Express-method of determination hidroactiviti of Portland cement

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Abstract. Basic problems are touched for existing methods of Portland cement binding properties control. Some of them consist in the fact that direct methods for Portland cement clinker and Portland cement physical-mechanical activity determination are too time-consuming, which does not enable timely correction of their properties directly in the course of production process. Others are connected with insufficient definitiveness of cement behavior with water depending on the value of its phase-forming minerals condition regulated parameters in their totality. We introduced the term “hydroactivity of Portland cement” for quantitative characterization of its part capable under certain conditions to transfer to liquid phase after cement mixing with water. An instant control method for produced Portland cement was developed based on direct connection between its hydroactivity and binding properties. Terms were substantiated for binder material hydroactivity determination under which the obtained results characterize more exactly the initial condition of material under analysis. A stage-wise description is given of application of the proposed shortcut method of hydroactivity determination for Portland cement clinkers, various classes of Portland cement and certain model systems. The proposed control method for properties of Portland cement clinker and Portland cement enables production of cement with assured activity under optimal relation between production expenses and obtained product quality.

Introduction

The essence of Portland cement (PC) quality control lies in determination of its parameters matching to valid requirements [1]. Methodology of this control includes two basic lines. One of them is connected with determination of PC behavior under interaction with water, such as under hardening [2]. Another one implies control of condition parameters of Portland cement clinker (PCC) and PC and subsequent prediction of their behavior, issuing from the results of such control [3, 4]. The first approach is too time-consuming, which makes difficult timely control action on clinker furnace and milling unit product quality control. Besides, the very part of PC interaction activity with water and obtained results of its physical-mechanical strength are blurred by properties of contact area formed on quartz filler surface.

The advantage of another approach lies in its promptitude. It was just this circumstance that enabled PCC burning process adjustment depending on appearance of unabsorbed calcium oxide (CaOfree) and crystallization pattern of its minerals determined by petrography directly at furnace head. Nevertheless,
the authors suppose that currently applied methods of PC minerals condition parameters estimate do not ensure in the totality of their results the ability to unambiguously predict cement behavior under its interaction with water.

Analysis of recent research
It should be noted that within last several decades methods of PC physical-mechanical properties control never actually changed as regards their essence [2]. At the same time methods of PCC and PC condition determination have been substantially improved. Thus, for instance, for determination of PCC and other cement materials phase composition X-ray phase analysis was widely applied using Rietveld method [5]. This method permits quite prompt determination by progressive approximation of not only quantitative phase composition of tested PCC, but also of crystallographic peculiarities of its phase-forming minerals structure. Besides, for evaluation of PC grinding fineness in addition to its specific surface determined by air permeability [6], laser analyzers are widely used which also enable to obtain cement particle size distribution function as well [7]. Nevertheless, as far as known to authors, Rietveld method fails to discover small catalytic-active impurities in tested samples, whereas laser analyzer and Blaine method are unable to determine condition of PC particles surface. Meanwhile, these factors are substantially important in formation of PC binding properties [8].

It follows from the above that a search of new efficient PC running quality control methods is prospective in analysis of PC behavior under accelerated interaction with water, as the latter is closely connected with all parameters defining condition of both Portland cement clinker and Portland cement.

Purpose and object of study
Development of a new method of PCC and PC behavior control under their interaction with water, which enables to obtain real-time information on current condition of these materials quality in the course of their manufacture.

Theoretical substantiation and development of method
The authors suppose that for online control of PCC and PC quality it is most feasible to make use of their ability of interaction with water, by determining it at an accelerated rate. The selected rate must ensure participation of a significant part of tested sample in formation of the results of said ability. Such an approach will enable real-time determination of all apparent factors connected with condition and behavior of phase-forming cement minerals and concomitant additives in tested materials.

The proposed method may be based on known truth that 28th hardening day ultimate compression strength of small-beam cement samples is in direct proportion to the number of hydrate compounds forming cement rock [8]. These compounds are formed in interaction of calcium silicates, aluminates and alumoferrites with water [9]. Their source in cement is Portland cement clinker and mineral additives which become able of demonstrating their latent activity due to alkaline properties of PC clinker parts [10]. Hydrate new formations are basis of hardening cement grout which unites cement fillers into a conglomerate strengthening in time.

To enable disclosure of PC binding properties, transfer of products of its minerals hydration, hydrolysis and dissolution into mixing water is necessary, but not sufficient, as certain terms are also required for solid formation from cement grout liquid phase. In case these terms do not meet their required values, PC binding resource may not be efficiently utilized. An example is PC hardening under too high water/cement ratio (W/C).

Within the frames of the above provisions, the results of small-beam cement sample strength determination from various cements may be interpreted as collation of the value of their active part which transferred to mixing water and was successfully realized as hardening binding material. The dynamics of
this phenomenon may be divided into two simultaneous processes, one of which is connected to PC mineral-forming materials being absorbed by mixing water, whereas the other one consists in cement grout solid phase formation on their basis. The first process depends on PC condition parameters, such as its phase composition, structure defects of phase-forming minerals, especially at phase borders, and appearance of catalytic-action impurities in them. The second process mostly depends on parameters of the cement grout being formed and on environment conditions. Both the first and the second processes may act as limiting factors as regards final results of PC hardening. This is due to the fact that dynamics of cement minerals matter transfer into liquid phase may also depend on release rate of new formations from it.

Our analysis shows that under the existing terms of PC physical-mechanical activity determination the obtained results depend on mutual behavior of tested material and products of its reaction with water. We may obtain necessary terms under which analysis results would better characterize initial material by itself, by way of PC active kneading at high W/C values. Measuring the residual amount of PC solid phase after such kneading would enable to define its part which transferred to liquid phase under experimental conditions, i.e., showed activity. The result obtained in this way would not actually depend on the behavior of PC reaction products with water. To designate this PC property we offer the term “Portland cement hydroactivity”. This term reflects the amount of PC matter which is able of transferring into water after its mixing. This amount may be expressed in per cent of tested material initial mass. This parameter, as distinct to its applicable counterparts, firstly characterizes the properties of PC matter by itself. For instance, the applied value of PC physical-mechanical or binding activity characterizes behavior of not only initial material, but also of forming cement grout and contact between cement rock and surface of added filler [8]. Other applied characteristics, such as PC hydraulic and hydration activity, are also connected with cement grout behavior in water and with condition of its liquid phase [8].

The ability of real-time determination of a parameter whose value firstly characterized properties of PCC and PC by themselves enables online control of condition of these binders directly in the course of their manufacture and consumption. The application of the control method may be presented as PCC and PC matter activity testing with water. In this case the totality of all properties inherent in tested materials takes part in formation of tested activity value. See below a description of the proposed determination sequence of cement matter hydroactive part.

**Equipment and materials**

In our work we applied: analytical balance, constant rpm impeller mixer, centrifuge, drying cabinet, muffle furnace below 1000 °C, photoelectric colorimeter, known concentration calcium chloride solution, double-distilled water, PCC, CEM 42.5 and CEM 32.5.

**Results and discussion**

**Results of method execution** Necessary amount (100 mg) of tested material sample was taken by quartering and brought to impeller mixer vessel with 100 ml of double-distilled water. Slurry concentration was 1 g/l, kneading time 10 minutes. After kneading the slurry was immediately brought into centrifuge working area to separate liquid and solid phases. After 3 minutes centrifuging liquid part was carefully drained, whereas vial with wet sediment brought into drying cabinet at 105 °C and dried up to constant mass. As drying took about 10 minutes and during this time a certain part of sample bound some water, the ignition loss of obtained dry residue at 1000 °C was also estimated. After that we calculated how much initial binder transferred to water under experimental conditions. The obtained results for samples of PCC, CEM 42.5, CEM 32.5 are shown in Table 1.

The authors have earlier developed a determination method for amount of calcium capable of transferring into water under similar terms [11]. If we use this method, having previously determined total calcium content in initial samples, we may estimate the degree of PC matter absorption at interaction with
water issuing from the amount of calcium that transferred into water relative to its initial content, with due consideration of the fact that it is uniformly distributed in fine-grained meal.

In the present work calcium content in cement slurry liquid phase was measured after centrifuging of the same samples than before as described in [11]. Calcium content in initial samples was determined beforehand. Results of second method application are also shown in Table 1.

| nn | Cement types | Initial mass (mg) | Mass residue (mg) | Hydroactivity (%) | Initial CaO mass (mg) | CaO mass in liquid phase (mg) | Hydroactivity (%) |
|----|--------------|------------------|------------------|------------------|----------------------|-------------------------------|------------------|
| 1  | PCC          | 100              | 69.4             | 30.6             | 66.7                 | 20.2                          | 30.3             |
| 2  | CEM 42.5     | 100              | 71.2             | 28.8             | 60.6                 | 17.4                          | 28.7             |
| 3  | CEM 32.5     | 100              | 75.9             | 24.1             | 56.1                 | 13.9                          | 24.8             |

As we see, the results of this measurement do not actually differ from previous one.

To determine the character of connection between PC hydroactivity and its physical-mechanical properties we used model systems obtained by mixing CEM 32.5 and CEM 42.5, gradually substituting less active cement for more active. After that we measured hydroactivity of obtained model cements and determined the hardness of cement-sand samples prepared on their basis. Thew samples hardened within 12 hours after their formation at 40 оC with cement/sand ratio 1:1 and W/C = 0.45. The revealed dependence between hydroactivity of model cements and hardness of samples made on their basis is shown in Fig.1.

Control of physical-mechanical properties of tested PCs by the value of cement rock hardness was already applied in earlier works by authors [12]. This method is simple and easily accessible.

![Fig. 1 Connection between hydroactivity of used model cement systems and hardness of cement-sand grouts made on their basis](image_url)

As seen from the plot, the obtained dependence is direct and sufficiently monotonous.
The materials of our research prove that PC absorption with water may be controlled by weight method using drying and calcination of solid residue, as well as by results of calcium double determination in initial sample and in liquid phase after kneading. Calcium content in PC is better determined by plant online quantometer, whereas in liquid phase preferred methods are ionometry; flame photometry; chemical methods or photoelectric colorimetry with special indicators. Single sample analysis never takes more than one hour.

**Conclusion**

The newly introduced parameter of hydroactivity first of all characterizes the condition of PCC and PC matter by itself.

The proposed control method for this parameter enables obtaining, on a par with PCC and PC characteristics, test of cement plant equipment operation efficiency. This capability permits output of cement with warranted properties at optimal relation between production expenses and quality of final product.

PC hydroactivity determination method may be also applied for accelerated quality control of cement incoming to plants manufacturing concrete and reinforced concrete articles.

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