Crystallisation occurs after a state of supersaturation is reached in the pore solution. The process includes an initial phase transition solid-fluid during dissociation and a further phase transition fluid-solid during crystallisation. Phase transitions are characterized by discrete volume changes. Fig. 1 shows the transition zone according the usual Van der Waal's theory.

The solution process is characterized by dominant repulsive forces. They are noticeable mainly in the early age of CSH-gel formation when a high dissociation rate occurs during solvation of the cement. The dispersion forces are also increased by the use of concrete admixtures like
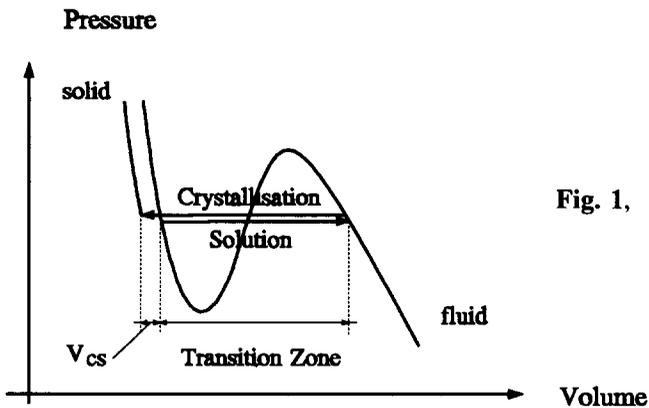
Pressure

Fig. 1, Phase Transition acc. VdW-Theory

plasticizer, retarders or water reducing agents [11]. Attraction forces dominate in the subsequent crystallisation process and lead to volume shrinkage. After total cement hydration a chemical shrinkage volume of 60-65 cm^3/kg cement is reached. These volume changes can be measured by hydrostatic weighing [3]. The binding forces can be expressed using volume changes and bulk modulus [4].

Changes of attractive and repulsive potentials are of high interest for the hydration and hardening of cement. They result in changes of particle distances and of volume. In this article we describe volume changes of cement hydration based on a TS-model and a consecutive reaction.

Phase Transition

Phase transitions are accompanied by discrete changes of their inner energy terms such as heat energy or bond energy. For a solution process the Gibbs free enthalpy becomes [5]

$$G = -T \cdot \delta n \cdot \ln\frac{c_s}{c} \tag{1}$$

Therein c is the material concentration, c_s the saturation concentration and δn the change of solved material. By differentiation of Gibbs free enthalpy G according to temperature we get the heat of solution Q_l for the solution of n mol material to

$$Q_l = T^2 \, n \, \frac{\partial \ln c_s}{\partial T} \tag{2}$$

Similarly the volume change V_l can be calculated by differentiating G according to the pressure

$$V_l = -T \, n \, \frac{\partial \ln c_s}{\partial p} \tag{3}$$

A positive heat of solution means that energy is absorbed from the system by an endothermic reaction. This happens since the expression $\partial c_s/\partial T$ remains positive, which is valid for most chemical solution reactions. Also for cement systems the solubility of CS-phases increases with

rising temperatures [6], which would imply an endothermic cement dissociation process. Such endothermic behaviour was found very rarely for cement reactions [7].

A direct use of eq.(3) is difficult for cement systems, because not much literature exists on pressure dependent solubility of CS-phases. The pressure dependence of solution reactions is normally expressed with van't Hoff's formula which was developed for osmotic pressures. Making use of the theory of activated states [8] the reaction rate k(p) is derived from eq.(3) to

$$k(p) = k_0 \, e^{-\frac{\Delta V^*}{RT} p} \qquad\qquad (4)$$

HHere ΔV means the volume change of the activated transition state and k_0 represents the reaction rate under normalized conditions. The reaction rate k(p) rises with increasing pressures until the activation volume remains negative and vice versa. Therefore, volume swelling as recorded with most solution processes leads to a decrease of the reaction rate, whereas volume shrinking of crystallisation accelerates the reaction. Equation (4) is similar to the Arrhenius law, if we understand the product of the activation volume ΔV^* and the binding pressure p as an activation energy ΔG^* .

An often used interpolation formula for phase transitions is Van der Waal's state equation

$$(p + \frac{a}{V^2}) (V-b) = RT \qquad\qquad (5)$$

where b accounts for the molecule volume and a/V^2 for the Van der Waal's attraction forces. Originally used just for gas-fluid transitions, VdW-state equation is now also applied to solid-fluid transitions. In more recent publications an interface layer is assumed, for which a density distribution $\rho(x)$ has to be found, which will minimize the binding energy and support the mass conservation. The binding energy is expressed with the VdW-potential enlarged by an elastic strain energy of the interface layer. The strain energy is calculated with the density gradient [9].

Repulsive solution forces, which cannot be explained with DLVO theory, are also described in [10]. They have been measured in the short action range up to 5 nm and were found to increase considerably with higher electrolyte concentrations. Repulsive forces are explained with the necessary dehydration energy of cations bound in solid matter.

All the theories for solution phase transitions mentioned here describe repulsive forces (dispersion forces) in the interface layer which lead to a volume swelling. Only in the subsequent crystallisation process, when attractive forces dominate, can volume shrinkage occur. Cement hydration includes a twofold phase transition. It seems therefore to be reasonable to describe volume changes of cement hydration with a through solution model.

Through Solution Model

Cement clinker exists of semistable, energy rich crystalline phase modifications of initial CS-phases. These phase modifications are stabilized on different energy levels depending on the clinker cooling rate. The higher the cooling rate, the shorter is the possible crystallisation time and the higher is the frozen free energy potential in the material. At room temperature semistable phase modifications are based on a local free energy minimum. In order to react in

contact with water, the free energy of the clinker phase has to be raised by a certain activation energy (Fig. 2). The required activation energy is absorbed as heat energy from the reacting system (endothermic process). From this activated state the further reaction to a final equilibrium state can occur.
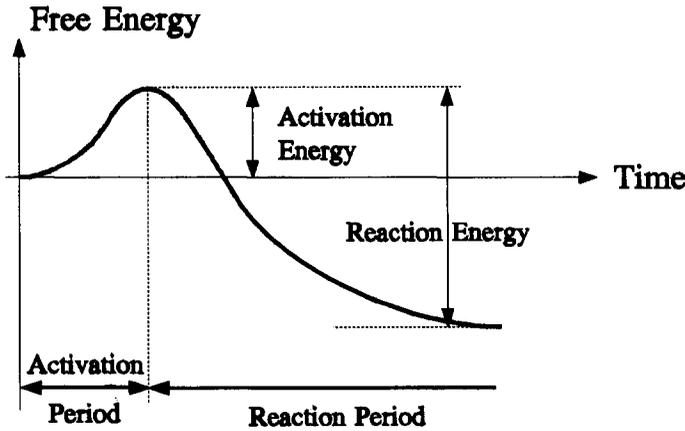
Free Energy

Fig. 2, Activated State

Transition state theory has been used for many chemical reactions and can be written as a simple consecutive reaction [8]

$$A \overset{k_x}{====>} X \overset{k_z}{====>} Z \tag{6}$$

A, X and Z are the material concentrations of initial, transition and final states, whereas k_x and k_z mean the rates of each partial reaction. Applying it to cement hydration A is understood to be the cement concentration per unit volume. The activated state is the dissolved state in pore solution, where X represents the concentration of dissociated CS-clinker phases. Z is the concentration of CS-phases in the final state of CSH-gel.

We obtain the solution for the consecutive reaction (6) using the law of mass action [8]. With the concentration A_0 at time 0 we get the initial product A(t) to

$$A(t) = A_0 \, e^{-k_y t} \tag{7}$$

and the transition state product X(t) to

$$X(t) = A_0 \, \frac{k_x}{k_z - k_x} \, (e^{-k_x t} - e^{-k_z t}) \tag{8}$$

The final product can be written with the law of mass conservation to

$$Z(t) = \frac{A_0}{k_z - k_x} \, [\, k_z \, (1 - e^{-k_x t}) - k_x \, (1 - e^{-k_z t}) \,] \tag{9}$$

A typical plot of concentration functions (7-9) is shown in Fig. 3.
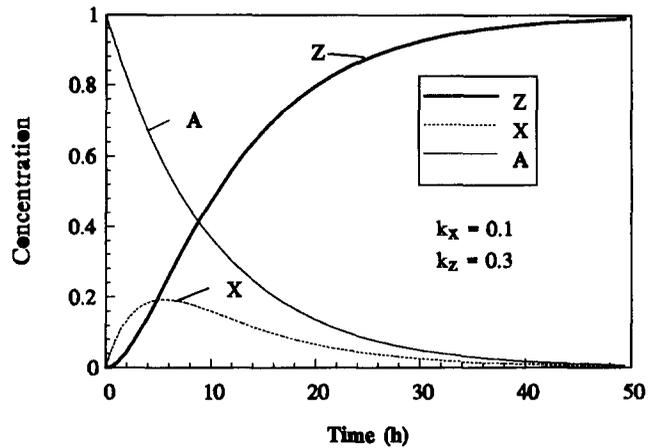
We recognize that the total reaction rate becomes

Fig. 3, TS-Concentrations A, X, Z

$$\frac{dZ(t)}{dt} = k_z \, X(t) \tag{10}$$

where the amount of the transition product $X(t)$ determines the reaction rate. Furthermore $Z(t)$ is a continuously increasing function towards 1 and can be defined as degree of hydration $\alpha(t)$.

$$\alpha(t) = Z(t) \tag{11}$$

In cement reaction kinetics a distinction is made between an immediate topochemical surface reaction and a diffusion controlled core reaction. The topochemical reaction considers influences of different cement fineness, surface activation of different grinding processes, SO_3 content, different nuclei content of prehydration or the influence of cement admixtures. The core reaction relates to the long term reaction behaviour of coarser cement grains and is controlled by the pore structure of CSH-gel.

To get a realistic model we divide the total cement reaction into a fraction A_1 for the surface reaction and into a remaining fraction A_2 for the core reaction. For both parts the reaction scheme (6) is applied but with different reaction rates.

$$
\begin{aligned}
A(t) &= A_1(t) + A_2(t) \\
X(t) &= X_1(t) + X_2(t) \\
Z(t) &= Z_1(t) + Z_2(t)
\end{aligned} \tag{12}
$$

The model has five unknown values which are defined as

A_1	cement fraction of surface reaction 1
k_{x1}	reaction rate of activation process 1
k_{z1}	reaction rate of final reaction 1
$A_2 = 1 - A_1$	cement fraction of core reaction 2 (known)
k_{x2}	reaction rate of activation process 2
k_{z2}	reaction rate of final reaction 2

The reaction rates $k_{x,i}$ and $k_{z,i}$ are assumed to be constant and not dependent on the CSH-gel

distribution or the degree of hydration. Equations (7-9) are valid for the kinetic values A, X and Z in each partial reaction i (i=1,2).

The volume changes of cement hydration during phase transitions are expressed with the kinetic values X and Z. We assume that an increase of the transition product X causes a volume swelling while a growth of the final product Z produces a volume shrinking. After full hydration there remains an ultimate chemical shrinkage volume $V_{cs,u}$ in the order of 60-65 cm^3/g cement. This can be calculated from stoichiometric CS-phase reactions knowing the clinker portions of CS-phases [3]. For the time dependent chemical shrinkage volume we write

$$V_{cs}(t) = V_{cs,u} [Z(t) - X(t)] \qquad (13)$$

In order to receive usual reaction plots the sign of volume changes has been changed in eq (13). Therefore positive V_{cs} values represent shrinkage volumes while negative ones mean swelling volumes.

Equation (13) includes a simultaneous occurrence of a surface and a core reaction. The use of a delay time t_0 for the core reaction would be formally better but could also only take into account a smeared influence of the cement grain size distribution. This effect is obtained in the TS-model with different reaction rates.

Application to measurements

Volume changes of hydraulic reactions can be measured by means of hydrostatic weighing [3]. Different reaction types are distinguished for the early cement reaction [3,4] (Fig.4).

Some cement types like sulphate resistant cements or blast furnace and slag modified cements show an early swelling behaviour (Type S). An early swelling is also obtained by adding admixtures like plasticizer, water reducers, or retarders [11] or by the addition of microsilica [4] to otherwise normally reacting cements. The initial swelling signifies an exceeding solvation process with subjected volume expansion. As long as repulsive solvation pressures dominate over attractive crystallisation forces no hardening effect can occur. Therefore, the induction period of cement hardening has been defined with the duration of the swelling period [3,4].
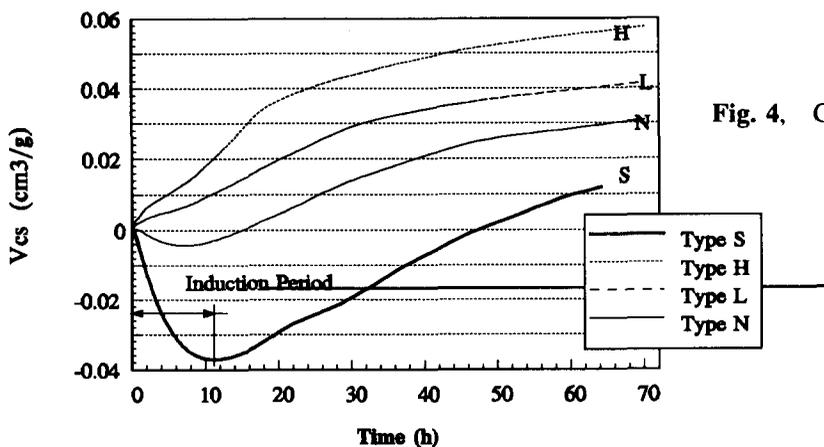

Fig. 4,   Cement Reaction Types

The mathematical problem is to calculate the five unknowns A_1, k_{x1}, k_{z1}, k_{x2}, and k_{z2} from the data set $V_{cs,i}(t)$. The usual stoichiometric CS-phase reactions cannot be assumed to hold for cements with higher glass contents or blended cements. For such cements the ultimate chemical shrinkage volume $V_{cs,u}$ is introduced as an additional unknown in eq. (13). Also for accelerated reactions an unknown additive term $V_{cs,0}$ has to be added in eq. (13). In such cases $V_{cs,0}$ considers the reaction in the first minutes, because hydrostatic weighing gives first values only one to two minutes after addition of mix water. Therefore, depending on the conditions, 5 to 7 unknown values have to be determined from the measured data set. The problem can be seen to minimize the square of the point errors

$$F = \sum_{i=1}^{m} \frac{(V_{cs}(t_i) - f(t_i, P_j))^2}{\sigma_i^2} \tag{14}$$

Therein $V_{cs,i}(t)$ are the measured volume changes at time t_i, and $f(t_i, P_j)$ are the calculated volume changes of the TS-model. An additional weight function for point errors can be applied with σ_i.

Numerical solution methods use a start vector P_0 and iterate according to a given algorithm until a predefined error level is reached. Different routines from standard libraries (BMDP, NAG) have been used. For practical use the NLOPT program [12] has proved to give quick and good results. Different algorithm like Nelder-Mead Simplex, Marquardt or gradient methods can be chosen and applied successively to the last calculated parameter set. Table 1 shows results obtained for the cement types of Fig. 4. The values $V_{cs,u}$ in Tab.1 have also been calculated. For the type S reaction a much higher ultimate chemical shrinkage is obtained as expected from stoichiometry, while type N and L reactions have lower values.

Fig. 5 and 6 show two examples of measured and calculated shrinkage volumes. All the TS-model curves calculated with the parameters of Tab. 1 give good agreement with the measurements. This proves that the TS-model can describe the main types of early cement reactions.

The TS-model includes two processes, a topochemical surface reaction and a core reaction. Often cement hydration shows a fluctuating reaction behaviour in the early age. This can be the result

Tab. 1,   TS-Model Parameters for different Cement Types

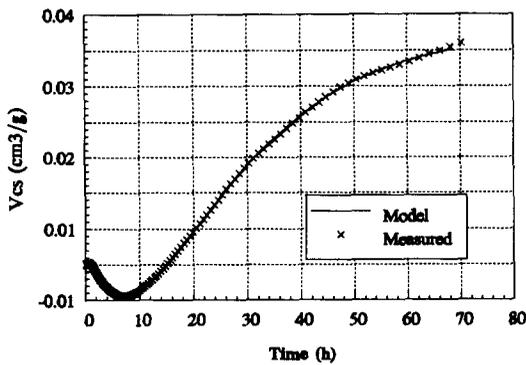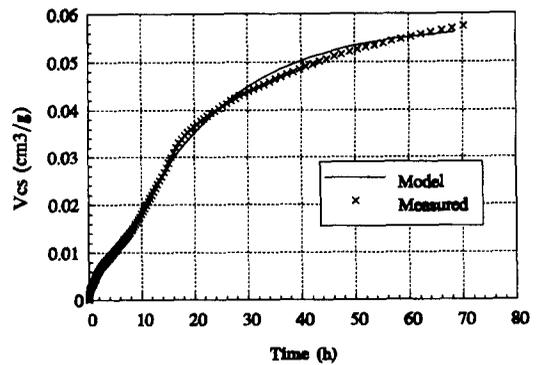| Param.	Type S	Type N	Type L	Type H
$V_{cs,u}$	0.09158	0.032495	0.045035	0.058915
A_1	0.57829	0.07487	0.130405	0.159724
k_{x1}	0.09388	2.0928	1.16515	0.78756
k_{z1}	0.0059099	28.4576	94.1051	15.1402
k_{x2}	0.083837	0.07453	0.038106	0.048637
k_{z2}	0.081433	0.06988	0.23984	0.390977

Fig. 5, Type N Cement Reaction

Fig. 6, Type H Cement Reaction

of the use of mineralisers, alkalis or other minor components. Such secondary processes cannot be taken into account with this TS-model.

Conclusion

Cement hydration is a process which is highly influenced by a twofold phase transition. In the transition zone strong changes of bulk volume take place. They lead to
-   volume swelling during solution and
-   volume shrinking during crystallisation or CSH-gel formation.

Total cement hydration is considered as a consecutive reaction A - X - Z, where X represents the dissociated state in a pore solution . A through solution model was defined, assuming a surface and a core reaction with constant reaction rates between different phase states. This model has been applied to the chemical shrinkage volume of cement reactions and was compared with measured data. Typical early shrinkage volumes of different cement types were fitted sufficiently accurately with this TS-model.

Reference

1   Mc Guiggan P.M., Israelachvili J.N.: *Short range and adhesion forces between surfaces in aqueous electrolyte solutions: interplay of DLVO and hydration forces*, in "Hydration and Setting", Rilem Proceedings 16, Ed. Nonat A., Mutin J.C., E&FN Spon, London, 1992, pp.205-217

2   Le Chatelier H.: *Recherches experimentales sur la constitution des mortiers hydrauliques*, Dunod, Paris, 1904

3   Paulini P.: *A weighing method for cement hydration*, Proc. 9th Int. Congr. Chemistry of Cement, New Delhi, 1992, Vol IV, pp 248-254

4   Paulini P.: *Thermodynamics of hydraulic hardening*, in "Hydration and Setting", Rilem Proceedings 16, Ed. Nonat A., Mutin J.C., E&FN Spon, London, 1992, pp.323-330

5   Landau L.D., Lifschitz E.M.: *Lehrbuch der theoretischen Physik*, Bd. V, Akademie Verlag, Berlin, 1984

6   Kondo R., Ueda S.: *Kinetics of hydration of cements*, Proc. 5th Int. Congr. Chem. Cement, Tokyo, 1968 Vol.II, pp.203-248

7   Bland C.H., Sharp J.H.: *A conduction calorimetric study of glasifier slag-portland cement*

blends, CCR, Vol.21(1991), pp.359-367

8   Laidler K.J., Meiser J.H.: *Physical Chemistry*, Benjamin Cummings Publ., Menlo Park, 1982

9   Gurtin M.E.: *The gradient theory of phase transitions on a finite interval*, in "Phase transformations and material instabilities in solids", Ed. Gurtin M.E., Academic Press, London, 1984, pp.99-112

10   Israelachvili J.N.: *Intermolecular and surface forces*, 2nd Ed., Academic Press, London, 1991

11   Paulini P.: *Reaction mechanisms of concrete admixtures*, CCR, Vol.20(1990), pp.910-918

12   Tirler G.: NLOPT-Manual, Universität Innsbruck, 1992, not published