Modelling of sand cement hydration in normal conditions

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Abstract. The paper considers the hardening mechanisms of the sand cement composition (0.75 sand and 0.25 Portland cement) during 28 days. In this study, the VCCTL tool is used for computer modelling of the sand cement hardening process. It is found that after 28 days, the sand cement hydration is ~0.75, the porosity is over 0.20 and 0.32 at the water-cement ratio of 0.40 and higher, respectively. Calcium silicate hydrate (C–S–H) and portlandite (CH) are the main hydration products of Portland cement and responsible for the sand cement strength. Owing to the high porosity of sand cement, free moisture is present in it in large quantities. It is shown that the effective elastic moduli of sand cement rapidly grow during 200 hours and then monotonically lower. The yield stress monotonically grows during sand cement curing, and at 0.40 and 0.44 water-cement ratios achieves the maximum value. This growth thus depends on the water-cement ratio and affects Young’s modulus during the curing process. At the qualitative level, a correlation is observed between the yield stress and Young’s modulus depending on the curing time of sand cement with the discussed water-cement ratios.

1. Introduction

The laboratory tests of Portland cement products are rather expensive and labour-intensive. The model-based testing of physicochemical properties of the calcium silicate hydrate (C–S–H) and sand composition after 28-day curing at room temperature allows to significantly reduce the time, materials, and resources. One of the most efficient tools of the predictive modelling of cement properties is the Virtual Cement and Concrete Testing Laboratory (VCCTL) [1–7]. Of certain interest is the investigation of the influence of the water-cement ratio on the hydration degree, pore volume, chemical shrinkage, the content of clinker minerals, hydration products and elastic moduli in products made of Portland cements with higher sand percentages. The correlation of the C–S–H elastic moduli and sand aggregate with the experimental stress-strain curves is detected depending on the curing time.

The aim of this work is to explore the curing mechanisms of the type CEM I 42.5B Portland cement with sand aggregate at 20 °C during 28 days. This cement type is similar to that manufactured at the Topki Cement Plant (the Novosibirsk region, Russia).

2. Materials and methods

The type CEM I 42.5B Portland cement was investigated in this experiment. Its chemical composition calculated by the Bogue equations [8] consisted of 61.06 g alite, 13.62 g belite, 12.79 g ferrite and 6.50 g aluminate in 100 g. The proportion of cement and non-reactive sand in the composition was 0.25 and 0.75, respectively. The specimens with 0.40, 0.44, 0.49 and 0.54 water-cement ratios were investigated. The mixture preparation was described in detail in [9]. The obtained sand cement composition was
placed in a 20×20×20 mm concrete form and cured in a binder chamber at 20 °C and 100% humidity. After curing for 24, 72, 168, 336 and 672 hours, the specimens were subjected to compressive testing on a test machine Instron-3382 (USA) at room temperature and a 0.5 mm/min deformation velocity. The strength properties of the specimens were determined by the yield stress and the elastic strain averaged over three points on the stress-strain curves.

Portland cement curing is a complex process that includes many mechanisms, each of which is described by its own group of variables. The identification of sand cement curing mechanisms requires the quantitative data on the initial phase composition, water-cement ratio, activation energy of dissolution of the clinker phases, heat generation during the formation of intermediate and final products, porosity, bound moisture, ion composition of aqueous solution, humidity, external conditions, elastic properties of hydration products, etc. The experimental study of the properties of sand cements as a multistage system is rather difficult and requires the curing process modelling. One of the most efficient tools of the predictive modelling of cement properties is the Virtual Cement and Concrete Testing Laboratory (VCCTL) [1–7]. The VCCTL modelling tool constructs a three-dimensional microstructure of the cement paste using the electron microscopical images of plane structures. Cement particles distribute at random in three-dimensional space in accordance with the two-dimensional particle-size distribution. Each unit volume (voxel) of the microstructure is assigned with a phase element. The interaction between neighboring voxels in the microstructure is based on the cellular automata rule. According to stoichiometry of the initial and intermediate compositions, autocorrelation of neighboring voxels, the growth in hydrates and water-filled pores is determined by the dissolution, growth and suppression of intermediate and accumulation of final hydrates. Within the VCCTL modelling, probabilistic automata provide many states and probabilistic transitions among them. Microstructures in the model are kept periodic in all calculations. Kinetics is influenced by temperature, water alkalinity and saturation in pores. Mechanical, physical and transport properties are calculated as a function of average parameters of the hydrate microstructure in the case of the known properties of initial clinkers, activation energy and chemical-reaction rates. A collection of quantitative data allows estimating the operating parameters of Portland cements over a long period of time.

Figures 1–3 plot the time dependences for sand cement hydration for 28 days at 20 °C and different water-cement ratios. One can see rather complex processes that occur in sand cement. In figure 1, the degree of hydration, specific heat capacity and chemical shrinkage are the highest at the initial stage of 10–200 hours, then these parameters monotonically decrease. After 650 hours, hydrates amount to 0.75 of the solid phase. The hydration degree in figure 1a correlates with the specific heat capacity in figure 1b, the pore volume in figure 1c and chemical shrinkage in figure 1d. The pore volume significantly decreases during the first 200 hours.
Figure 1. Time dependences of sand cement curing at 0.40, 0.44, 0.49 and 0.54 water-cement ratios: (a) – hydration; (b) – specific heat capacity; (c) – pore volume; (d) – chemical shrinkage.
Figure 2. Time dependences of clinker mineral curing \((a, b, c, d)\) and hydrates \((e, f, g, h)\) at 0.40, 0.44, 0.49 and 0.54 water-cement ratios.

Figure 3. Time dependences of sand cement mechanical properties: \((a)\) – bulk modulus; \((b)\) – shear modulus; \((c)\) – Young’s modulus; \((d)\) – Poisson’s ratio at different water-cement ratios:
1 – 0.40, 2 – 0.44, 3 – 0.49, 4 – 0.54.

The increase in the water-cement ratio up to 0.49 and 0.54 has a significant effect on the pore volume, which is close to 0.30 after 650 hours of curing. This indicates the high content of free moisture in sand cement. Chemical shrinkage almost does not depend on the water-cement ratio. According to figure 2a–d, the amount of C\(_3\)S (alite), C\(_2\)S (belite), C\(_3\)A (calcium aluminate), C\(_3\)AF (calcium aluminoferrite) clinker minerals considerably lowers. These clinker minerals do not fully dissolve after 650 hours. The different water-cement ratios of 0.40, 0.44, 0.49, 0.54 do not change much the degree of reduction in the C\(_3\)S and C\(_3\)A content. As can be seen from figure 2e–h, the following products appear during the
hydration process: C₃AH (hydrogarnet), C–S–H (calcium silicate hydrate), CH (calcium hydroxide or portlandite), and ETTR (ettringite). And C–S–H and CH are the main hydration products that provide the sand cement strength. The ettringite content is unimportant, it accumulates during the first 50–70 hours of curing and then lowers. With the water-cement ratio of 0.40, the C–S–H content grows more intensively during the curing process, and after 650 hours it is noticeably higher than at 0.54 and 0.49 water-cement ratio. In figure 3, one can see the time dependencies of the elastic properties of sand cement, viz. elastic bulk modulus, shear modulus, Young’s modulus and Poisson’s ratio, respectively for 0.40, 0.44, 0.49 and 0.54 water-cement ratios. Figure 3 shows that the highest growth in the effective elastic moduli during 150 hours, and then the curves achieve plateau. The water-cement ratio has a substantial effect on the elastic moduli. During the curing process, these moduli monotonically increase. However, the growth in the water-cement ratio significantly reduces the bulk, Young’s and shear moduli. The highest values of the elastic moduli are found at a 0.40 water-cement ratio. The VCCTL tool does not provide the parameters for calculating the stress-strain curves of the materials at issue [10–13]. It is found, that the yield stress monotonically increases and reaches the greatest values at 0.44 and 0.40 water-cement ratios, but with increasing curing time the difference in the values gradually lowers. The highest values of Young’s modulus are achieved at a 0.40 water-cement ratio, while at lower values of the latter, Young’s modulus considerably lowers, which is in agreement with the yield stress. The figures also show a good correlation between Young’s modulus and the yield stress, depending on the curing time. Figure 4 contains the plots for the yield stress and curing time at different water-cement ratios.

![Graphs of elastic properties and yield stress](image)

**Figure 4.** Time dependences of sand cement mechanical properties: 1 – Young’s modulus, 2 – yield stress at different water-cement ratios: a – 0.40, b – 0.44, c – 0.49, d – 0.54.

The addition of Young’s modulus and the respective values of the water-cement ratio in figure 4 allows us to determine the correlation between the experimental data on the yield stress and elastic
moduli. According to figure 4, the correlation is observed for these parameters at all the indicated ratios of water and cement. The similar dependencies are obtained in [14].

3. Conclusion
Using the VCCTL tool for the predictive modelling of sand cement curing during 28 days we obtained the time dependences for the degree of hydration, specific heat capacity, clinker phase and hydrate content and pore volume. It was found that after 28 days, the sand cement hydration was ~0.75. After 28-day curing, the pore volume was over 0.20 at 0.40 water-cement ratio, and increased to 0.32 at higher water-cement ratios. C–S–H predominated among other hydration products of sand cement. C–S–H and CH hydrates mainly determined the strength properties of sand cement. In the assumption of water-filled pores, sand cement retained a high content of free moisture. It was shown that the effective elastic moduli of sand cement rapidly grew during the first 200 hours and then monotonically lowered. The yield stress monotonically grew during the curing process, and at a 0.40 and 0.44 water-cement ratio achieved the maximum value, which correlated with the influence of the water-cement ratio on Young’s modulus. The high content of free moisture in the porous volume could cause an unfavorable fatigue effect during the operation.

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