

# CALCIUM ALUMINATE CEMENT MASS BALANCE MODEL BASED ON $\text{CaAl}_2\text{O}_4$ HYDRATION

Neven Ukrainczyk, Juraj Šipušić, Tomislav Matusinović

FKIT, University of Zagreb, Marulicev trg 20, Zagreb, Croatia,  
e-mail: nukrainc@fkit.hr

## 1. INTRODUCTION

During the cement setting and hardening, microstructure of material and amounts of individual phases (hydraulic cement minerals, water and formed hydrates) are changing continuously<sup>1,2</sup>. 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<sup>3-5</sup>, yielding  $\text{CAH}_{10}$  (cement notation: C=CaO, A=Al<sub>2</sub>O<sub>3</sub>, H=H<sub>2</sub>O) as main products at temperatures lower than 20 °C,  $\text{C}_2\text{AH}_8$  and  $\text{AH}_3$  at about 30 °C and  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  at temperatures higher than 55 °C.  $\text{CAH}_{10}$  and  $\text{C}_2\text{AH}_8$  are known to be metastable at ambient temperature and convert<sup>6</sup> to the more stable  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  with consequent material porosity and permeability increase and loss of strength. The conversion is accelerated by temperature and moisture availability.

## 2. EXPERIMENTAL

The CAC (iron-rich) used was taken from a regular production of Istra Cement International, Pula, Croatia. Cement pastes with w/c = 0.3, 0.4, 0.5 and 1 were prepared by mixing the distilled water and cement stabilized at required temperature. Wafers of about 10 g of cement paste were placed in small capped plastic vials and cured in thermostated bath at 5, 10, 14 and 20 °C. The composition of cement and hydrates formed had been investigated by quantitative powder X-ray diffraction (QXRD) after Chung<sup>7</sup>. Chemically bound water in the cement samples was determined by loss on ignition.

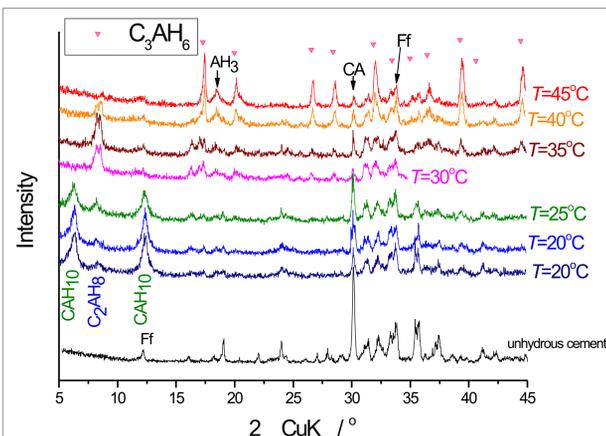
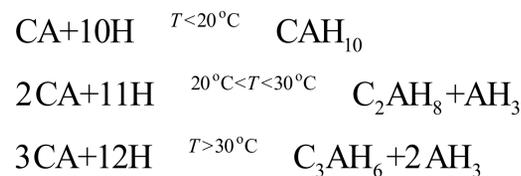


Figure 1. XRD analysis of cement and hardened pastes hydrated at different temperatures.

**Cement notation:**  
C=CaO, A=Al<sub>2</sub>O<sub>3</sub>, H=H<sub>2</sub>O



XRD analysis on samples obtained from hydrated specimens cured at appropriate temperature, Figure 1, confirmed the hydrate compositions expected from the literature<sup>3-5</sup>. Main diffraction peaks of metastable hydrates are fairly broadened, indicating poor crystallinity, while that of the stable hydrated material showed good crystallinity.

Table 1. Comparison of the hydration degree obtained from measured bond water,  $\alpha_{bw}$  with the CA QXRD analysis,  $\alpha_{CA}$ . Sample notation in Table 1 indicates experimental variables, i.e. temperature and w/c ratio (5C04 indicates hydration at 5 °C and the w/c ratio of 0.4)

Sample	$t_h$ , h	$bw$ , g/g	$\alpha_{CA} = \alpha_{active}$	$\alpha_{bw}$	error, %
5C04	30	0.3278	0.62	0.640	3.20
5C04	24	0.3159	0.61	0.617	1.08
5C05	30	0.3683	0.71	0.719	1.25
5C03	30	0.2591	0.50	0.506	1.15
10C04	30	0.3380	0.65	0.660	1.50
10C05	30	0.3880	0.74	0.757	2.34
10C10	30	0.4272	0.84	0.834	-0.73
14C04	30	0.3438	0.67	0.671	0.16
14C05	30	0.3995	0.78	0.780	-0.03
20C04	30	0.3512	0.70	0.686	-2.07
20C05	30	0.4119	0.82	0.804	-1.95
20C10	30	0.4439	0.88	0.866	-1.54

## 3. MASS BALANCE MODEL

In this work three main reactions schemes of the CA hydration at different temperatures are applied to predict the composition of cement paste. The model predictions are compared to experimental results for hydration at  $T < 20^\circ\text{C}$ , Table 1. The model enables the quantification of volume fractions of the various hydration products, free water, unreacted cement and chemical shrinkage as a function of the degree of hydration, Figure 2. The model input variables are mass fraction of CA and  $\text{C}_{12}\text{A}_7$  in cement, water to cement ratio, functions of individual reactions partition during the hydration, while stoichiometry of individual reactions, densities, and molar masses of reactants and products are known. The developed model, written for the setting of MATLAB<sup>®</sup> is capable to deal with simultaneous hydration reactions, both in saturated and in sealed conditions. Constant or variable individual reaction partition during the hydration can be also handled by the model.

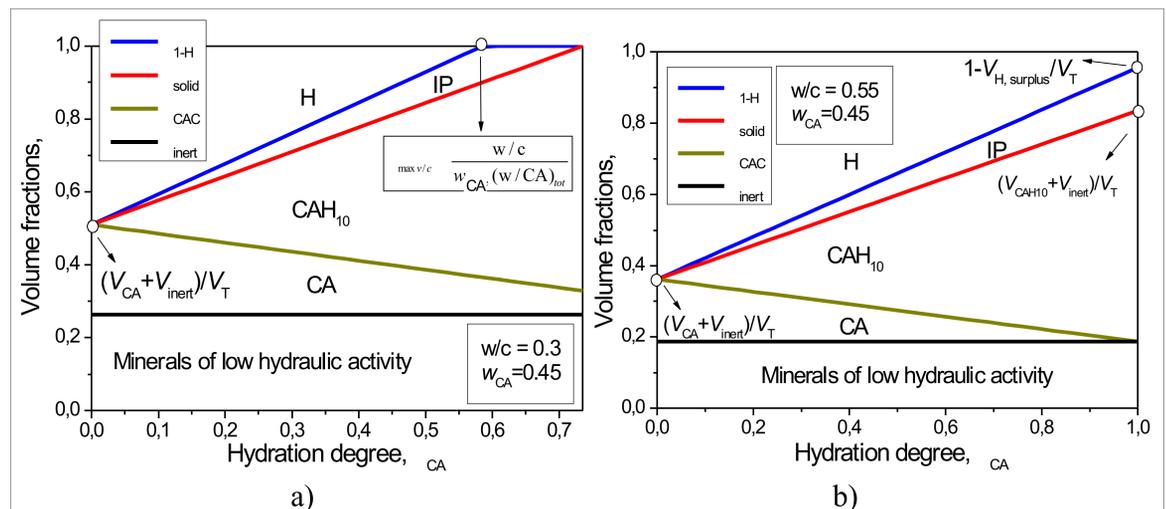


Figure 2. The microstructural model shown on examples of volume fractions during hydration at: a) w/c = 0.3 and  $w_{CA} = 0.45$ ; and b) w/c = 0.55 and  $w_{CA} = 0.45$ , where:  $w_{CA}$  - initial CA phase mass fraction in CAC,  $V_i$  - initial volume of  $i$ -th phase: (H - water, T - total paste volume) w/c - water to cement mass ratio,  $(w/CA)_{tot}$  - stoichiometric ratio for complete hydration, IP - internal porosity(chemical shrinkage)

## 4. CONCLUSION

A relatively simple and robust cement hydration model obtained is suitable for engineering purposes. Main reaction scheme of the CA hydration at temperatures less than 20 °C can be applied to predict the composition of iron-rich calcium aluminate cement paste. Evolution of the fractional changes of chemical shrinkage, solid content and active cement should be measured to additionally validate the proposed model.

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