Studying the Structure Formation of Cement Stone in the Presence of Fine-Disperse Additives

V. D. Cherkasov, V. V. Avdonin, D. N. Pronin, D. A. Varankina, and R. S. Rogozhkin

Abstract The study and creation of highly effective chemical additives and their complexes for the modification of cement systems is an urgent scientific and applied task of building materials science. The article discusses the role of the used finely dispersed additives in the process of structure formation of cement stone, provides data on the effect of these additives on the strength of the MZB. The possibility of creating an effective additive for hardening cement composites on average by 30%, with a dosage of not more than 1.5% by weight of cement based on fine carbon, is shown. This approach is distinguished by environmental safety, technological simplicity and economic efficiency.

Keywords Cement · Finely dispersed additives · Strength · X-ray diffractometry · Structure please · Carbon · Calcium titanate

1 Introduction

Obtaining concretes based on Portland cement binder with high performance properties and low cost is an important task of building materials science [1–4]. One of the ways to solve this problem is the addition of solid-phase finely dispersed additives (SDA) of a certain nature into the initial cement blend [5–15]. These are the TDD of particle surfaces, which, in our opinion, can interact with calcium ions in a solution of blended cement, either by an ion-exchange mechanism or by the principle of formation of colloidal micelles, depending on the nature of the additive.

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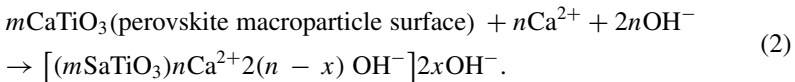Vyatka State University, Moskovskaya Street 36, Kirov, Russia

2 Methodologies

According to the first mechanism, the adsorption of calcium ions can occur on the surface of such adsorbents as coals of various types, according to the following scheme [16]:

$$coal^{2-}2H^+ + Ca^{2+} + 2OH^- \Leftrightarrow coal^{2-}Ca^{2+} + 2H^+ + 2OH^-. \tag{1}$$
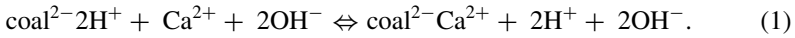
At the same time, calcium ions quite strongly bind to the surface of the coal; as a result, the formed charged particles can later play the role of additional crystallization centers for the products of primary hydration of cement (and this is mainly calcium hydroxide) from a supersaturated cement slurry. The uniform distribution of TDD particles in the original cement-containing system will ensure a more uniform flow of structure formation processes, and ultimately, an increase in the strength of the cement composite.

According to the second mechanism, the adsorption of calcium ions from an aqueous solution of lime can occur on the surface of hardly soluble solids, in the crystal structure of which there are calcium cations, in accordance with the Fajans-Panet rule. Such substances include, for example, natural mineral perovskite; calcium titanate. In this case the adsorption process will proceed according to the following scheme:

$$mCaTiO_3(\text{perovskite macroparticle surface}) + nCa^{2+} + 2nOH^-$$
$$\rightarrow \left[(mSaTiO_3)nCa^{2+}2(n-x)\,OH^-\right]2xOH^-. \tag{2}$$

3 Results and Discussion

To confirm the above assumption the experiments were carried out to study the effect of fine particles of coals of various types and calcium titanate on the strength characteristics of fine-grained concrete, which are shown in Fig. 1.

From the presented data it follows that the additives used in relatively small amounts relative to the mass of the binder significantly increase the strength of cement concrete. So the maximum increase in strength is achieved with an additive amount of about 1% by weight of cement, and is: 34%—for carbon MUI 99; 28%—BAU-A coal; 23%—for calcium titanate. The most effective TDD tested was carbon MUI 99.

To establish the possibility of interaction of calcium ions with the surface of the particles of the additives used in the cement mortar, X-ray diffraction research [17] of cement composites modified with carbon, coal, and calcium titanate was carried out on an Empyrean Panalytical X-ray diffractometer in the filtered radiation of a copper anode with a Pixel 3D semiconductor detector. Portland cement M500
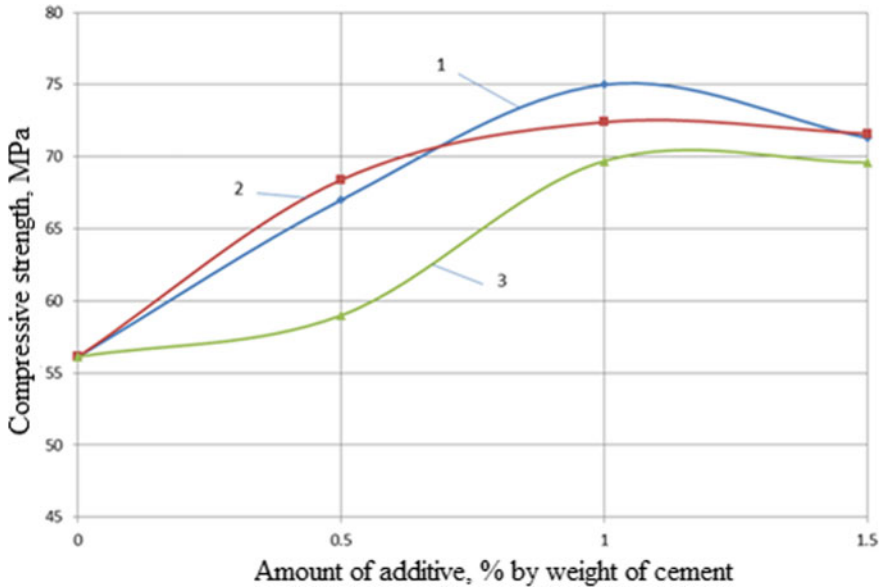
Fig. 1 The strength of the MZB depending on the amount of additives from the mass of cement, where: 1—carbon MUI 99; 2—BAU-A coal; 3—calcium titanate. Materials: cement—750 kg/m^3; sand (0.8–2 mm)—1000 kg/m^3; sand (0.16–0.63 mm)—500 kg/m^3; W/C $= 0.3$; GP (MasterGleniun) $= 1\%$

was used as the initial binder. X-rays were taken after 28 days of hardening. The analysis of the obtained results showed that for the sample without additive (C-1) (Fig. 2) the intensity of Ca(OH)$_2$ reflections (interplanar distances d = 4.93; 3.11; 2.63; 1.79; 1,69 Å and double Bragg angles 2θ = 17.98; 28.60; 34.04; 50.75; 54.28°, respectively) are significantly larger than for samples with additives. The lowest values of the intensity of reflections of lime are noted for the sample with the addition of carbon (G-1). In samples with additions of charcoal and CaTiO$_3$ (Y-1 and K-1, respectively), these values are approximately equal, but higher than in the sample with carbon addition. Possibly, the lower reflection intensities of lime in the presence of carbon-containing additives compared to the control sample are associated with the adsorption of Ca(OH)$_2$ on carbon particles.

At the same time, the intensity of the diffraction lines of calcite (Fig. 3), in particular at d = 3.029 Å (2θ = 29.47°) is much greater for the sample with the addition of carbon, which may indicate the activation of the carbonization process in the presence of a large amount of lime F.
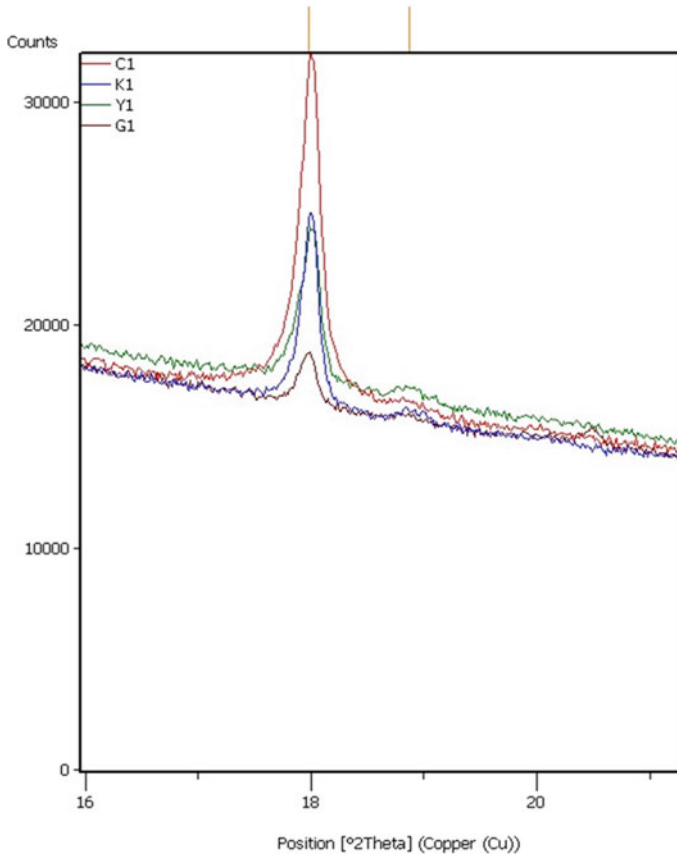
Fig. 2 Intensity of reflections of lime, where: C 1—cement without additives; K 1—calcium titanate; Y 1—BAU-A coal; G 1—MUI 99 carbon

For the sample without additive, the lowest value of the intensity of calcite reflections was noted. In samples with the addition of charcoal and $CaTiO_3$, the value of $CaCO_3$ reflections is higher than in the control sample, but significantly lower than in the sample with the addition of carbon. This allows us to assume that in samples with additives (and especially in the sample with the addition of carbon), the increase in strength can partially occur through the carbonate mechanism.

The value of the reflection intensities of anhydrous calcium silicates (Fig. 4) (d = 2.706–2.607 Å; 2θ = 32.22–32.61°) for all samples is approximately equal, but for samples with carbon and $CaTiO_3$ additions, it is slightly less than for the control composition and composition with the addition of charcoal. This may indicate that the hydration process in the samples with carbon additions proceeds in a more active form. The difference in the degree of conversion for the samples with the addition of carbon black and charcoal may be due to the difference in particle sizes and their specific surface area.
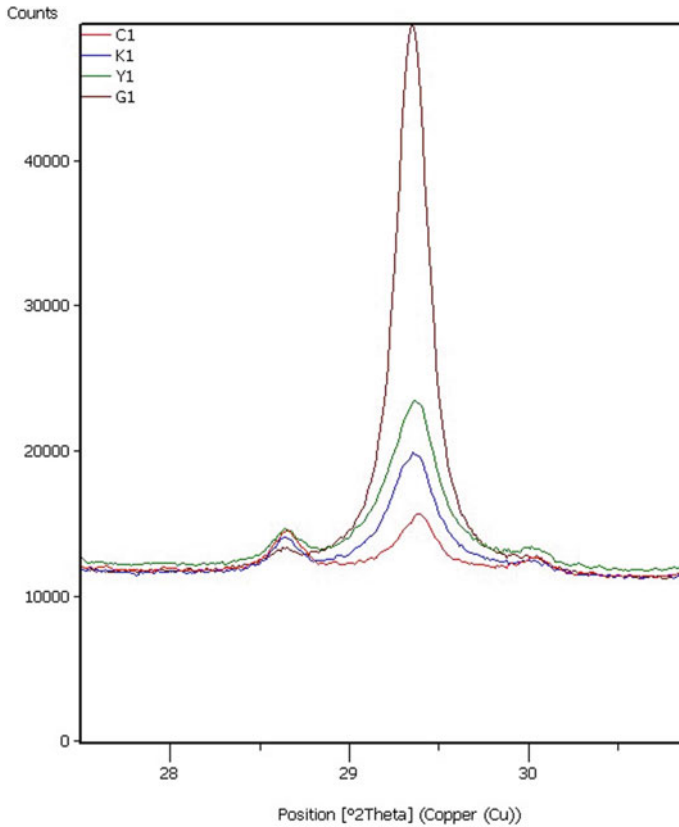
Fig. 3 Intensity of calcite reflections, where: C 1—cement without additives; K 1—calcium titanate; Y 1—BAU-A coal; G 1—MUI 99 carbon

At the same time a corresponding change in the intensity of lime reflections is clearly not observed. It can be assumed that part of $Ca(OH)_2$ binds to other hydrated phases (part of Ca^{2+} ions may be in the structure of ettringite formed at the early stages of hydration) or is adsorbed in crystalline form on particles of charcoal or carbon.

The intensity of ettringite reflections (Fig. 5), (d $=$ 3.88; 2.29; 2.23 Å; $2\theta =$ 22.9; 39.31; 40.42º) is somewhat higher in samples with the addition of carbon and charcoal, which probably indicates the activation of the formation of this phase.
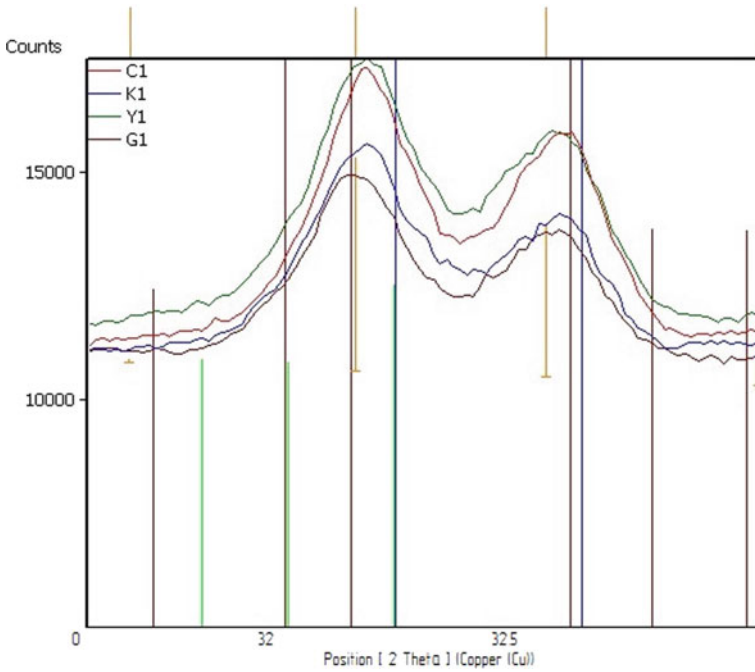
Fig. 4 Intensity of reflections of anhydrous calcium silicates, where: C 1—cement without additives; K1—calcium titanate; Y1—BAU-A coal; G1—carbon MUI 99
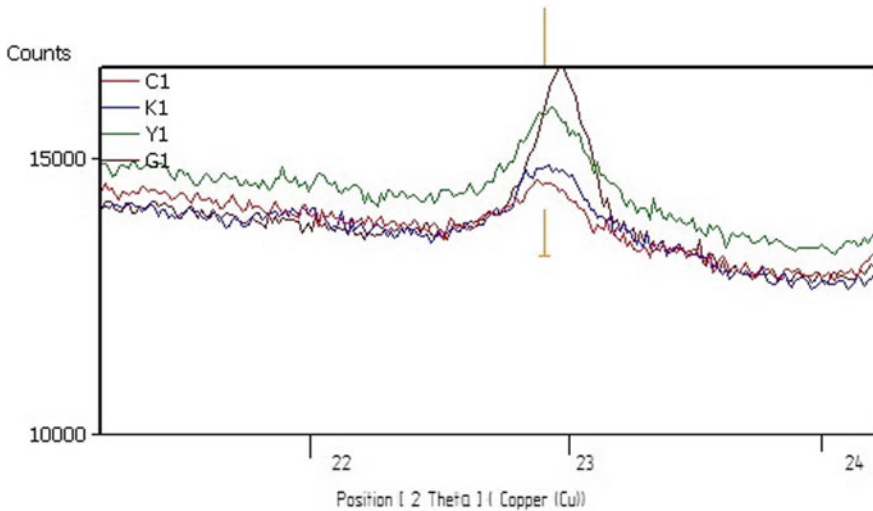

Fig. 5 The intensity of reflections of ettringite, where: C 1—cement without additives; K 1—calcium titanate; Y 1—BAU-A coal; G 1—MUI 99 carbon

4 Conclusions

The obtained results of X-ray phase analysis confirm, to a certain extent, the theoretical assumptions about the active participation of the used additives in interaction with calcium ions in the blended cement slurry in the primary processes.

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