MODELING OF SOLID FRACTION EVOLUTION DURING CALCIUM ALUMINATE CEMENT HYDRATION

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ABSTRACT

Calcium aluminate cement (CAC) is a special cement advantageously employed with high performance in many specific applications. Knowledge of the hydration reactions and microstructure evolution is important from the viewpoint of safe usage, good durability and functionality. The hydration of CAC is highly temperature dependent, yielding different hydration products that alter material properties. During the setting and hardening, microstructure of material and amounts of certain phases are changing. The solid fraction comprises the formed hydration products and the fraction of non-reacted cement.
This paper presents a study of the solid volume evolution during early age hydration of CAC. The hydration of specimens of commercial iron-rich CAC (*Istra 40*) has been investigated by thermo-gravimetric analysis, density measurements and powder X-ray diffraction (XRD).
Mathematical model of the solid volume evolution based on the main reaction scheme of the principal mineral hydration is presented. The model predictions are compared to the experimental results.

1 INTRODUCTION

Calcium aluminate cement (CAC) is a versatile special cement that is used in high performance applications [Ben02, Man01, Man90, Scr99, Geo83] such as those requiring: resistance to chemical attack, high early strength, refractory, resistance to abrasion, and/or low ambient temperature placement. Setting and hardening of CAC is primarily due to the hydration of CA (cement notation: C=CaO, A=Al_2O_3, F=Fe_2O_3, S=SiO_2, H=H_2O), but other compounds also participate in the hardening process especially in long term strength development [Ben02] and at higher temperatures of hydration. The hydration of CAC is highly temperature dependent [Ben02, Man01, Man90], yielding following main hydration products at approximate temperature ranges:

$$\mathrm{CA} + 10\,\mathrm{H} \rightarrow \mathrm{CAH_{10}} \qquad T < 20\ ^\circ\mathrm{C} \qquad (1.1)$$

$$2\,\mathrm{CA} + 11\,\mathrm{H} \rightarrow \mathrm{C_2AH_8} + \mathrm{AH_3} \qquad T \sim 30\ ^\circ\mathrm{C} \qquad (1.2)$$

$$3\,\mathrm{CA} + 12\,\mathrm{H} \rightarrow \mathrm{C_3AH_6} + 2\,\mathrm{AH_3} \qquad T > 55\ ^\circ\mathrm{C} \qquad (1.3)$$

At ambient temperature metastable hydrates, CAH_{10} and C_2AH_8 convert to the more stable C_3AH_6 and AH_3 with consequent material porosity and permeability increase and loss of strength. The conversion is accelerated by temperature and moisture availability. George [Geo90] discussed the criticality of the water to cement ratio to long-term performance of CAC concrete. He concluded that a very simple straightforward model based on the stoichiometric water content required for complete hydration, allows the impact of both water to cement ratio and the conversion phenomenon on the porosity to be reasonably predicted. By relating porosity to strength [Mat03] and durability of CAC concrete, predictions provided a sound basis for safe usage and explanation of the well documented [Man01] construction failures since the 1970's.

In literature there is still not yet an adequate cement paste model for CAC hydration analog to Powers' model for PC hydration [Bro04]. Furthermore, there are still no systematic experimental data showing the evolution of the volume of the solid during the hydration of CAC. In recent attempt [Ukr08a] the main reaction scheme of the CA hydration was applied to predict the compositional evolution during early age hydration of iron-rich CAC paste. The model was validated on hydrated pastes at T = 5 – 20 °C by comparison of the predicted degree of the reacted CA based on measured chemically bound water content (see further eq. (1.7)) with the values obtained by the quantitative XRD analysis. Systematic measurement data on evolution of the chemical shrinkage, solid content and cement minerals are still needed to additionally validate the proposed model.

This paper is concerned with the solid volume evolution during early age of CAC hydration process. The hydration of specimens of commercial iron-rich CAC *Istra 40* (manufactured by: *Istra Cement*, Croatia) with different water to cement mass ratio (H/CAC = 0.4 – 1.0) where investigated by thermo-gravimetric analysis, density measurements and powder X-ray diffraction (XRD).

1.1 Mass balance model of CAC early age hydration

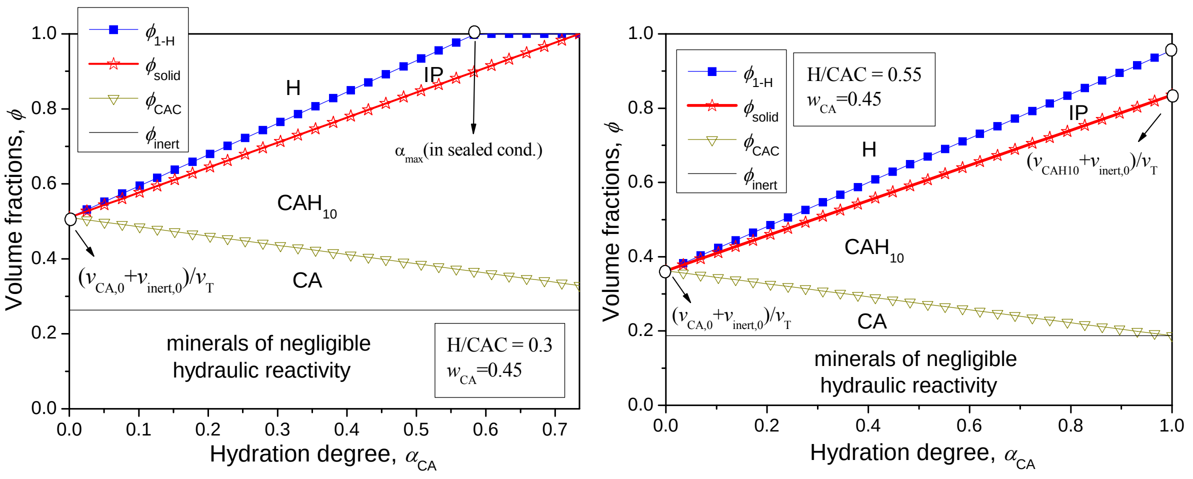
In the case of CAC, the most hydraulic phases are CA and $C_{12}A_7$, while C_2AS, C_2S and ferrite phase (C_4AF) are considered to have no significant reactivity at early ages (first 48 hours) below 20 °C [Ben02, Scr98]. However, although C_4AF reactivity has usually been disregarded in studies of CAC hydration, because of its high quantities (up to 30 %) one should be careful in considering its contribution. The main effects of $C_{12}A_7$ are on the dissolution rate, which is accelerated, and on the occurrence of the small quantity of C_2AH_8. Moreover, $C_{12}A_7$ is present in much smaller quantities (~2-5%) than CA (40-70 %) and gives similar products as CA hydration, so its hydration, in first approximation can be treated together with CA hydration (CA quantity increased by $C_{12}A_7$). As typically 70% - 90% of the heat evolved is liberated in the first 24 h [Geo83, Ukr08b, Ukr10], simplified thermodynamic (non-kinetic) modeling of early age hydration process (below 20 °C) based only on CA hydraulicity **eq.** (1.1) seems reasonable.

1.2 The solid volume evolution model

During individual hydration reactions, volume fractions of the non-reacted cement and the free water components decrease, while the fractions of the formed hydration products and the internal porosity, IP increase (Fig. 1.1.). In case of sealed conditions the internal porosity is filled with air and water vapour, while in water saturated conditions additional environmental water enters into cement paste system. Considering only one (independent) hydration reaction, in this paper eq. (1.1), (1.2) or (1.3), a general form for the phases i volume fraction evolution during hydration is linear:

$$\phi_i(\alpha) = A_i + B_i\,\alpha \tag{1.4}$$

where intercept A_i and slope B_i can be deduced from Fig. 1.1.



(a) (b)

Fig. 1.1. The CAC paste model [Ukr08a, Ukr09] shown on examples of volume fractions evolution during hydration at: **(a)** H/CAC = 0.3 and w_{CA}= 0.45; and **(b)** H/CAC = 0.55 and w_{CA} = 0.45, where: H/CAC is water to cement mass ratio, w_{CA} is initial CA (and $C_{12}A_7$) mineral mass fraction in CAC; $v_{i,0}$ is initial volume of i-th phase per mass of CAC: (H - free water, T - total paste volume, inert - minerals of negligible hydraulic reactivity) [cm^3/g of CAC]; and IP is internal porosity (chemical shrinkage).

The deduction of the solid volume model is based on 1 g of CAC. From the characteristic points (start and end of reaction), marked with ^{O} in Fig. 1.1., a general form of slope and intercept of the model in eq. (1.4) are deduced in [Ukr08a]. By inference to Fig. 1.1.(b), the increase of the volume of solids [cm^3/g of CAC] during hydration is:

$$v_{\text{solid}} = v_{\text{CA,0}} + v_{\text{inert,0}} + \left(v_{\text{hydrates}} - v_{\text{CA,0}} \right) \alpha_{\text{CA}} \tag{1.5}$$

where the initial volumes (at α_{CA} = 0) of the components $v_{CA,0}$ and $v_{inert,0}$ are for mineral CA (increased by the amount of $C_{12}A_7$) and minerals of negligible hydraulic reactivity, respectively. The volume of h hydration products (in eq. (1.1) only CAH_{10}) at complete hydration (α_{CA}=1) is:

$$v_{\text{hydrates}} = \sum_h \left(\frac{M_h \, \upsilon_h \, w_{\text{CA}}}{M_{\text{CA}} \, \upsilon_{\text{CA}} \, \rho_h} \right) \tag{1.6}$$

where υ and M are stoichiometric coefficient and molar masses of the reaction components, respectively, and ρ_h is the density of hydration product [Scr98, Lea76], Table 1.1.

The degree of hydration can be formulated on the basis of actual bond water and possible stoichiometric bound water [Ukr08a]:

$$\alpha_{bw} = \frac{bw}{\left(\text{H/CAC}\right)_{\text{tot}}} \tag{1.7}$$

where $(H/CAC)_{tot}$ is the stoichiometric water to cement mass ratio for complete hydration of active mineral components with water (H):

$$(\text{H/CAC})_{\text{tot}} = (\text{H/CA})_{tot} \, w_{\text{CA}}; \qquad (\text{H/CA})_{tot} = \frac{M_{\text{H}} \, \upsilon_{\text{H}}}{M_{\text{CA}} \, \upsilon_{\text{CA}}} \tag{1.8}$$

Table 1.1. Densities [Scr98, Lea76] and molar masses of the minerals.

Mineral	ρ / g cm^{-3}	M / g mol^{-1}
CA	2.98	158.1
$C_{12}A_7$	2.85	1387
C_4AF	3.77	485.9
CAH_{10}	1.72	338.1
C_2AH_8	1.96	358.2
C_3AH_6	2.52	378.3
AH_3	2.44	156.0

It should be noted that this calculated degree of hydration is based on the simplified stoichiometric model of the early age hydration reactions; in this paper eqs. (1.1)-(1.3) by assuming that the only reactive minerals are CA and $C_{12}A_7$ (CA quantity increased by $C_{12}A_7$, see further in **1.1** Mass balance model of CAC early age hydration).

By combining (1.7), (1.6) and (1.5), the solid volume evolution per 1 gram of CAC (v_i, cm^3/g CAC) versus chemically bound water, *bw* (g/g of CAC) can be expressed as:

$$v_{solid} = v_{\mathrm{CAC},0} + \frac{\sum\left(\frac{M_h \upsilon_h}{M_{\mathrm{CA}} \upsilon_{\mathrm{CA}} \rho_h}\right) - v_{\mathrm{CA}}}{(\mathrm{H/CA})_{\mathrm{tot}}} bw \tag{1.9}$$

In the model equation (1.9) the intercept (v_{CAC}) changes only slightly depending on the mineralogical composition of CAC, while the slope is a constant (i.e. non-dependant on the amount of active minerals in CAC). Differently, in model eq. (1.5) the principal variable (beside the degree of hydration) is the amount of the active minerals (in this paper, w_{CA}).

Depending on the water to cement mass ratio, H/CAC and amount of reactive minerals the reaction of hydration can be stopped by an insufficiency of free water (Fig. 1.1.(a)) or by a run out of reactive cement minerals (Fig. 1.1.(b)). Another possibility to terminate the hydration, in the case of water saturated conditions, is insufficient free space for growth of reaction products. Thus the model eqs. (1.9) and (1.5) are valid for $0 \le bw \le (\mathrm{H/CA})_{\mathrm{tot}}$ and for $v_{\mathrm{cac},0} \le v_{\mathrm{s}} \le (v_{\mathrm{H},0} + v_{\mathrm{cac},0})$.

2 EXPERIMENTAL

This paper examines the hydration of sample of commercial CAC ISTRA 40 taken from a regular production of *Istra Cement*, Croatia (CALUCEM Group). The cement has the oxide mass fraction composition listed in Table 2.1. Physical properties of used cement are given in Table 2.2. The main compounds are CA and ferrite phase (C_4AF-C_6AF_2), with mayenite, $C_{12}A_7$, gehlenite, C_2AS and β-C_2S as minor compounds.

Table 2.1. Chemical composition of investigated CAC.

CaO	Al_2O_3	Fe_2O_3	FeO	SiO_2	TiO_2	MgO	SO_3	Na_2O	K_2O	Sum
37.10	38.47	14.39	2.90	4.43	1.05	0.90	0.20	0.14	0.17	99.8

Table 2.2. Physical properties of investigated CAC.

>90 µm, %	<40 µm, %	Blaine, cm^2/g	Specific gravity, g/cm^3	Setting time, min		Standard consistency, %
				initial	final	
3.76	80.50	3508	3.20	298	329	24.0

Cement pastes with different H/CAC were prepared, Table 2.3. by mixing the demineralised water and 8 g of cement. Prior mixing the components were thermally stabilized at required temperature. Wafers of cement paste were placed in small sealed plastic cylindrical vials ($2r$ = 30 mm) and cured in thermostated bath. Specimen notation in Table 2.3. indicates experimental variables for hydration at T = 5 °C, namely the H/CAC ratio and time of hydration, t_h (e.g. W05t12h indicates specimen hydrated for 12 h with the H/CAC ration of 0.5000). At the hydration time t_h (h) given in Table 2.3., specimens were removed from their vials and crushed to a fine powder. The hydration was blocked and free water removed by addition of acetone. This was done by grinding and mudding the sample in three doses with acetone in agate mortar and CO_2 free atmosphere.

Table 2.3. Experimental plan for investigating the bound water and density of solids at different H/CAC ratios, hydration time t_h, and T = 5 °C.

Specimen label	H/CAC (mas. %)	t_h (h)
W10t12h	1.0000	12
W10t24h	1.0000	24
W10t48h	1.0000	48
W05t12h	0.5000	12
W05t24h	0.5000	24
W05t48h	0.5000	48
W04t12h	0.4000	12
W04t24h	0.4000	24
W04t48h	0.4000	48

The bound water content (*bw*, g/g of CAC) was determined as loss on ignition at 1000 °C in laboratory furnace divided by the mass of the ignited sample and corrected for the loss on ignition of the unhydrated cement. In these conditions the samples do not convert but dehydrate [Ukr07].

Average density of acetone-dried CAC paste, which includes the formed hydration products and the fraction of non-reacted cement, is determined according to the ASTM C 188-89.

The composition of used cement and hydration products formed after 30 h at T = 5, 20 and 30 °C was investigated by X-ray diffraction (XRD). Quantitative XRD analysis of investigated CAC was done by using the adiabatic principle with auto flushing [Chu74, Mid76].

3 RESULTS AND DISCUSSION

Quantitative XRD analysis of the used CAC gave the mass proportion of CA and $C_{12}A_7$ in CAC to be 41 % and 4 %, respectively. The XRD analysis on specimens hydrated at appropriate temperature for 30 h confirmed the hydrate compositions expected from the literature. At 5 ^{o}C only CAH_{10} was observed, while at 20 ^{o}C a small quantity of C_2AH_8 and AH_3 could be detected. At 30 ^{o}C C_2AH_8 and AH_3 are the main products with appearance of C_3AH_6 but no CAH_{10} was observed.

For higher H/CAC ratios (above 0.4) the significance of cement paste sedimentation has to be recognized. Cement paste is a concentrated flocculated suspension that sediment under gravity in a hindered settling mode in which all particles whatever their sizes settle at the same rate [Kin76]. This results in a movement of the interface between the concentrated suspension and the clear water above solids during the hydration induction period. The CAC paste model in Fig. 1.1. considers the total volume of the system to be comprised of the settling mass (concentrated cement paste) and the clear water above it. The chemical shrinkage results in a suction of this clear water into the settling mass and a reduction of the actual volume. Maximally, this volume reduction equals the theoretical amount of the internal porosity, IP, but in practice it is less due to a mass transfer phenomenon and depends on the geometry of the specimen.

After hydration upon experimental plan in Table 2.3. the amount of clear free water above the solid paste was measured by gravimetry. Specimens hydrated at H/CAC = 0.4 and 0.5 showed no clear water after hydration for time t_h (Table 2.3.). On the other hand, the highest H/CAC ratio resulted in the clear water to cement mass ratio ~ 0.5 to be above the specimen hydrated for 48 h.

The results of chemically bond water investigation (*bw*, g/g of CAC) are given in Table 3.1. The results of all methods are presented as an average of at least 3 separate measurements carried out for one hydration condition. The statistical analysis on experimental results calculated the measurement uncertainty (with 95 % confidence level) of chemically bond water and solid density to be ± 0.004 g/g of cement and ± 0.02 g cm^{-3}, respectively.

Reported [Lea76] values on densities of samples of CAC to the extent of about 90 % by successive regrinding and then dried over $CaCl_2\ 4H_2O$ (relative humidity of 37 %), are 2.11 g cm^{-3} and 2.64 g cm^{-3} for hydration at 18 °C and 45 °C, respectively. The obtained value on sample W10t48h (Table 3.1.) is in reasonable accord with the literature value (note that the conditions of hydration and drying of the samples are somewhat different).

Table 3.1. Experimental results of the chemically bound water and solid density measurements.

Specimen	*bw*, g/g of CAC	ρ_{solid}, g cm^{-3}
W10t12h	0.3495	2.28
W10t24h	0.4263	2.18
W10t48h	0.4551	2.16
W05t12h	0.2910	2.36
W05t24h	0.3678	2.28
W05t48h	0.3941	2.24
W04t12h	0.2835	2.39
W04t24h	0.3273	2.31
W04t48h	0.3481	2.28

The solid volume of specimens [cm^3/g of CAC] is obtained from the measurements of chemically bound water and density:

$$v_{\text{solid}} = (1 + bw) / \rho_{\text{solid}} \tag{3.1}$$

Based on a propagation of error analysis of eq. (3.1), the estimated combined uncertainty of the calculated solid volume is ± 0.0055 cm^3/g of cement (with 95 % confidence level).

Results of the change in the volume of the solid during the hydration of the CAC cement are shown in Fig. 3.1. and Fig. 3.2.

As mentioned earlier the slope of the linear model eq. (1.9) is not dependant on the amount of active minerals in CAC. For stoichiometric model of the hydration reactions given by eq. (1.1) the slope is $tg\alpha = 0.7973$. By applying eq. (1.9), slopes for other (higher temperature) independent hydration reactions of CAC are: $tg\alpha = 0.7100$ and $tg\alpha = 0.5501$ for stoichiometric models (1.2) and (1.3), respectively (see Fig. 3.1.). The decrease of the slope of individual reactions in order of eq. (1.1) - (1.3), Fig. 3.1., is attributed to the specific volumes of the formed hydration products and the stoichiometric water requirement, $(H/CA)_{tot}$ for their formation.

The specific volumes of the formed hydration products, according to reaction eq. (1.1), (1.2) and (1.3), are 0.560 cm^3/g, 0.484 cm^3/g and 0.410 cm^3/g, respectively. Furthermore, by inference to eq. (1.8), the $(H/CA)_{tot}$ for the individual CA hydration (1.1), (1.2) and (1.3) is 1.1385, 0.6262 and 0.4557, respectively. With increasing temperatures the hydration products contain more crystalline water (OH^-), higher crystalline level, and the hydration degree is higher due to the lower stoichiometric water requirement of the higher temperature hydration reactions. On the other hand, the hydration products formed at lower hydration temperatures have a greater capacity for filling the capillary porosity in CAC paste. This results in lower porosity (and hence better performances) at lower temperatures although the hydration degree increases with temperature. Chemically bound water for complete hydration of active minerals (CA and $C_{12}A_7$ in investigated cement), the $(H/CAC)_{tot}$ upon reaction eq. (1.1), (1.2) and (1.3) is calculated by eq. (1.8) to be 0.5123 g/g CAC, 0.2881 g/g CAC and 0.2051 g/g CAC, respectively. A reported value of $(H/CAC)_{tot} \sim 0.33$ for a completely converted CAC [Geo90] indicates that other minerals beside CA (and $C_{12}A_7$) should be accounted for to yield a more detailed stoichiometric model of CAC long term hydration and at higher temperatures.

In Fig. 3.1. and Fig. 3.2. one can see that the simplified model for reaction eq. (1.1) is in excellent accord with the experimental results obtained on specimens hydrated at $T = 5$ °C for up to 48 h. Once again the reactivity of other phases but CA have been disregarded in the simplified stoichiometric model eq. (1.7). It can be concluded that the volume evolution of the solids during low temperature hydration of CAC during early age ($t_h \leq 24$ h) can be predicted well by the presented simplified model of the CA hydration.

The presented modeling methodology can be extended to develop more complex models to describe all three reactions of CA hydration scheme simultaneously, and even to include other hydraulically active minerals (e.g. $C_{12}A_7$, C_4AF and C_2S).

Cement pastes mixed with less than the stoichiometric water content hydrated under sealed conditions will contain non-hydrated active cement minerals after consumption of all water, Fig. 1.1.(a). On the other hand, cement pastes prepared above the stoichiometric water content will contain unused water after all the active cement minerals have reacted, Fig. 1.1.(b), especially when yielding stable hydration products. This excess water contributes only to the porosity of the cement paste (with an adverse effect on strength). As a consequence the curve of porosity versus initially mixed H/CAC ratio is not smooth with a characteristic discontinuity at point of the stoichiometric water content.

Previous publications [Cot70, Geo90, Scr98] have shown that the calculated porosity agrees well with experimental data for hydration at 70 °C, while at 10 °C agrees only for the H/CAC ratios below 0.4 (range?). It has to be noted that the quantity of CA in iron rich and low grade CAC can vary from 40 - 70 % [Ben02]. The model porosities for the low density hydration products give also good predictions above the H/CAC of 0.4 if the quantities of reacted minerals are known, as is demonstrated in Fig. 3.2. (from the data on solid volume one can easily obtain porosity, as shown in Fig. 1.1.). Degree of hydration can be obtained by QXRD analysis or by measurements of chemically bound water and usage of proper stoichiometric model (eq. (1.7)) [Ukr08a, Ukr09].

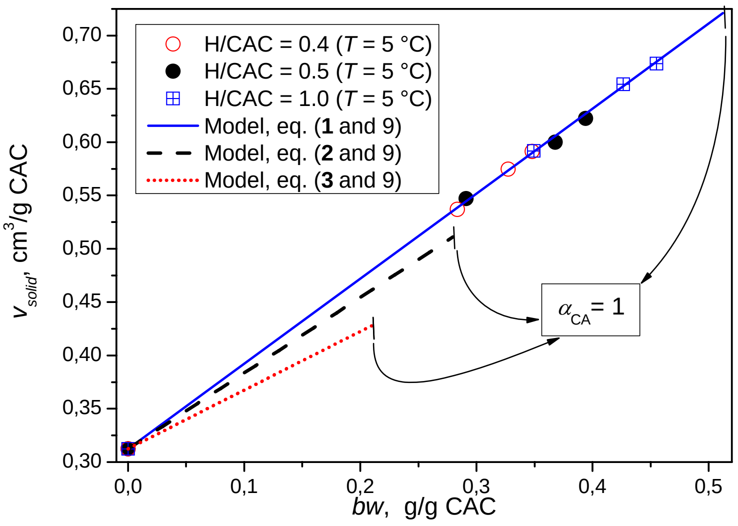


Fig. 3.1. Comparison of experimental and theoretical results of the solid volume evolution as a function of chemically bound water (limited by the amount of reactive mineral components).

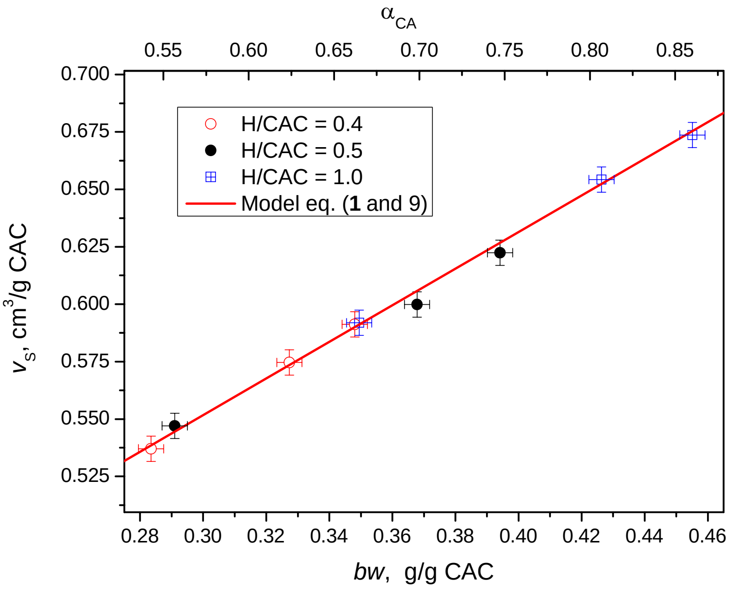


Fig. 3.2. A detail of Fig. 3.1. comprising the corresponding calculated degree of hydration upon eq. (1.7).

Finally, to stress out again, the stoichiometric requirement, $(H/CAC)_{tot}$ depends on the amount of active minerals in CAC. So, beside the commonly addressed H/CAC ratio as the principal variable governing the porosity and strength development during conversion of metastabile hydration products one should also consider the amount of the most reactive minerals in CAC.

4 CONCLUSIONS

The paper presents a relatively simple and robust model of solid fraction evolution during early age of CAC hydration. The model is based on the main reaction scheme of the CA hydration.

The water to cement ratio and the amount of the most active minerals in CAC are the principal variables governing the porosity and strength development during conversion of metastabile hydration products.

Predictions of the solid volume versus chemically bound water during early age hydration of iron-rich CAC at $T = 5$ °C are in good agreement with the experimental data.

In future work, the given modeling methodology should be extended to simultaneously model all three reactions of the CA hydration scheme (at various temperatures), and even to include the other hydraulically active minerals (e.g. $C_{12}A_7$, C_4AF and C_2S).

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REFERENCES

[Ben02] Bensted J., Calcium Aluminate Cements, Chapter 4 in Structure and Performance of Cements, 2end ed., (ed. Bensted J, Barnes P), London, 2002. 114-138. ISBN 0-419-23330-X

[Bro04] Brouwers H.J.H., The work of Powers and Brownyard revisited: Part 1, *Cem Concr Res* 34 (9) (2004) 1697–1716.

[Chu74] Chung, F.H., Quantitative interpretation of X-ray diffraction patterns of mixtures. II. Adiabatic principle of X-ray diffraction analysis of mixtures, Journal of Applied Crystalography **7** (1974) 526-531.

[Cot70] Cottin B., Reif P. Parameter Physiques regissant les properties mechaniques de pastes pures de liants alumineux, Revues des Materiaux et Construction 661 (1970), 294-295.

[Geo83] George C.M., Industrial aluminous cements in Structure and Performance of Cements (ed. P.Barnes), Applied Science, London, (1983) 415-470.

[Geo90] George C.M., Manufacture and Performance of Aluminous Cement: a New Perspective, in [Man90], 181-207.

[Kin76] King A., Raffle J.F., Studies on the settlement of hydrating cement suspensions, J. Phys. D: Appl. Phys., 9 (1976) 1425-1443.

[Lea76] Lea F.M., The Chemistry of Cement and Concrete, 3rd ed., Edward Arnold, London, (1976) ISBN 0-7131-2277-3.

[Man90] Mangabhai R.J., Ed, *Proc. Int. Conf. on CAC*, Chapman and Hall, London, 1990. ISBN 0-419-15200-8

[Man01] Mangabhai R.J., Glasser F.P., Ed, *Proc. Int. Conf. on CAC*, Edinburgh, UK, 2001. ISBN 1-86125-142-4

[Mat03] Matusinović T, Šipušić J, Vrbos N, Porosity-strength relation in calcium aluminate cement pastes, *Cement Concrete Research* 33 (2003) 1801-1806.

[Mid76] Midgley H.G., quantitative Determination of Phases in High Alumina Cement Clinkers by X-ray Diffraction, Cement Concrete Research 6 (1976), 217-224.

[Scr99] Scrivener K.L., Cabiron J.L. and Letourneux R., High-performance concretes from calcium aluminate cements, Cement and Concrete Research, 29 (8) (1999) 1215-1223.

[Scr98] Scrivener K.L., Capmas A., Calcium Aluminate Cements, Chapter 13 in Lea's Chemistry of Cement and Concrete, 4th ed. P. C. Hewlett, John Wiley & Sons, NY, 1998. ISBN 0-340-56589-6

[Ukr07] Ukrainczyk N., Matusinović T., Kurajica S., Zimmermann B., Šipušić J., Dehydration of a Layered Double Hydroxide-C_2AH_8, Thermochimica Acta 464 (1) (2007) 7–15.

[Ukr08a] Ukrainczyk N., Matusinović T., Šipušić J., Microstructural Model of Calcium Aluminate Cement Hydration, Minerals to Materials Conference - M2M08 Bridging the Gap between Minerals and Materials: Central Metallurgical Research and Development Institute of Egypt, Cairo 2008, Proc. on CD, 8p.
(http://bib.irb.hr/datoteka/377077.Ukrainczyk_m2m08.pdf)

[Ukr08b] Ukrainczyk N., Šipušić J., Dabić P., Matusinović T., Microcalorimetric Study On Calcium Aluminate Cement Hydration, 13. International conference on Materials, Processes, Friction and Wear - MATRIB'08, Vela Luka, Croatia, June (2008) 382-388. (http://bib.irb.hr/datoteka/360481.Ukrainczyk.pdf)

[Ukr09] Ukrainczyk N., Calcium Aluminate Cement Hydration Model Development, PhD thesis, University of Zagreb, 2009.

[Ukr10] Ukrainczyk N., Matusinović T., Thermal Properties of Hydrating Calcium Aluminate Cement Pastes, Cement and Concrete Research 40 (2010) 128–136.