EPJ Web of Conferences **221**, 01001 (2019) https://doi.org/10.1051/epjconf/201922101001
EPPS 2019

In-situ curing mechanism of Portland cement

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Abstract. The paper presents the results of predictive modelling of the curing mechanism of the type CEM I 42.5B Portland cement using the VCCTL tool. The curing lasts during 28 days at 20 ºC and the water-cement (W/C) ratio of 0.26, 0.30, 0.35 and 0.40. It is shown that the degree of Portland cement hydration is ~0.70 after 28-day curing. The growth in the W/C ratio significantly intensifies the hydration rate and the dissolution of clinker minerals. The amount of the main hydration products calcium silicate hydrate (C-S-H) and portlandite considerably increases with the W/C ratio. In Portland cement, the fraction of hydrated cement achieves 0.60 of the solid phase and the pore space. It is found that the effective elastic moduli rapidly increase during 400 hours, and then monotonely lower down to 16.79 GPa for the bulk modulus, 8.90 GPa for the shear modulus and 22.69 GPa for Young's modulus. Relatively high values of the effective elastic moduli are explained by the higher content of the clinker phases and, probably, the higher degree of C-S-H crystallinity. The dependence between the yield stress and Young's modulus is in good agreement with the VCCTL microstructural model of Portland cement curing.

1 Introduction

The model-based testing of physicochemical properties of concretes after 28-day curing allows a user to significantly reduce the time, materials, and human resources. Portland cement curing is a complex process which includes many mechanisms. A consistent description of this process requires the quantitative data on the initial phase composition, water-cement (W/C) ratio, activation energy of clinker phase dissolution, heat generation in forming the intermediate and final products, porosity, bound moisture, ion composition (electrical conductivity) of aqueous solution, humidity, external conditions, composition, amount, and elastic properties of hydration products. The experimental study of these properties is rather difficult. One of the most efficient tools of predictive modelling of the Portland cement hydration and strength gain is the Virtual Cement and Concrete Testing Laboratory (VCCTL) [1–6]. It seems to be very interesting to study the hydration process mechanisms and search for the correlation between the experimental parameters of stress-strain curves and elastic moduli of hydrated cement in ordinary conditions as well as the influence of the water-cement ratio on this correlation.

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The aim of this work is to explore the hydration process and predict the strength properties of CEM I 42.5B using the VCCTL computer modelling tool. The mechanical tests of Portland cement are carried out after 4 hours and 1, 3, 7, 14 and 28 days of curing. The analysis is performed for the curing mechanism of Portland cement having different water-cement ratio and its effect on the correlation between the strength properties.

2 Materials and methods

The type CEM I 42.5B Portland cement was used in this experiment to investigate its mechanical properties. The Bogue calculations were used for the cement composition of 61.06 g C_3S, 13.62 g C_2S, 12.79 g C_4AF and 6.50 g C_3A in ~100 g [7]. The cement paste with the water-cement ratio of 0.26, 0.30, 0.35 and 0.40 was prepared in a common form 20×20×20 mm in size. 20 specimens were then compacted on a vibrating table [8, 9]. The experiment focused on the identification of strength properties of Portland cement depending on the curing time, water-cement ratio at room temperature and a search for correlations between the cement strength and theoretical elastic properties. Not less than 3 specimens were used in the experiment, which were deformed after each 4 hours and after 1, 3, 7, 14 and 28 days of curing. The specimens deformation was performed on a test machine INSTRON at a 0.5 mm/min loading rate and room temperature. The yield stress of Portland cement was used as its strength property, and its values were averaged over three points. These experiments constituted a part of our previous research [10, 11].

Prediction of the concrete hardening is performed using the Virtual Cement and Concrete Testing Laboratory (VCCTL) [1, 2]. The VCCTL is used to model concrete structure at the micro-scale level based on two-dimensional images of the initial phases and hydration products obtained by a scanning electron microscopy. A plane, random distribution of single elements obtained by Voronoi decomposition [3] is converted to a three-dimensional model. Each unit volume (voxel) of the microstructure is assigned with a phase element. The interaction between neighbouring voxels is based on the cellular automata rule. According to stoichiometry of the current states, autocorrelation of neighbouring voxels, development of phases and water-filled pores, the composition of Portland cement can be determined by the dissolution, growth, the intermediate phase suppression and the formation of final products (hydrates). The main hydration products, such as low-crystallized, almost amorphous, calcium silicate hydrate (C-S-H) having the properties of gel, and calcium hydroxide (CH) form with reasonable certainty, on the grain surface contacting with water, and appear in the available pore space. The initial random three-dimensional model of the microstructure is recovered by means of autocorrelation functions and contains four mineral clinker phases and different forms of calcium sulphate. Calcium silicate hydrate (amorphous or low-crystallized) forming during C_2S and C_3S hydration occupies a wide area of C-S-H gel. The amount of C-S-H gel of variable Si/Ca ratio based on tobermorite and jennite is about 60 at.%, while AFt phase (ettringite) and AFm phase (hydrocalumite) constitute about 10 and 18 at.%, respectively. The alkalinity of water in pores and its saturation have an effect on the kinetics of chemical reactions. At the initial stages of modelling, we utilize a quadratic dependence of the normalized volume of C-S-H gel, while at later stages the probability of the partial surface dissolution relative to the surface of the initial cement is determined. The quantitative phase composition of the solid substance allows us to estimate the effective elastic moduli of Portland cement during its curing using the moduli of the individual phases in the initial and final products [12].

3 Results and discussion

Figures 1–4 show the main results of modelling and mechanical tests of hydrated cement with the water-cement ratio of 0.26, 0.30, 0.35 and 0.40. The curing lasts for 28 days at 20 ºC.

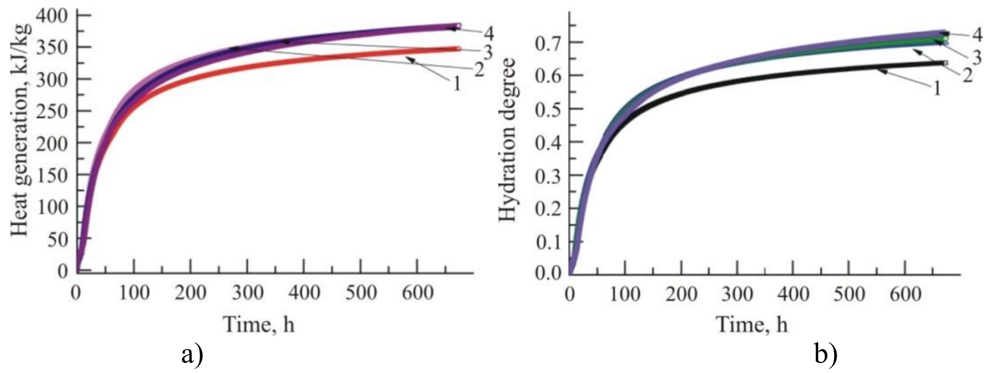


Fig. 1. Time dependences of heat generation (a) and hydration (b). W/C ratio: *1* – 0.26; *2* – 0.30; *3* – 0.35; *4* – 0.40.

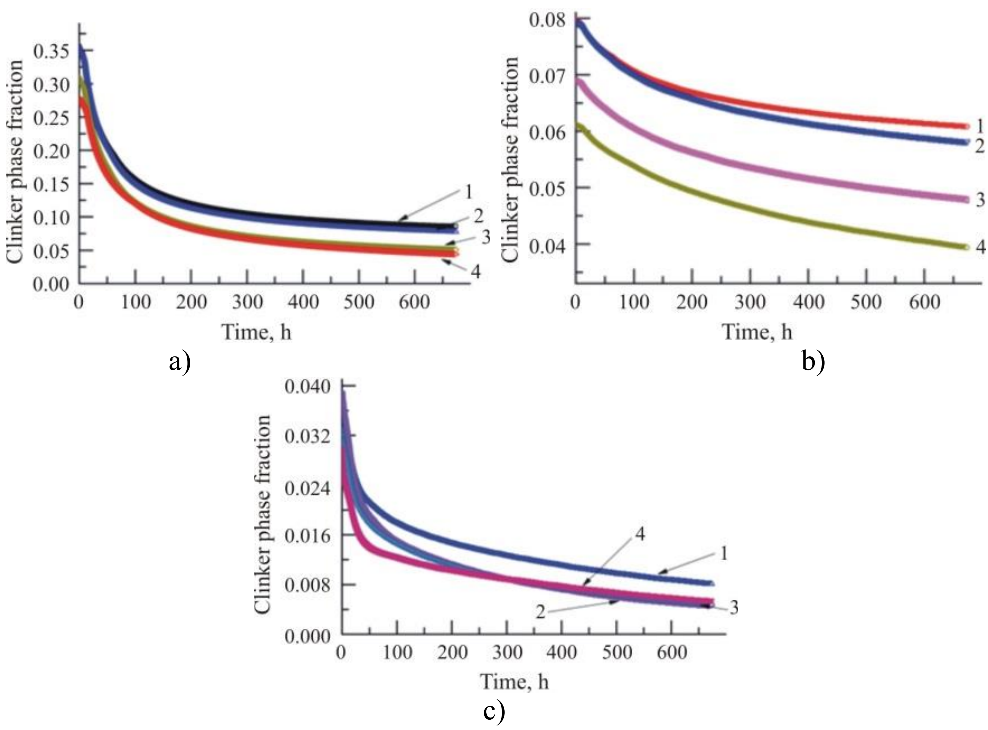


Fig. 2. Time dependencies of clinker phase fractions: *a* – alite (C_3S); *b* – belite (C_2S); *c* – aluminate (C_3A). W/C ratio: *1* – 0.26; *2* – 0.30; *3* – 0.35; *4* – 0.40.

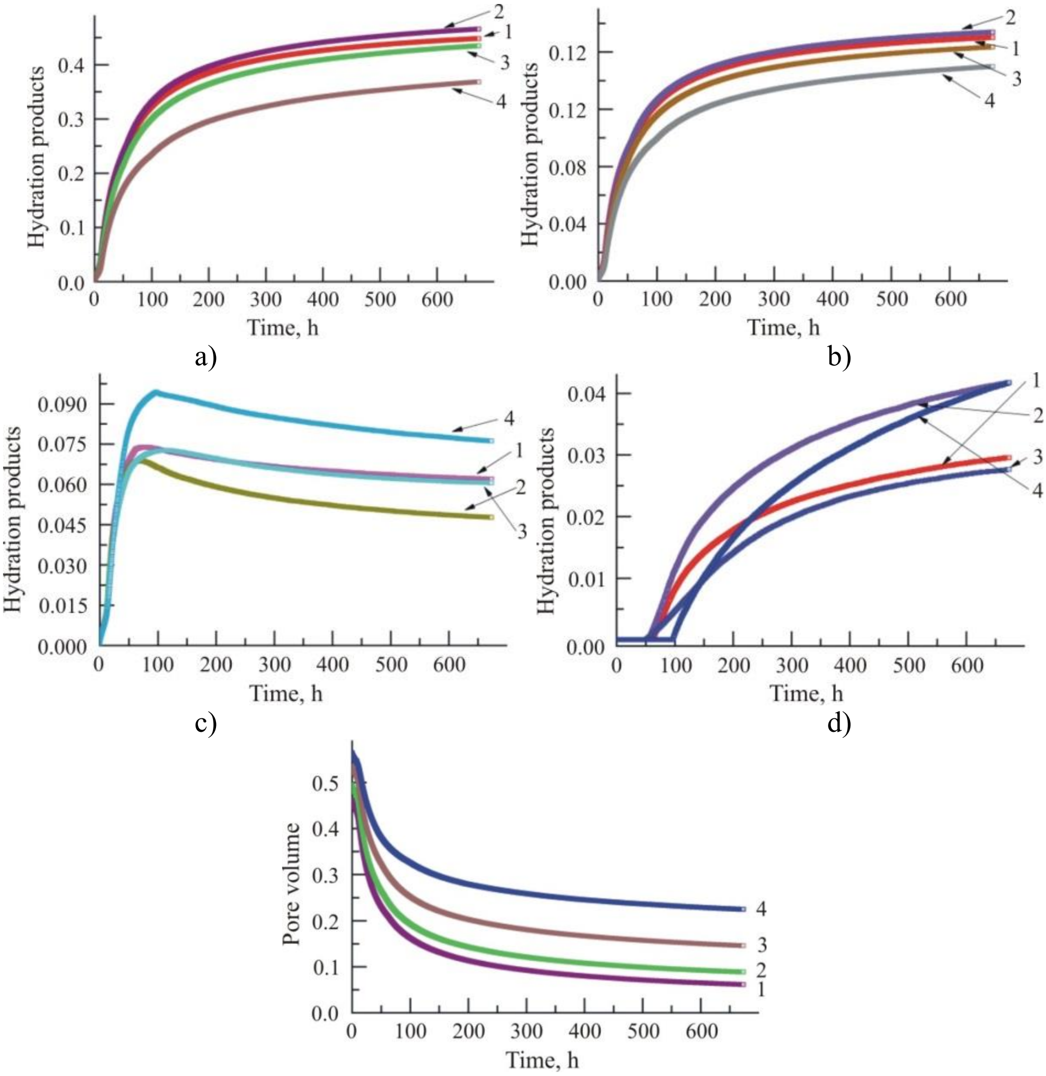
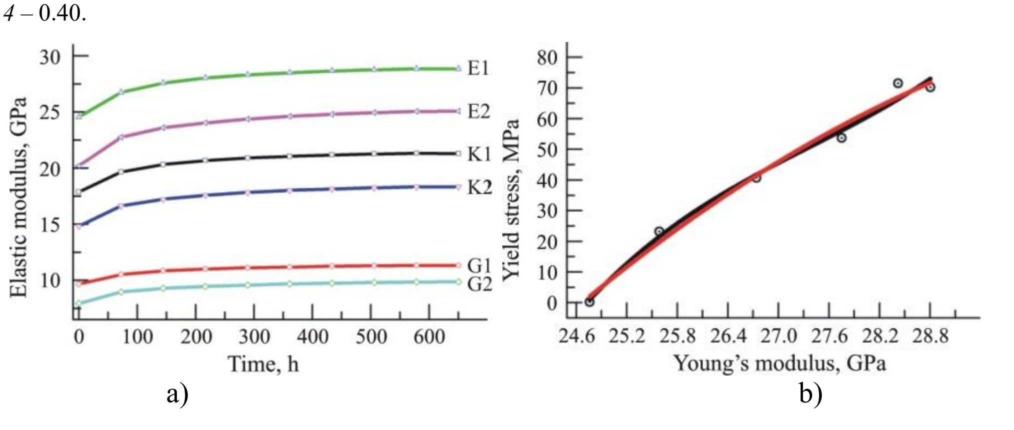


Fig. 3. Time dependencies of hydration products and pore fractions: *a* – C-S-H; *b* – portlandite (CH); *c* – ettringite, *d* – monosulfate (AFm phase); *e* – pore volume, W/C ratio: *1* – 0.26; *2* – 0.30; *3* – 0.35; *4* – 0.40.



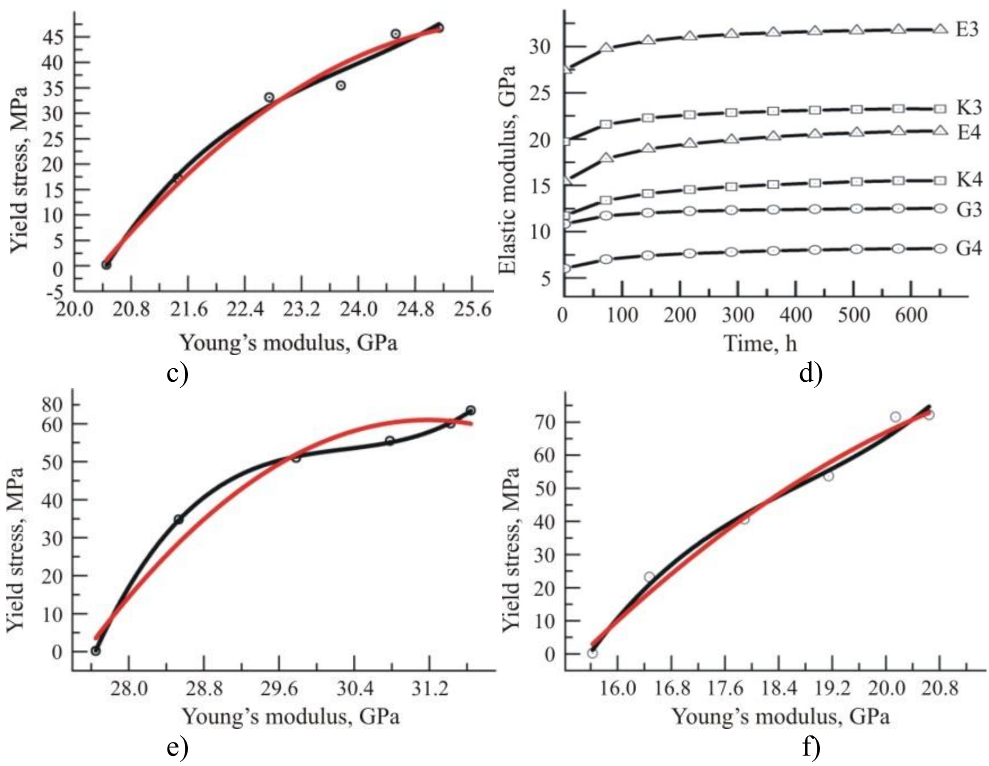


Fig. 4. Time dependences of strength properties of Portland cement: *a, d* – Young's modulus, W/C = 0.30 (curve *E*1), W/C = 0.35 (curve *E*2), W/C = 0.26 (curve *E*3), W/C = 0.40 (curve *E*4); bulk modulus, W/C = 0.30 (curve *K*1), W/C = 0.35 (curve *K2*), W/C = 0.26 (curve *K3*), W/C = 0.40 (curve *K4*); shear modulus, W/C = 0.30 (curve *G*1), W/C = 0.35 (curve *G2*), W/C = 0.26 (curve *G3*), W/C = 0.40 (curve *G4*). Yield stress: *b* – W/C = 0.30; *c* – 0.35; *e* – 0.26; *f* – approximation points. Approximations use quadratic (red curve) and cubic (black curve) polynomials.

These figures show that the hydration process develops within the first 100 hours. Within this period, we observe the intensive heat generation and strength gain which correlate with each other. The water-cement ratio insignificantly affects these processes (fig. 1). After 100 hours, the hydration rate monotonely decreases. The clinker phase fraction substantially lowers during 100 hours. However, the initial clinker phases do not completely vanish (fig. 2). It is found that the water-cement ratio notably affects the process of clinker dissolution. Since the cement paste was prepared, the amount of alite, belite and particularly alumoferrite lowers with the increasing W/C ratio (fig. 2). The rate of alite and aluminate dissolution is the highest during the first 100 hours, and at W/C=0.40 the highest is the rate of aluminate dissolution. As can be seen from fig. 3, the main hydration products are C–S–H, portlandite, ettringite and to a lesser extent, monosulfate (AFm phase). With the curing time, the amount of the indicated products increases, except for ettringite which changes non-monotonely. The highest hydration rate (see fig. 3) is observed during the first 100 hours and then it monotonely lowers. The hydration degree correlates with the heat generation and the accumulation rate of hydration products (see figs 1–3). In modelling, it is assumed that the pore space is filled with water. According to fig. 3*e,* the amount of free moisture in pores is higher at a 0.30 water-cement ratio. These results indicate that at W/C ratio ranging between 0.26 and 0.35, the hydration process occurs under conditions close to saturation. Indeed, the processes of the C-S-H accumulation are more intensive within this water-cement ratio. As presented in fig. 4, the effective elastic moduli are obtained for

Young's modulus *E*, the bulk modulus *K* and the shear modulus *G*, depending on the curing time and the water-cement ratio. The latter significantly affects the elastic properties of the material, although the behaviour of *E, K* and *G* curves is almost the same during the curing process. The lower water-cement ratio enhances the strength properties of cement despite the large pore space. These dependencies of the elastic moduli indicate to the variable composition of crystal lattices of the major phases of hydration products. The values of the effective elastic moduli are strongly affected by the clinker phases. The analysis presented in [12] for the correlation between the models of hardening and strength properties of cements shows that the most suitable are models based on the dependencies in the form of polynomials of ~2.5–3 degrees. Figure 4 contains the approximated dependences between the yield stress and Young's modulus. With a high degree of reliability (≈0.97), the experimental values of the yield stress can be approximated using either quadratic or cubic polynomials. This is proved by the results obtained in [12]. A comparison of the parameters of cubic polynomials shows that the strength gain rate at a 0.26 water-cement ratio is higher than at 0.35, and 4.2 times higher than at 0.30 water-cement ratio (see Table 1). The parameters of quadratic polynomials are less sensitive to the water-cement ratio, but at W/C = 0.26, the strength gain rate is 3.1, 3.2 and 5.1 times higher than at 0.30, 0.35 and 0.40 water-cement ratio, respectively.

Table 1. Parameters of quadratic and cubic polynomials.

Parameters	W/C	A[a]	B	C	D
Cubic	0.26	–75067.09316	7456.36708	–246.78961	2.72363
	0.30	–15827.170	1712.59335	–62.06803	0.75599
	0.35	–5924.28961	735.06165	–30.4467	0.4239
	0.40	–4035,77249	633.2368	–33.21594	0.59033
Quadratic	0.26	–4260.9055	276.7963	–4.43239	–
	0.30	–1356.23386	87.17665	–1.30545	–
	0.35	–932.66324	74.94812	–1.43216	–
	0.40	–559.28657	52.65684	–1.06735	–

[a] A, B, C, D are cubic and quadratic polynomial approximation parameters.

4 Conclusions

The analysis of the predicted phase compositions in cement hydration under normal conditions showed that the water-cement ratio had a notable effect on the parameters investigated. At W/C = 0.26, the curing process was slower than at higher values of the W/C ratio: the amount of clinker phases was rather high. And the amount of hydration products was higher than at W/C=0.40. The free moisture in the pore space was higher also. The high values of the effective elastic moduli were provided by the larger content of clinker phases and, probably, by the higher C-S-H crystallinity. The results of the VCCTL modelling of Portland cement curing were supported by the exponential function of the yield stress and Young's modulus with a high degree of reliability.

Authors wish to acknowledge the financial support from the Russian Foundation for Basic Research (Grant N 18-08-01025).

References

1. J. Bullard, E. Garboczi, P. Stutzman, *VCCTL software* In: Overview and Opportunities, 1–17 (Gaithersburg, National Institute of Standards and Technology, USA, 2013)

2. D. P. Bentz, *A Three-dimensional cement hydration and microstructures program,* Pt I Hydratation Rate, Heat of Hydration and Chemical Shrinkage, Report NISTIR 5756, 1–47 (Gaithersburg, U.S. Department of Commerce, 1995)
3. D. P. Bentz, P. V. Coveney, E. J. Garboczi, M. F. Kleyn, P. E. Stutzman, Modelling Simul. Mater. Sci. Eng. **2,** 783-808 (1994)
4. D. P. Bentz *CEMHYD3D: A Three-dimensional cement hydration and microstructure development modelling package version 2.0,* Report NISTIR 6485 (U.S. Department of Commerce, 2000)
5. D. P. Bentz, C. J. Haecker, X. P. Feng, P. E. Stutzman *Proc. 5th Int. VDZ Cong. on Process Technology of Cement Manufacturing*, 53–63 (Düsseldorf, Germany, 2003)
6. P. E. Stutzman, J. W. Bullard, X. P. Feng *Quantitative imaging of clinker and cement microstructure*, Report NISTIR 1877 (U.S. Department of Commerce, 2015)
7. H. F. W. Taylor, *Cement chemistry* (Moscow, Mir, 1996)
8. SNiP 310.3-76 «Cements. Definition of normal density, setting time and uniform volume distribution» (in Russian)
9. SNiP 22685-89 «Molds for concrete test samples» (in Russian)
10. A. I. Gnyrya, Yu. A. Abzaev, S. V. Korobkov, K. S. Gauss, IOP Conf. Series: EES, **193** 012010 (2018)
11. Yu. A. Abzaev, A. I. Gnyrya, S. V. Korobkov, K. S. Gauss, A. Boyarintsev, S. Tomrachev, *Proc. 15th Int. Conf. of Students and Young Scientists Prospects of Fundamental Sciences Development* In: Journal of Physics: Conf. Series **1145** 012016, 1-8 (2019)
12. S. T. Erdogan, E. J. Garboczi, J. W. Bullard, *Proc. Int. Conf. on Durability of Building Materials and Components*, 1-8 (Istanbul, Turkey, 2008)