Flowability and durability of cement containing technological additives during grinding process

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Abstract—This paper considers the major factors influencing cement flowability and its conservation in humid environment with the presence of processing additives during grinding. It describes cement flowability quantitative measurement methods developed and introduced by the authors and implemented on the basis of several cement plants of Russia. The influence of storage conditions on altering cement flowability in humid environments, which simulate absorption of significant moisture quantity in the accelerated mode, was studied. The influence of grinding intensifiers on cement flour rheological characteristics and their conservation under the conditions of storing cement in humid environments was studied as well. The correlation regression analysis of the impact of physical and chemical characteristics of the samples of cement on its flowability was performed. As follows from the analysis, cement flowability has weak correlation dependence on studying variables, which indicates it being influenced by a variable factor not quantitatively measured yet.

Keywords—grinding intensifiers, cement flowability, flowability conservation, humid environment.

I. INTRODUCTION

According to the structure systems’ classification, offered by N.B. Urjev [1], cement flour can be categorized as disperse systems with the condensation structure and with the strength reversibility of junctions between particles as a result of plastic deformation when compacting. Along with the elaborate interphase surface, which specifies the characteristics of many cement flours being highly dispersive systems, their structure-rheological properties, such as irreversible shear deformability (flow), emerging of reversibly destroyable junctions between particles (structuring), etc. are of a great importance. Transition from the free disperse structure (aerated flour) to cohesive-disperse systems (after being stored in silos for a long time) drastically changes major structural-mechanical properties, such as mobility and flowability. Flours structure rheological characteristics are vital with such technological operations as homogenizing, piping, under the conditions of loading and unloading a transport vehicle. Flowability is, basically, a combination of physical properties of material, environmental conditions and equipment used for materials processing and storing [2]. Anticipating cement flour flowability assists in preventing stoppage in production with regard to all loading-unloading operations.

Cement flour flowability problems occurred under the conditions of excessive demand for the bagged cement and adoption of the technology of grinding cement along the close-loop lines with separators. The causes of degradation of cement flour flowability have not been fully studied yet. The major reason supported by a lot of research is the complicated correlation between the surface energy of specific cement grains and the flow of the same particles. The surface energy depends on many factors during cement manufacturing: grinding fineness, the type of grinding equipment, types of rotating furnaces and the method of production (wet or dry), burning and cooling temperature, the cooling rate [3].

Flowability of mineral flour is influenced by a great variety of factors being as follows: particles’ size and shape, percentage of moisture, temperature, airflow rate with aerating transportation, etc. The particles’ size and shape and their classification according to the size play the significant role in flowability and other properties such as packed density, angle of friction, flours compressibility. Even a minor change of
particles can lead to significant changes of flours mobility. A decrease of the particles size leads to the reduction of the flowability of certain flour [4-5]. The smaller the size of particles and the larger the range of particles size distribution, the higher the adhesive power and the lower the flowability are [1, 6]. There are several empirical regularities: hydrophobic flours disperse better than the hydrophilic ones; the flours derived from solid minerals disperse better than the flours derived from the soft ones; the monodisperse flour disperses better than the polydisperse one. Flowability can be improved by fluidization [7].

Caking is triggered by non-coherent material having been at rest for a long time [8]. Caking causes the following concurrent processes:

1) The first one is connected with the increase of junctions amount N caused by gradual penetration of small particles into the space between the large ones.

2) The second one is invoked by gaining the strength of junctions due to the gaps filling. Both processes lead to non-coherent material strengthening in general and to the loss of its mobility right up to monolith formation.

When storing cement and other powdery material in silos and bins, lower layers intensely densify under the pressure of the overlying layers. As a result, the material cakes forming the craters with firm walls, which drastically hinders material unloading. Caked material loses flowability, herewith, the angle of friction grows. Specifically, the angle of friction of the compacted cement reaches 90°. The density of the low layers of cement kept in silo reaches 1.7 t/m³ due to the gradual compacting, while its overlying layer has the bulk weight equal to 0.75 t/m³ at air-feeding and has a high flowability.

To add flowability, silos bottoms are equipped with aerating elements, which direct the compressed air into a silo. Compressed air flow rate required for aerating cement in a silo is equal to 0.4 nm³/min over the surface 1 m² large; herewith, the compressed air must be unoiled and cleared from moisture. According to experimental findings, compressed air rate required for the pneumatic unloading is equal to 2-3 nm³/min per 1 ton of cement depending on the haul length [9]. In the absence of due air dehumidification in spring and autumn, from 1 to 4 kg of water can get into a silo. In case of continuous storage of cements under the conditions of interaction with moisture and CO₂ new products emerge [10]. As a consequence, cement flowability can drastically decrease according to the storage time and the environment conditions.

Cement surface hydration can start during the material production due to dehydration of gypsum in the cement mill or with the application of water solution being the intensifier in case of poor mill aspiration. Water absorption can continue during the storage of fresh cement in bins, while gypsum continuous transpiring crystallization water favouring hydration at elevated temperature (>42°C) [10].

Research [11] has shown that surface hydration can drastically alter cement properties with regard to the characteristics of flowability and durability. The paper [12] determined threshold values of air humidity for all types of clinker cement and sulfate carriers, as well as for calcium oxide, which trigger moisture absorption. The research has shown that the amount of moisture vapor absorbed by its separate components in a multicomponent system is rather different. Calcium oxide and tricalcium aluminate C₃A of rhombic crystal system, which absorb water at 55% of relative humidity, are especially hydroscopic. As for C₂S of rhombic crystal system, water absorption starts at 80% of relative humidity, while silicates (C₃S and C₄S) absorb only a small quantity of water at 64% of atmospheric relative humidity. Water is absorbed due to the chemical and physical processes such as water film which is only several millimicron thick.

The most efficient way of caking flours is the modification of particles surface with the help of surface active agents, hermetization of storage facilities and thorough dehumidification of aerating air.

The corresponding test equipment is used for detecting the flours rheological characteristics [13-14]. However, the practice of consistency measurement indicates that there is not even a single test capable of complete quantitative correlation of the mobility of various mineral powders and different influencing factors [14-15]. Cement flour can produce the effect of arching, thus, the application of standard flow tests is not suitable in such fields as food or pharmaceutical industries. Generally, the cement flowability is estimated by indirect indicators at cement plants. American Society for Testing Materials suggests the qualitative method of determining cement flowability by the ASTM 1565-04 method [14-15]. The essence of this method lies in sifting weighed cement through sieve number 05 on a shaking table Hagerman (Fig.1). Cement flowability is high if more than 50% of material gets through the sieve when shaking.

Let us suggest applying the second method of determining cement flowability at cement plants which have the vibrating sieves with the option enabling one to control the amplitude and time of vibration.

![Fig. 1. Method of determining cement flowability by the ASTM 1565-04 method: a) a shaking table Hagerman with sieve number 05 installed on it; b) loading material on sieve number 05](image-url)
conversely, the reduction of remainders amount on the sieve equal to more than 50% denotes the increase of material flowability. This method was developed by the authors of the given paper with the objective to control cement quality for JSC “Sengeleevsk cement plant”. The stated methods were implemented at the cement plants of international industrial Holding company “Eurocement group”, CJSC “Serebryakovsk cement plant”, a set of plants of “LafargeHolcim” holding, etc. with the objective to control grinding intensifiers operating efficiency according to the recommendation of the authors and with their direct involvement.

The objective of the given research was to study the impact of grinding intensifiers on rheological cement characteristics and their properties retaining under the conditions of humid environment.

II. METHODOLOGY

The study of cement flowability and of the influence of various factors on this characteristic was carried out under the conditions of production experiments over a processing additive being a grinding intensifier of the range Litoplast AI, produced by LLC «Polyplast » in open-cycle mill 4x13.5 m. The grinding intensifier was transferred to the clinker conveyor with the ratio of 200 g to 1 ton of cement during the production of cement of CEM II/A-S 32.5B type. 30 cement samples have been taken immediately after being taken out of the mill at regular intervals during 2 days. The samples taken were analysed according to the following parameters: cement temperature, chemical and material compositions, fineness of grinding over the surface area and distribution of granulometric particles size. Cement flowability was checked by the ASTM method immediately after its exiting the mill and after cooling samples to room temperature.

The environments with the temperature equal to 25°C and relative humidity of 30, 75 and 100% were created in closed bins with the objective to carry out the research on the impact of storage conditions on altering the cement flowability. The environments in which the cement samples were stored were created by:

a) saturated solution of sodium chloride NaCl at the following concentration c=33 %; relative humidity of 75% in a bin (the stated storage conditions were created according to State Standard 29244-91);

b) solution of glycerin (CH\(_2\)OH)\(_2\)CHOH (with the following density \(\rho=1.225 \, g/cm^3\) at the following concentration c=97.9 %); relative humidity of 30% in a bin (State Standard 29244-91);

c) water \(H_2O\); relative humidity of 100% in a bin.

In spite of the fact that these conditions do not meet the requirements of storing cement in silos and closed bins, they enable one to simulate the absorption of a significant amount of moisture in the fast mode.

Two freshly ground cements of laboratory milling taken from industrial clinkers with the content of tricalcium aluminate 9.6% (pattern index OC) and 3.1% (pattern index KC) respectively were applied to study the conservation of properties in humid conditions.

The industrial sample of grinding intensifier Litoplast AI (pattern index AI) produced by LLC “Polyplast Novosmoskovsk” was selected to act as a processing additive during grinding. For comparison, cements with the water-repellent agent of oleinic acid (pattern index OL) were ground.

The alterations of the properties of cement kept in these environments were fixed according to the changes of such parameters as appearance, loss on ignition (LoI) and flowability with regard to three parallel samples.

III. MAIN PART

In the course of research, the party of cement CEM II/A-S 32.5B was manufactured in one silo. Cement CEM II/A-S 32.5B included blast-furnace granulated slag whose content, regulated by State Standard 30108, made from 6 to 20 pts. Ranges of blast-furnace slag in cement composition during the grinding process are demonstrated in figure 2. An average amount of slag in the party over the time of research was equal to 16.5%. As one can see, the fluctuation limits of slag weight ratio are rather large: from 7 to 25%. The graph shows rather rapid jumps of blast-furnace slag content (samples 5, 17, 18). These fluctuations were caused by slag hanging in bins and irregularity of its loading into the mill. This has adversely affected cement grinding capacity and flowability. In case of increasing the quantity of slag in cement composition with the aim to provide a required grinding fineness over the remainders on the sieve number 008, the mill productivity decreased by 1-2 tons.

The temperature of cement after the mill was measured by a built-in device and was displayed on the mill operator panel, while surface area was measured by Blaine apparatus. Cement particle composition was determined by the device ANALYSETTE 22 produced by the firm FRITSCH. According to the analysis report, the particles weight ratio up to 3mkm, from 3 to 30 mkm, from 30 to 80 mkm and more than 80 mkm were singled out.

The outcomes of alteration of physico-chemical characteristics of the selected cement samples are introduced in Table 1.

The method of correlation regression analysis was applied for studying the dependence of cement flowability on various factors. This method studies the correlation of indicators when
the dependence between them is not strictly functional and is distorted by the influence of secondary random factors. Correlational-regressive analysis is carried out in module Descriptive statistics of the program STATISTICA.

Covariance analysis was applied for quantitative measurement of tightness and direction of pairwise correlation between sampling variables (factors) \((P_i)\) and output parameters \(B_1\) and \(B_2\) – flowability determined at different temperatures. Assessment of bonding force was made via Cheddok scale: weak – from 0.1 to 0.3; moderate – from 0.3 to 0.5; prominent – from 0.5 to 0.7; high – from 0.7 to 0.9; very high (strong) – from 0.9 to 1.0.

An algorithm in module Descriptive statistics implies calculating the coefficient of Pearson correlation in supposition that the variables under research are distributed along the normal law. The results of correlation analysis are demonstrated in Table 2.

The results of correlation analysis have shown that the coefficient of linear correlation of two variables changed from \(-0.04\) (factor \(P_6\)) to 0.31 (factor \(P_2\)) for the output variable coefficient of linear correlation of two variables.

The coefficient of Pearson correlation is calculated by the following equation:

\[
y = b_0 + b_1 P_1 + b_2 P_2 + \ldots + b_i P_i, \tag{1}
\]

where \(b_0, b_1, b_2, \ldots, b_i\) are regression coefficients.

Regression coefficients indicate the effect of variable factors on the exit indicator. Coefficient \(b_0\) is equal to the resulting indicator value collectively. Coefficients \(b_1, b_2, bi\) show the number of units, which the level of exit indicator \(B_1\) or \(B_2\) deviates its average value by, if the variable factors values deviate from the medium one, which equals zero, by one standard deviation. Thus, regression coefficients characterize the degree of significance of particular factors for increasing the level of exit indicator. Specific regression coefficients values are determined by empirical data according to the least square method (as a result of solving system of normal equations).

The significance probability level was given as \(a = 95\%\). The significance of the coefficients of multiple correlation \(R\) in the equation was checked by \(F\)-Fisher LSD by calculating its actual value and comparing with the tabular data.

Squared correlation coefficients are the determination coefficients which determine the degree of variation certainty of one variable factor in table 1 indicating of variable factors in table 1.

The results of regression analysis are presented in Table 3.

The results of regression analysis have shown that all coefficients in the regression equation have very low values, i.e. almost all variable factors have insignificant influence on the exit parameter. This fact is proved by low determination coefficients \(R^2\), whose values do not exceed the point 0.43 for

| TABLE II. COEFFICIENT OF DOUBLE CORRELATION DEPENDENCE |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Output parameter | Variables* | \(P_1\) | \(P_2\) | \(P_3\) | \(P_4\) | \(P_5\) | \(P_6\) | \(P_7\) |
| Fluidity after the mill | 0.05 | 0.31 | 0.01 | 0.05 | 0.03 | -0.04 | -0.05 |
| Fluidity at the temperature of 25°C | -0.36 | 0.33 | 0.08 | -0.09 | -0.09 | 0.2 | -0.04 |

* - indication of variable factors in table 1

To provide the concurrent interconnection between the outer parameter \(B_2\) (flowability at 25°C) and several independent variables \((P_i)\) the regression analysis of Pearson correlation was applied. Linear dependence of multiple-factor regression is described by the following equation:

\[
y = b_0 + b_1 P_1 + b_2 P_2 + \ldots + b_i P_i, \tag{1}
\]

where \(b_0, b_1, b_2, \ldots, b_i\) are regression coefficients.

Regression coefficients indicate the effect of variable factors on the exit indicator. Coefficient \(b_0\) is equal to the resulting indicator value collectively. Coefficients \(b_1, b_2, bi\) show the number of units, which the level of exit indicator \(B_1\) or \(B_2\) deviates its average value by, if the variable factors values deviate from the medium one, which equals zero, by one standard deviation. Thus, regression coefficients characterize the degree of significance of particular factors for increasing the level of exit indicator. Specific regression coefficients values are determined by empirical data according to the least square method (as a result of solving system of normal equations).

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the concurrent influence of tree factors \((P1+P2+P3)\). In other words, there is 43% of certainty that these factors influence flowability. The remainder 57% refer to the influence of unknown factors. Coefficient \(R^2\) has the value equal to 0.12 for the particle composition \((P4+P5+P6+P7)\), which also failed to prove the influence of particle composition on cement flowability. Presumably, this insignificant fluctuation of particle composition leads to slight alteration of cement flour composition.

The assessment of adequacy of the computational model of the flowability dependence on all the variables selected by the Fisher criterion has also proved insignificance of statistical models: inequation \(F_{\text{comp}} < F_{\text{tabl}}\) fulfilled in all considered combinations.

Apparently, the correlation between cement flowability and all selected variable parameters was not found. It justifies the fact that cement flowability is influenced by other random parameters not considered in the given experiment.

A set of experiments was conducted with the objective to study the influence of processing additives on moisture absorption and conservation of cement flour characteristics in the situations of storing under the conditions of different humidity. Cements from the industrial clinkers of two cement plants were ground in the laboratory. Flowability, appearance and losses during firing and storing in humid environments were determined for the mentioned cements. Tables 4 – 6 present the average results on three samples.

**TABLE III. COEFFICIENT OF REGRESSION LINEAR EQUATION AND FISHER CRITERIA**

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Variables*</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
<th>(P1+P2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
<td>(P1+P2)</td>
</tr>
<tr>
<td>Coefficient(R^2) (coefficient of determination)</td>
<td>0.19</td>
<td>0.43</td>
<td>0.19</td>
<td>0.12</td>
<td>0.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fisher (c)</td>
<td>2.399</td>
<td>2.92</td>
<td>2.69</td>
<td>2.495</td>
<td>2.245</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The coefficient of determination</td>
<td>3.32</td>
<td>2.29</td>
<td>2.435</td>
<td>2.69</td>
<td>2.495</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*- indication of variable factors in table 1

**TABLE IV. ALTERATIONS OF CEMENT SAMPLES APPEARANCE AFTER BEING STORED IN HUMID ENVIRONMENTS DURING 6 DAYS**

<table>
<thead>
<tr>
<th>The storage/environment settings:</th>
<th>Relative humidity</th>
<th>30%</th>
<th>50%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>The index of the sample of clinker</td>
<td></td>
<td>OC</td>
<td>KC</td>
<td>OC</td>
</tr>
<tr>
<td>The index of technological additives in the grinding of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The appearance of the sample powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The outcomes testify that the surface fractionally gains hydrophobic characteristics in the presence of processing additives, which must favour time elongation of storing cement in closed bins.

With the increase of the relative humidity of storage environment, the amount of agglomerates increases in all cement samples. The amount of agglomerated particles with the presence of processing additives is between the clear sample and sample with oleinic acid. It indicates active absorption of organic intensifier’s molecules on the surface of cement flour. The procedure of absorption of intensifiers’ anion-active molecules implies that solid particles are to be arranged by polar groups and by hydrophobic ends outwards the surface. Such arrangement results in slower vapour absorption along with surface particles hydration avoidance.

**TABLE V. CHANGING LOSSES ON SAMPLES IGNITION AFTER 6 DAYS OF STORING IN HUMID ENVIRONMENTS**

<table>
<thead>
<tr>
<th>The index of the sample of clinker</th>
<th>The index of intensifier</th>
<th>The loss at calcination after conditioning at a relative humidity of storage environment, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>The index of the sample of clinker</td>
<td>The index of intensifier</td>
<td>30%</td>
</tr>
<tr>
<td>OC</td>
<td>clear</td>
<td>0.755</td>
</tr>
<tr>
<td>KC</td>
<td>clear</td>
<td>0.790</td>
</tr>
<tr>
<td>OC</td>
<td>1AI</td>
<td>0.11</td>
</tr>
<tr>
<td>OC</td>
<td>OL</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Significant change of losses on sample ignition occurs when they are stored in the environment with the relative humidity which is higher than 75%. Changes of flour under such conditions can be compared with the accuracy of the moisture determination method. It is worth mentioning that a significant increase of samples’ humidity was indicated under the conditions of their storage at 100% humidity; however, it is true for clear compositions.
Flowability of cement flour (Table 6) decreases with the increase of the relative humidity of storage environment, notably, the percent of flowability reduction is significantly higher for clear compositions. The decrease of cement flowability under the conditions of storage characterized by 30% of relative humidity does not exceed the value of accuracy of the determination technique.

IV. CONCLUSION

Structural-rheological properties of cement flour, particularly, its flowability, play a significant role in providing continuous execution of a set of technological operations in the process of its production and loading for the customers.

Notwithstanding this, nowadays the opportunities to adjust and anticipate these characteristics, specifically, by means of applying grinding intensifiers are not studied sufficiently.

The research results given in this paper enabled one to evaluate the influence of cement physical-chemical parameters and its storage conditions on rheological properties of material – flowability and cement conservation in the situation of applying technological additives when grinding.

V. OUTCOMES

Application of the developed techniques of determining cement flowability on the basis of ASTM1565-04 standard and with the use of vibrating sieve enable one to evaluate cement flowability in a qualitative way and obtain consistent results concerning the efficiency of the applied grinding intensifier.

The outcomes of correlation-regression analysis of the flowability of cement with grinding intensifier indicate that cement flowability has a weak correlation dependence on the studied variables being cement temperature after being processed in a mill, slag content and grinding fineness. Obviously, apart from the stated variables, flowability is influenced by a stronger factor, which has not been qualitatively determined yet. This factor can be represented by static characteristics, appearing on the surface of particles in the process of grinding.

The results of studying the flowability and LoI of cement stored in humid environments prove that the application of grinding intensifiers of the range Litoplast AI does not pose significant impact on the alteration of cement flowability under the conditions of it being stored in silos, which relative humidity does not exceed 30%.

Acknowledgment

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