

Reaction Mechanisms of Concrete Admixtures

P. Paulini
Institut für Baustofflehre und Materialprüfung
Universität Innsbruck, A-6020 Innsbruck, Austria

(Communicated by F.W. Locher)
(Received May 21, 1990)

ABSTRACT

Concrete admixtures influence the kinetic of cement hydration mainly during the dormant period. The dominant influence of admixtures seems to lie in different bound forces between dissociated ions in the pore water solution. Repulsive forces characterize the solvation process while attractive forces dominate during crystallization. These changes of ion bound forces lead twice to volume changes during phase transitions of hydration. Volume changes measured with an immersion weighing setup show clearly the effect of concrete admixtures on cement reaction. Retarder agents produce a volume swelling while accelerators force an immediate shrinkage behaviour. A mechanism as introduced by Le Chatelier involving a solution-crystallization step seems to describe the hydration process most adequately. As long as repulsive forces dominate, a volume swelling occurs and no strength gain can take place. The dormant period is defined by the length of the swelling process. Hardening and strength growth start at the point at which volume shrinkage appears.

Introduction

Concrete admixtures are used to influence concrete hardening mainly in the early phase of hydration. By adding very small amounts of admixtures, properties of fresh concrete can be influenced in a wide range. The hydraulic reaction can be accelerated or retarded using appropriate agents and workability can be improved using superplasticizers. Many mechanisms have been suggested to explain all these effects [1],[2]. There is still no full understanding of hydration mechanisms including all these phenomena at once. In this contribution emphasis shall be put at energy transformations occurring during physico-chemical processes of cement hydration.

Hydration Mechanisms

Cement hydration evolves in a way which includes two phase transitions. In contact with water, metastable solid cement phases dissolve into an aqueous solution. This dissociation leads to an increase of CaO concentration up to 20-40 mmol/l in the first hours of C₃S hydration [3]. Reaching a state of supersaturation in the pore water solution, crystallization into stable and solid CSH-products can follow. In both phase transitions a sudden volume change occurs, resulting from changes in bound forces. Figure 1 shows this phenomenon in a plot according to the Van-der-Waals theory.

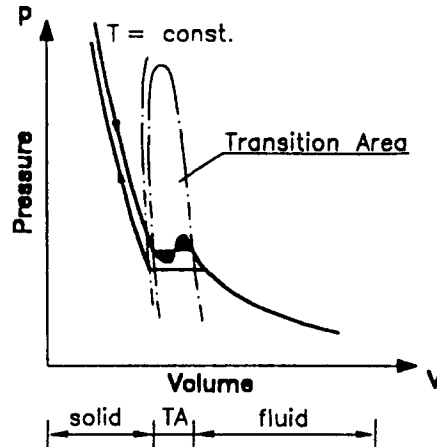


Figure 1
Phase Transition acc.
Van-der-Waals-Theory

During the solvation process a solid-fluid phase transition leads to an increase in volume (swelling). Crystallization involves a volume contraction (shrinkage) which is higher in absolute terms than the previous volume swelling. A shrinkage volume remains after fluid-solid transition and can be measured volumetrically or gravimetrically. Both processes interact simultaneously, but with different velocities. Hydration can be seen as a solvation-crystallization step and was first described by Le Chatelier [4].

An other physico-chemical phenomenon can be noted during hydration, namely an exothermic heat production during the reaction. Figure 2 shows the Ca²⁺ ion concentration and the reaction heat rate of a C₃S hydration according to Vernet [5].

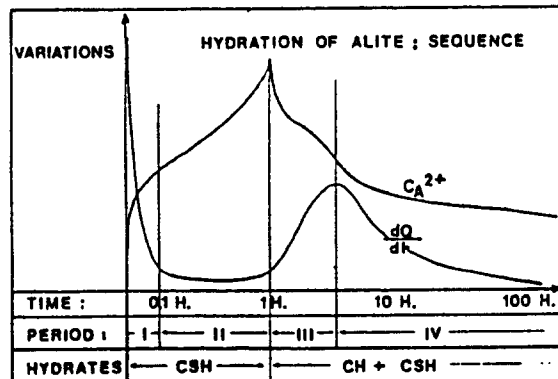


Figure 2
Hydration of C₃S,
acc. [5]

This plot shows some very interesting facts :

- 1) In period I - the initial period of hydration - a high increase of Ca^{2+} ion concentration is accompanied by a severe drop of exothermic heat rate. According to the Arrhenius law, a higher temperature should accelerate the reaction. This is obviously not valid during period I. The solvation process requires an activation energy, which is taken as heat energy from the system, resulting in an endothermic process with decreasing heat rates.
- 2) In period II - the dormant period - the solvation proceeds, still producing a gain of Ca^{2+} concentration. During this period, the exothermic heat rate (if present?) is low.
- 3) Period III - the acceleration period - is characterized by a sudden drop of Ca^{2+} ion concentration. The starting point of period III is defined by a state of supersaturation in the pore water solution. Once nucleation is initiated in the area of supersaturation, the subsequent reaction kinetic is determined by a simultaneous process of solvation - transport - and crystallization. During this period the exothermic heat rate reaches a peak, after which a continuously decreasing reaction rate follows.

Concrete admixtures are of interest within periods I and II. Once the accelerated period is reached, no strong effects of admixtures on hydration kinetics can be expected. The main purpose of concrete admixtures lies therefore in influencing the solvation process of cement hydration.

Thermodynamics of Hydration

Hydraulic reactions are irreversible processes evolving from an energetic state of nonequilibrium towards an equilibrium. During the reaction an energy transformation occurs from a high free energy level towards a lower one. This results in two types of opposite directed energies, a reaction heat and a volume work (bound energy). In order to start the hydration process, metastable crystalline CS-phases need a certain amount of activation energy. The reaction path may be described either by entropy changes or by free energy changes. Figure 3 shows a schematic plot of a reaction path which requires an activation energy G^\ddagger .

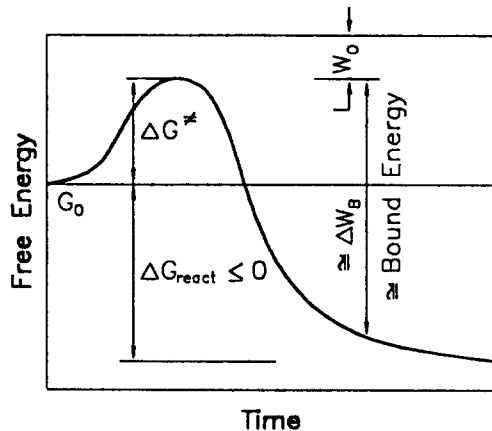


Figure 3 Activated reaction path in free energies

According the 2nd law of thermodynamics, entropy changes must be positive :

$$dS = dS_i + dS_e \geq 0$$

By decomposing entropy production into an inner term dS_i remaining in the system, and a term dS_e , which reacts with the environment, it can be shown [6]:

$$dS_i \geq -dS_e \geq 0$$

Both entropy production terms are counteracting terms, whereby the remaining term dS_i dominates the flux term dS_e .

A chemical reaction can equally be described in terms of free energies. Helmholtz free energy and Gibbs free enthalpy must decline continuously during a chemical reaction.

$$dF = -p \cdot dV - S \cdot dT \leq 0$$

$$dG = V \cdot dp - S \cdot dT \leq 0$$

The chemical potential μ is normally defined as the difference between the starting and end point of Gibbs free enthalpy. We have seen that CS-phases need a certain activation energy G^\ddagger in order to start the reaction. This energy is supplied as heat energy to the reacting agents and is derived from the mix components and the surrounding. The total chemical potential is therefore

$$\mu_{tot} = (G_0 - G_{eq}) + G^\ddagger$$

Hydraulic reactions don't show any global electrical or magnetical effects. We can therefore measure the total energy transformation during hydration using a vector (p, T, V) . We consider an adiabatic state function as shown on Figure 4 .

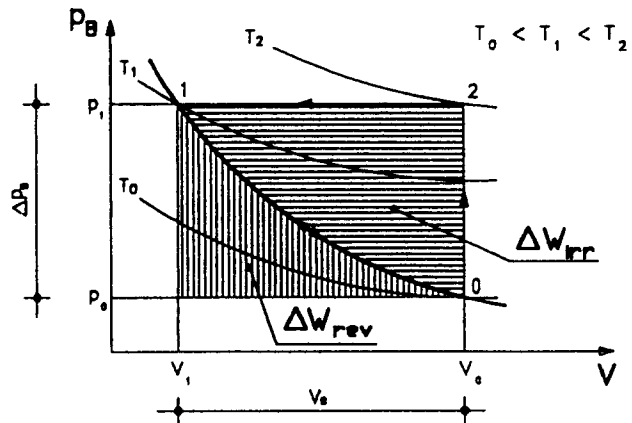


Figure 4
Adiabatic State Function

In this case we understand under the pressure term p_B an inner bound pressure, and not as usual an exterior pressure working on the system. The volume change between original state 0 and end state 1 represents a shrinkage volume V_s resulting from increasing bound stresses.

By following an adiabatic reversible equilibrium process along the path 0-1 one finds, that reversible volume work and reversible heat are opposite energies of an equal absolute amount. This behaviour of counteracting energies is known as the Le Chatelier principle.

$$\Delta W_{rev} = - \int p_B \cdot dV = - \Delta Q_{rev} = S_{eq} (T_1 - T_0)$$

Focusing now on an irreversible process taking place between states 0-2-1 we see, that the material undergoes not only reversible, but also irreversible volume work. The total volume work done on the material is

$$\Delta W = \Delta W_{rev} + \Delta W_{irr} = - \Delta p_B \cdot V_S$$

Structure formation and strength growth of a material depend only on the irreversible part of volume work.

$$\Delta W_{irr} = - \Delta p_B \cdot V_S + \int p_B \cdot dV$$

Simultaneous to the irreversible work, an opposite directed heat of reaction ΔQ_R occurs. By applying the 2nd law it can be shown [7], that for exothermic processes, the reaction heat is smaller in absolute terms than irreversible volume work remaining in the system. The contrary is true for endothermic reactions.

	$T \cdot dS_e \leq 0 \leq T \cdot dS_i$
exothermic reactions	$dQ_R \leq 0 \leq dW_{irr}$
endothermic reactions	$dW_{irr} \leq 0 \leq dQ_R$

That means, that exothermic reactions are accompanied by a volume shrinkage and increasing bound forces. Endothermic reactions show a volume swelling and decreasing bounds. Chemical hardening is therefore always of exothermic nature.

These thermodynamic relations hold even for hydration processes. We have seen that exothermic hydration heat and irreversible volume work are opposite energy terms. They can be regarded as energies, responsible for both terms of counteracting entropy production. Only the part of irreversible volume work remaining in the system can influence a hydraulic stiffening and hardening process. In this sense a main interest has to be put on the irreversible volume work occurring during hydration.

Kinetics of Hydration

Kinetic measurements of chemical reactions can be performed based on the above explanations recording either heat energies or volume work. Until now mostly calorimetric recordings have been used interpreting hydraulic reactions.

In order to describe the irreversible volume work remaining in the material we would have to record both, bound stresses and shrinkage volumes during a reaction. A direct measurement of intermolecular bound stresses is a rather difficult task. It is much easier to record volume changes during a reaction and to calculate bound pressures. This can be done using

$$dp_B = - K \cdot dV_S / V_0$$

where K is the bulk modulus, V_S the shrinkage volume and V_0 the initial volume. We have therefore used a setup based on the immersion weighing method (Fig. 5). In this way volume shrinkages during cement reaction can be easily and accurately recorded [8].

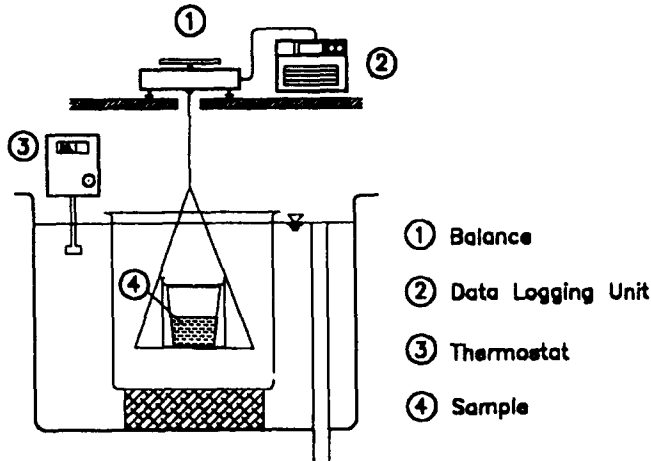


Figure 5 Immersion Weighing Setup

Reaction rates recorded by volume shrinkage show the same characteristics as recorded by calorimetric methods. The total shrinkage volume for cement hydration depends on the fractions of the hydraulic phases and lies in the range of 0.06-0.07 cm^3/g cement. All the following recordings have been taken from cement paste reactions with a w/c-ratio of 0.40, and if not otherwise mentioned with a isothermal temperature of 20 $^{\circ}\text{C}$.

The early phase of cement hydration can present a complete different behaviour as known from calorimetric records. Early volume changes of cement hydration can produce an increase in volume (swelling process) which turns into a shrinkage process after the dormant period. Figure 6 shows the wide range of early cement reactions without use of any admixture.

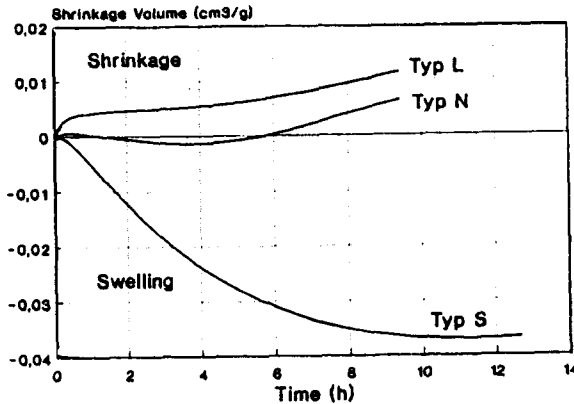


Figure 6 Range of early Cement Reactions

Type L cements have a low initial reaction and were found by finer ground cement types. Type N cements show no clear initial reaction and were found in normal portland cements and sulphate resistant cements. Swelling processes of type S cements were observed especially in slag cements, old cements and fresh ground cements.

In order to prove that the time during which swelling occurs can be defined as dormant period, accelerated cement reactions with different isothermal temperatures are represented in Figure 7. Leaving out the swelling phase, Figure 7 shows

only volume contractions, starting at the time where chemical shrinkage appears. We note the well known behaviour of temperature-accelerated cement reactions which have shorter dormant periods, react faster at the beginning, and reach lower degrees of hydration at the end.

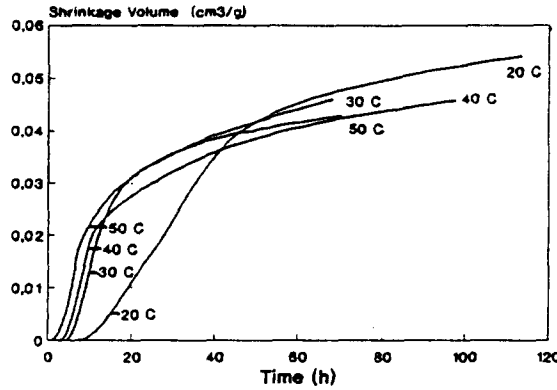


Figure 7 Isothermal Cement Reactions

The following plots give an insight into the working mechanisms of concrete admixtures. Adding accelerator agents leads to an increase of early volume shrinkage. This is illustrated in Figure 8 using 5% accelerators of different brands and a rather fast reacting CE II S cement. Figure 9 shows the same result with a slow-reacting sulphate-resistant portland cement. Both, dry and fluid agents have been used.

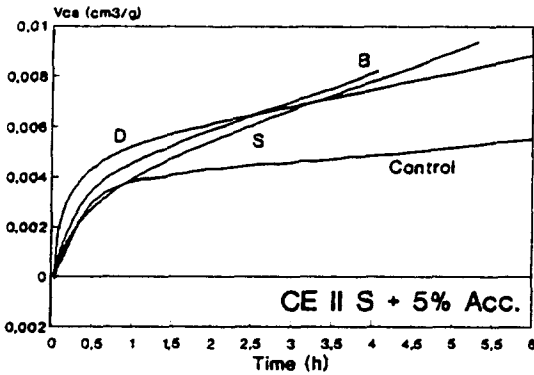


Figure 8 Cement Reaction w. 5% acc. Control = CE II S Cement

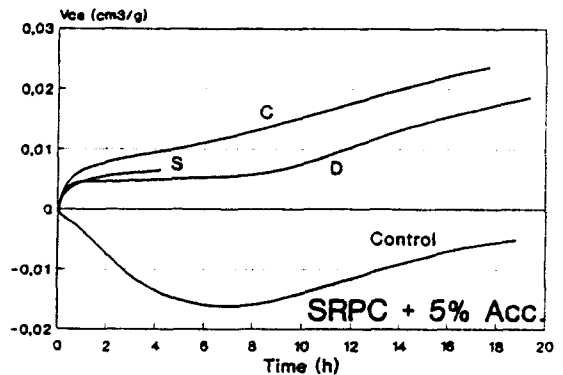


Figure 9 Cement reaction w. 5% acc. Control = SRPC Cement

On the other hand, the use of retarders leads to an increase of volume swelling. Figure 10 shows this, using 0.4% retarder with an ordinary CE I cement and a CE II S slag cement. Increasing the dosage of retarder leads to a higher propagation of swelling volumes. This is shown in Figure 11 with an ordinary PC 35F cement using a retarder based on hydroxycarboxilic acid.

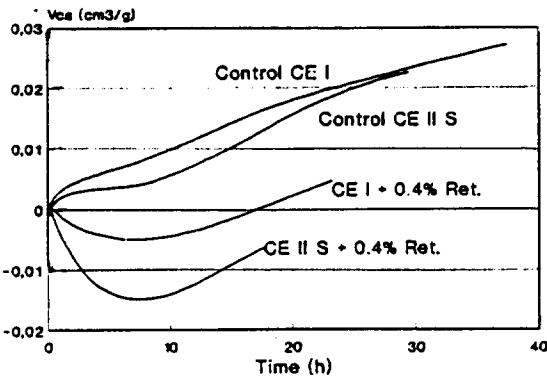


Figure 10 Cement Reaction with 0.4% Retarder

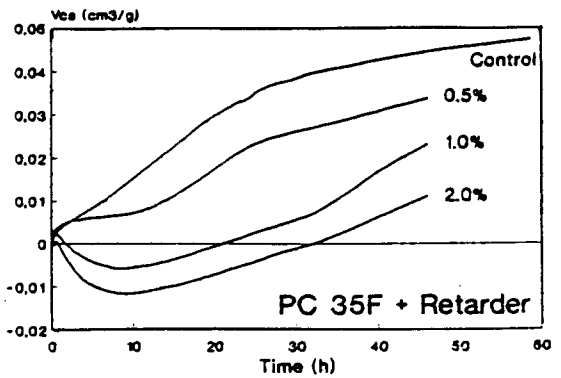


Figure 11 Cement Reaction with incr. Retarder Dosage

Portland cement consists of metastable crystal modifications which are influenced by many factors, like burning-cooling processes, chemical composition, type of grinding and state of prehydration. Metastable modifications are to be found in a frozen state of high free energy and tend to reorder themselves into stable crystals even in solid state reactions. The influence of a concrete admixture on the cement reaction can vary widely. The specific action of expected admixture effects should therefore be proved in every different cement. An example is given in the two following figures.

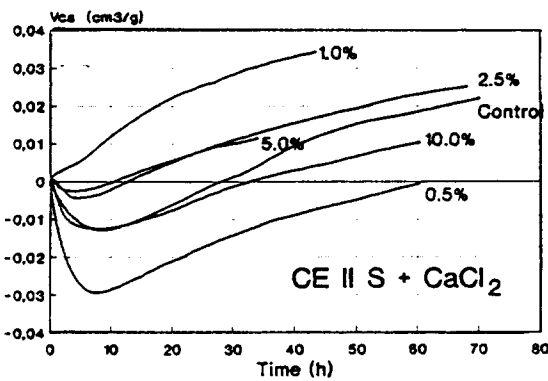


Figure 12 CaCl₂ influence on PC II S slag cement

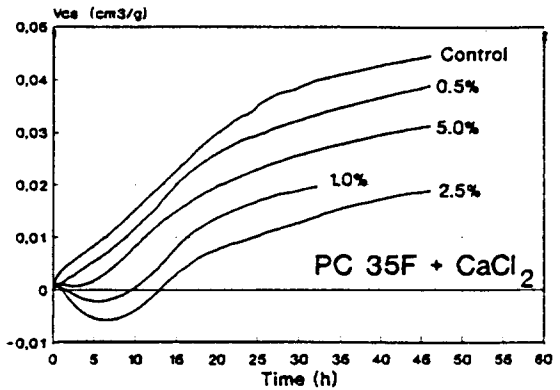


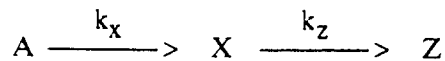
Figure 13 CaCl₂ influence on PC 35F reaction

Calcium chlorides are known as strong accelerators. Figure 12 shows the influence of different dosages on the reaction of a slag cement. A low dosage of 0.5% leads to a stronger solvation and swelling process compared to the control reaction. Using 1% leads to an immediate initial reaction while higher percentages show again a short swelling period.

Picture 13 shows the reaction influence of CaCl₂ on a fast reacting PC 35F. Increasing the dosage up to 2.5% leads to declining shrinkage volumes and to a swelling period. A dosage of 5% shows again a faster reaction.

Conclusion

Kinetic reactions recorded by the immersion weighing method give a clear insight in the working mechanisms of cement hydration. They are determined by a double phase transition of the solvation-crystallisation step of cement hydration. During solvation a solid-fluid transition takes place in which repulsive forces are released and ions from solid state crystals are converted to an aqueous solution. This process leads to lower ion bounds and higher distances between ions resulting in a volume swelling. After reaching a state of supersaturation in the pore water solution the crystallization step to CSH-phases, including a fluid-solid transition, can follow. Here attractive ion forces dominate the process - ion distances become smaller - and an total shrinkage volume of 0,06-0,07 cm³/g cement remains after complete hydration. This Le Chatelier Through Solution model can be described by a consecutive reaction



with constant velocities k_x and k_z . Such a model, applied to cement reactions, was presented in [7].

The addition of concrete admixtures influence these mechanisms in a clear way. The usage of retarder agents increases repulsive forces of the solvation process and leads to high swelling volumes in the first hours after mixing. As long as repulsive forces prevail over attractive forces of the crystallization process, no strength gain can occur. The dormant period is defined by the length of the swelling period. Superplasticizers accelerate the solution process and lead as well to swelling volumes during the early reaction. The following CSH-crystallization runs faster because of higher CS-ion concentrations in the pore water solution. This is a well known behaviour of many superplasticizing agents. Accelerators show an immediate shrinkage volume just after mixing. This can be the result of a higher chemical potential, so that just a low activation energy is needed in order to start the reaction. An other possibility is to increase the number of crystalline nuclei using stone or quartz powders. All these mechanisms can be shown with a sensitive volumetric measurement setup.

References

- 1 Ramachandran V.S., Concrete Admixtures Handbook, Noyes Publ., New Jersey, 1984
- 2 Rixom M.R., Mailvaganam N.P., Chemical Admixtures for Concrete, 2nd ed., Spon LTD., London, 1986
- 3 RILEM Comm. 68-MMH, Task Group 3, The Hydration of Tricalciumsilicate, Materials and Structures, Vol.17, (1984), pp.457-468
- 4 Le Chatelier H., Recherches experimentales sur la constitution des mortiers hydrauliques, These, Paris, 1887
- 5 Vernet C., Flux thermique et cinetique d'hydratation, Proc.8th.Int. Congr. Chemistry of Cement, Rio de Janeiro, 1986, Vol.III, pp.64-69
- 6 Glansdorff P., Prigogine I., Thermodynamic Theory of Structure, Stability and Fluctuations, Wiley Interscience, London, 1971
- 7 Paulini P., Kinetik der Zementhydratation und ihr Einfluss auf die Festigkeit von Beton im jungen Alter, Dissertation, Universität Innsbruck, 1988
- 8 Paulini P., Kinetic reaction measurements in cement hydration with the immersion weighing method, Zement-Kalk-Gips International, 41.Jg, 10, (1988), pp.525-531, 12,(1988), pp.297-300