

DETERMINATION OF Ca^{2+} IONS AT EARLY STAGE OF HYDRATING CEMENT PASTE

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Novel procedure to determine instantaneous concentrations of Ca^{2+} ions in hydrating cement paste is suggested. Using EDTA and following indirect Ca^{2+} determination titrated with Mg^{2+} ions in Schwarzenbach buffer medium allows to determine calcium ion concentrations for different times.

INTRODUCTION

One of the frequently used materials in practice are cementitious-based systems with broad applications spanned from stomatology to the civil engineering. Although the properties of such systems (in particular, mechanical) are intensively studied for many decades, the problems connected with the processes occurring at very first stage of their setting are still open and unanswered.

Indeed, when commonly used Portland cement is mixed with water, the intensive exothermic chemical reaction starts, followed by massive release of hydration heat.

Chemically, tricalcium (resp. minor dicalcium) silicates react with water to produce calcium silicate hydrates and calcium hydroxide (so-called portlandite). Further setting of this mixture is then associated with hydration of the two calcium-based silicate constituents. Consequently, one of the essential entities strongly influencing this process is a time-dependent concentration of free calcium ions. Ca^{2+} ions then play the role of building units (monomers) from which the newly-forming solid phase is successively built up: primarily by nucleation and then by subsequent growth of nucleated solid clusters.

Various chemical methods have been proposed for extracting free calcium hydroxide, $\text{Ca}(\text{OH})_2$, in hydrating cement paste and different solvents for dissolving free CH in hydrating cement paste, which can be later determine by titrating of the resulting solution with a suitable acid and indicator. Frequently applied procedure that uses ethyl acetoacetate and isobutyl alcohol to

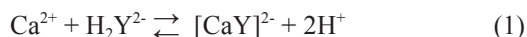
dissolve free C or CH is called Franke method [1,2]. This method is based on extraction of cement mixture with ethyl acetoacetate and isobutyl alcohol, then refluxing the solution on a hot plate (for one hour). The mixture is cooled down and filtered (with suction pump using dense filter paper). Then wash the flask, residue, and filter paper with isobutyl alcohol CH, dissolved in the filtrated solution, is titrated with 0.1M hydrochloric acid. Singh et al. stopped hydration at different time intervals with isopropyl alcohol and ether [3]. The solution chemistry of Portland cement pastes was studied [4] within context of concentrations of calcium and silicon in the aqueous phase during early stages of hydration. Apparatus for mixing and filtering of cement in nitrogen environment (to prevent carbonation) was used and followed by titration against standard EDTA solution using glyoxal bis(2-hydroxyanil) indicator. Ca^{2+} ions concentrations in the liquid phase without/with malic acid as retarder were extracted by Franke method [2] from the hydrating cement paste and determined by titrating against 0.01 M EDTA solution using Eriochrome Black T indicator [5]. On the other hand, Franke and Sisomphon [6] proposed a new extraction of CH taking into account the stability of cement hydration phases at various pH conditions, because hydrated cement phases are stable in specific defined ranges of alkalinity environment. The phases are subjected to decomposition when pH of the test solution is lower than this stability level. At first, portlandite, CH is destabilized, and further the calcium silicate hydrates C-S-H, calcium aluminate hydrates C-A-H, and the others are dissolved at lower pH values. "The target of the testing is to extract CH from the cement paste into the solvent without deteriorating other hydrated phases" [6].

We suggest a novel procedure, firstly applied in this context, allowing to determine Ca^{2+} in hydrating cement paste. The method is based on addition in excess of EDTA to mixture of cement with water at given w/c ratios followed by indirect Ca^{2+} titration with Mg^{2+} ions in Schwarzenbach buffer medium with Eriochrome black T as indicator at different times (4, 9, 12, 16, 24, 50, 70, 120 and 150 minutes).

As known, anion H_2Y^{2-} forms stable complex compounds, chelates with certain bi-, tri- and tetravalent metals (Ca, Mg, Cd, Cu, Pb, Bi, Ni, Zn) [7,8]. Formation and stability of chelates are strongly influenced by pH-value of solution. While the chelates of tri- and tetravalent metals are stable in acid medium, in contrast to the chelates of bivalent metals, which are stable in alkali, resp. weak acid medium. Bi- and trivalent cations exhibit, in addition, a relatively high strength and solubility of chelates in water. Above mentioned facts are represented in Figure 1, where the dependency of conditional formation constants K' on pH-value for some cations is shown.

Since the reaction rate constant of reaction of Ca^{2+} with $\text{Na}_2\text{H}_2\text{Y}$ (1) is of order $\sim 10^8 \text{ s}^{-1}$ [9], the process occurs practically immediately and quantitatively. It has been stressed out, however, that this reaction takes place in alkali medium.

As follows from Figure 1, chelate Ca^{2+} with EDTA is stable just in this pH interval.



Proposed novel procedure of Ca^{2+} ions determination is simple and reproducible. Due to very high level of Ca^{2+} ions concentrations (about 300 mg Ca^{2+} ions per 1g hydrated cement mixture), the application of titrimetric method for cement paste seems to be suitable.

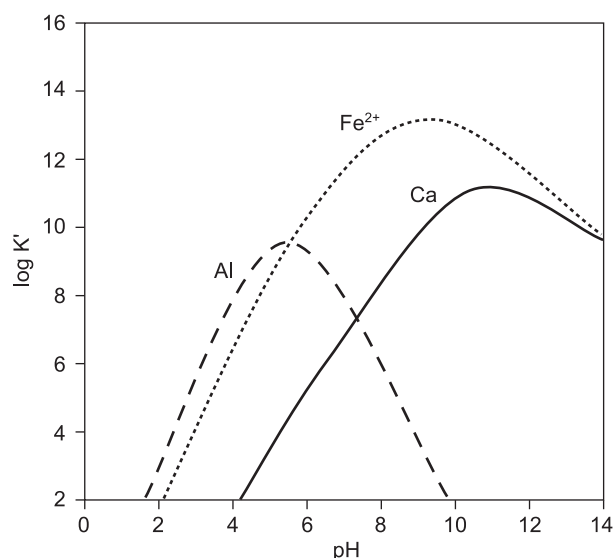


Figure 1. Dependency of conditional formation constants K' on pH-value for some cations (schematically according to [8]).

As known, EDTA, ($\text{Na}_2\text{H}_2\text{Y}$) belongs to strong calcium binding agent, releasing a flush of silicon into solution within the first few minutes of hydration [10].

Since our proposed method allows to determine Ca^{2+} ions concentration at a very beginning of the setting process, let us to summarize shortly the main features of this complex process. The initial state of cement setting is divided into two inductive periods occurring within about 10-15 minutes. During this stage, the cement grains are wetted and also first reactions of clinker minerals with water start [11]. Basically, this period may be characterized by relatively massive hydration heat release, resp. by dissolution of calcium aluminate phases followed by portlandite CH and ettringite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ formations (see Figure 2, [12]).

During second part of inductive period, the release of hydration heat decreases and the viscosity of the system markedly increases. At this stage, the process of setting starts: amount of calcium silicates is lowered and the clusters of a new, solid phases - CH, calcium silicate hydrates are formed.

Moreover, concentration of Ca^{2+} ions reaches the supersaturated values and the formation of ettringite and other new products still continues. This inductive period ends during 1-2 hours from the moment, at which the cement was mixed with water.

When tricalcium silicate (C_3S) is suspended in water, it dissolves in agreement and produces Ca^{2+} , (OH^-) and silicate ions [13]. The solution reaches few minute later, the maximum of supersaturation with respect to C-S-H which precipitates. As the Ca^{2+} ions produced by dissolution are not consumed all by formation of C-S-H , calcium hydroxide concentration increases and $\text{Ca}(\text{OH})_2$ precipitation occurs when the maximum supersaturation is reached (see Figure 3).

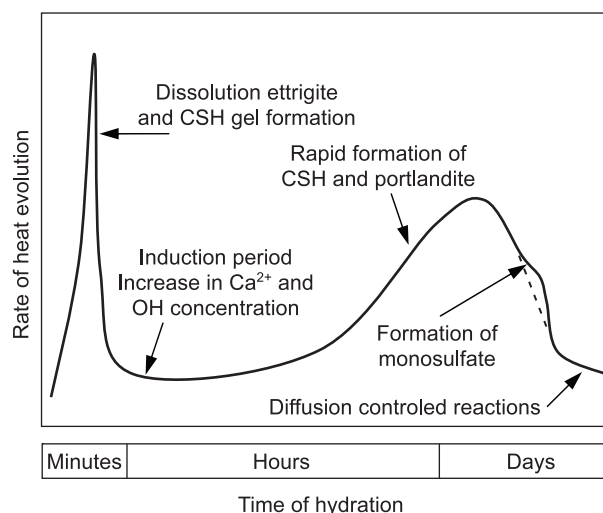
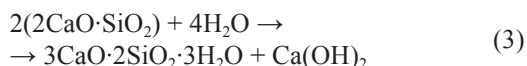
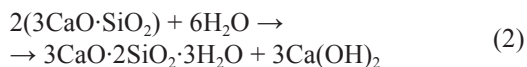
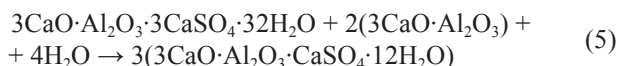
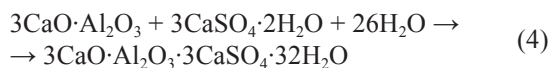


Figure 2. Sketch of Portland cement hydration development [12].

Due to reaction of calcium silicate C_3S , C_2S with water, the calcium silicate hydrates C-S-H gel and crystalline calcium hydroxide as the products are formed [14]:



Tricalcium aluminate, C_3A , reacts with the water and in presence of gypsum, $CaSO_4 \cdot 2H_2O$ resulting in hexagonal-like prisms of ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (see (4)), followed by their transformation into pseudo-hexagonal plates of monosulfate, $CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 2H_2O$ (see, (5)).



One of the applicable methods how to estimate the amount of Ca^{2+} ions in the chemically-reacting system [cement + water] is based on application of a certain type of retarding admixture. In generally, the retarding admixtures act in two possible ways [15,16]:

- 1) They react with hydration products to form partially soluble compounds on the cement grains surfaces. This layer inhibits the access of water molecules

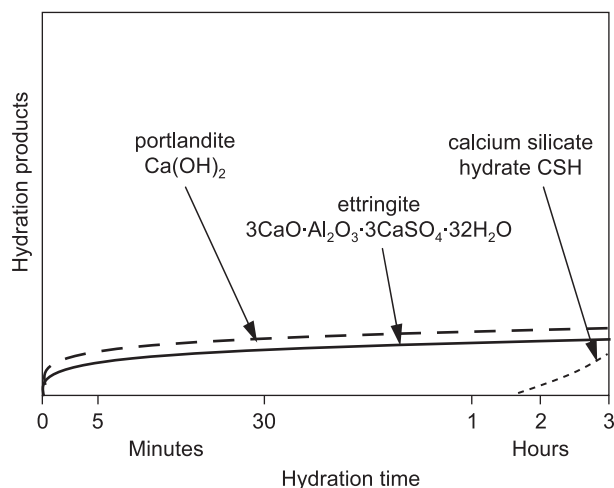


Figure 3. Principal sketch of first products of hydration at early stage of evolution [11].

Table 1. Oxide composition of CEM I 42.5 R.

Oxide	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	MnO
Comp. (wt.%)	63.77	20.51	4.74	3.3	1.05	3.07	0.15	0.95	0.09

to hydration nucleus of the cement grain and, consequently the transition of ions from surface of hydrated layer to solution is retarded.

- 2) Retarding admixtures may also act as protective colloid, inhibiting the gel swelling and eliminating capillary forces. However, as the cement hydration proceeds, the formation of solid state structure is excluded at advanced state of evolution. Moreover, the formation of crystallization seeds from supersaturated solution is also blocked. It has to be pointed out, however, that the retarding effect depends on the amount of admixture.

Among retarding substances EDTA-belonging to carboxylic acids/carboxylates and borates [19] has been chosen for our purposes. It is found to be very effective in altering the nucleation and subsequent growth of calcium minerals. EDTA may bind to calcium ions on the crystal surfaces to prevent further heterogeneous nucleation and further growth of newly-formed clusters of portlandite.

EXPERIMENTAL

Materials

Ordinary Portland cement (OPC) CEM I 42,5 R, Mokrá, Czech Republic was used for hydration studies. The oxide and mineralogical composition of the cement are given in Tables 1 and 2.

Chemicals

All chemical agents applied are of purity p.a. 0.05 M EDTA, disodium ethylenediaminetetraacetate, 0.05 M MgSO₄. Schwarzenbach buffer, Eriochrome black T.

Methods

To prepare hydrated samples, 40g cement was inserted in tall-form beaker and given amount of distilled water was added (water to cement (w/c) ratios were chosen to be 0.40, 0.45, 0.50, and 0.60). Before

Table 2. Phase composition of CEM I 42.5 R (Bogue).

Mineral	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₂ F	SO ₃ -bound CaO
Comp. (wt.%)	58.34	14.80	6.81	10.31	0	2.149

this operation, cement and distilled water have been kept in thermostat at 25°C. Cement with water have been thoroughly mixed by hand for 1 min and then the beaker with cement mixture was kept again in thermostat at 25°C.

At fixed times 4, 10, 12, 16, 20, 24, 50, 70, 90, 120 and 150 minutes the cement mixture in thermostat has been removed from the beaker and hydration was immediately stopped by adding of a very strong retardant 0,05 M EDTA, which is excess in solution. Filtering of mixture of cement paste with EDTA was realized through a fine filter paper and instantaneous Ca^{2+} ion concentrations in the filtrate were determined by indirect titration together with Mg^{2+} ions in Schwarzenbach buffer medium with Eriochrome black T (as the indicator) allows to obtain calcium ion concentrations for different times.

RESULTS AND DISCUSSION

Concentrations of Ca^{2+} ions have been measured for various water to cement ratios ($w/c = 0.35; 0.40; 0.45; 0.50; 0.60$) as a functions of time. It may be readily seen

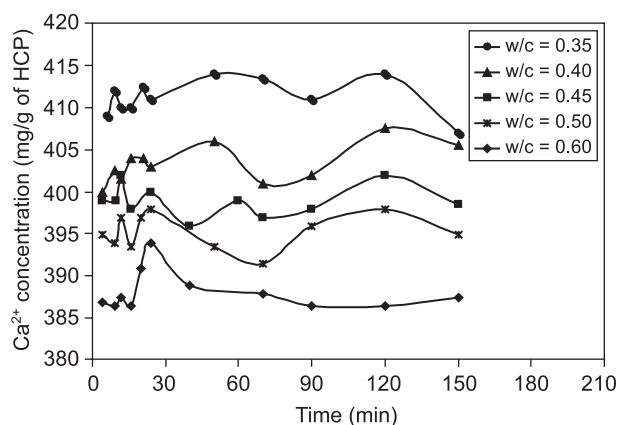


Figure 4. Concentration of Ca^{2+} (in mg) in HCP versus time related to total mass of HCP (at temperature 25°C).

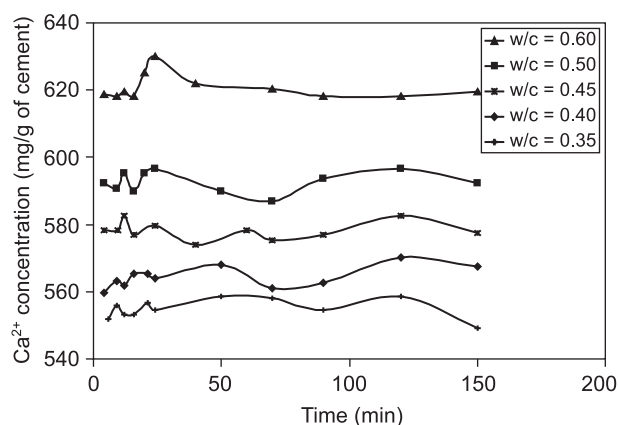


Figure 5. Concentration of Ca^{2+} ions (in mg) in HCP versus time weighted to mass of cement. (temperature 25°C).

that with increasing water content, the concentration of Ca^{2+} ions decreases with time (see Figures 4, 5). In Figure 4, the amount of calcium ions (in mg) is related to the total mass of hydrating cement paste (HCP), while the concentration of Ca^{2+} in Figure 5 is expressed in terms of amount of cement. Standard deviations indicating the accuracy, resp. the interval of reproducibility of our results, are represented in Figure 6 (for $w/c = 0.5$). Situation is the same also for other w/c ration curves as well.

Furthermore, each of these curves consists, at least, of two peaks at a very beginning of hydration process. Increasing of Ca^{2+} ions concentration for short time interval is caused by rapid exothermic chemical reactions for. This fact is demonstrated in Figure 7, representing initial stage in hydration process in HCP measured by SETARAM C 80 calorimeter.

Our results (for w/c ratio 0.5) are in good agreement with those obtained with help of completely different method – Franke extraction [3,5].

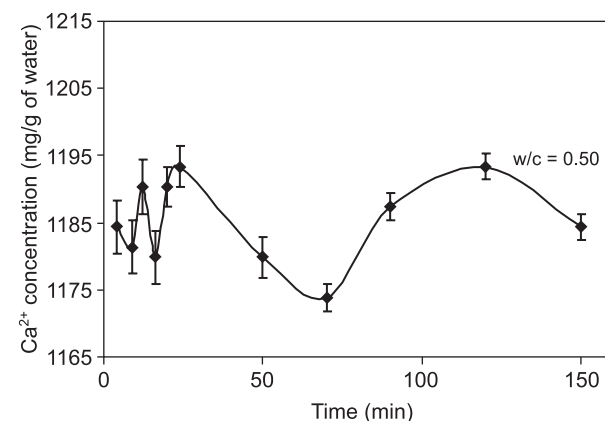


Figure 6. Error bars for concentration of Ca^{2+} ions (in mg) in HCP versus time weighted to mass of water ($w/c = 0.5$, temperature 25°C).

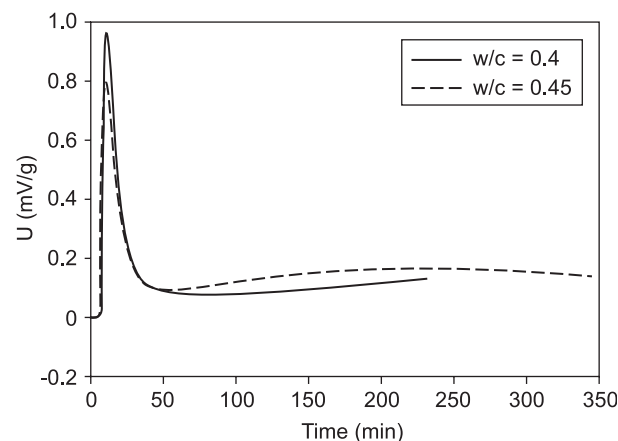


Figure 7. Initial stage of hydration process in HCP of Portland cement, Mokrá, ($w/c = 0.40; 0.45$) measured by SETARAM C 80 calorimeter.

Then the concentration of ions decreases: within context of the standard models [17,18] this behaviour is caused by creation of some protective layers. Due to osmotic pressure, the membranes are destroyed followed by releasing of further Ca^{2+} ions. This mechanism corresponds to further increasing of concentration of Ca^{2+} ions (see Figures 4 and 5). This monotonic dependence then slowly decreases with increasing time. Origin of this behaviour can be related to a very early stage of phase transformation (solidification) – nucleation. Indeed, relatively freely moving Ca^{2+} ions can be understood to be a monomers, i.e., building units for the formation of clusters of a new, solid phase - $\text{Ca}(\text{OH})_2$, portlandite, hexagonal plate-like crystals. In this sense, results of our analysis can be served to be input parameters for more general, nucleation model, in which the concentration of Ca^{2+} ions plays a role of time-dependent concentration of monomers.

CONCLUSIONS

We present a novel procedure allowing to determine concentration of dissolved calcium in HCP for different water to cement ratios (w/c) and at various times. (Temperature is held at 25°C). This analytical method is based on application of strong retarder EDTA solution whose addition to hydrating HCP immediately stops these reactions. By further indirect determination of Ca^{2+} titrated with Mg^{2+} ions in special buffer medium then we obtain resulting dependency of Ca^{2+} concentration on time. Our procedure is relatively simple, effective and well reproducible. Resulting curves-i.e., nontrivial temporal dependencies of calcium ions at different temperatures and for various w/c ratios-serve as important input parameters for more general, nonstationary nucleation model in closed systems.

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