Composite low-water demand cements – one of the most promising and available technologies in terms of “Ecology” national project

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Abstract. In current article results of research of composite low-water demand cement (LWDC) based on Angarsk plant’s cement CEMII/A-F 32,5R, dump ash from TPP-10, marble powder from Sludjanskoi quarry and micro silica from LLC “Bratsk ferritic alloys plant” (Irkutsk region) are performed. Goal of the study is development of efficient ecology-friendly technology for high-quality cements with raw materials local to Irkutsk region. As a result of the study, technological, physical and mechanical properties of cement paste in fresh and hardened state were determined. Standard consistency W/B of LWDC-based cement pastes’ could be changed in range between 19 and 26%, and compressive strength of hardened cement paste can be varied from 22 to 60 MP. 2-stage 3-factor regressive analysis for compressive strength values of hardened cement paste at age 3,7,28 and after thermal curing was done, regression equations were obtained.

1 Introduction
In Russian Federation ecology problem is escalated in status of national project, which main goal is efficient by-products and wastes usage. It will be realized in terms of 11 federal projects, e.g.”Implementation the best available technology”, which is agreed with Irkutsk region aims of realization of strategy of construction materials industry’ development strategy, initiated by government of the region. As foundation of this strategy, development of construction materials based on by-products and local raw materials was chosen.

It is absolutely obvious that industry of construction materials could have one of the biggest capacity of large by-products and wastes range, e.g. fly ashes of thermal power plant (TPP). Basing on this fact, industry of construction materials could be considered as implementation of this project in near future.

In European countries raw material mining, goods production, its consumption and waste generation are considered as chain link [1-5]. It is believed that such an approach will allow to preserve environment from deterioration. Due to this principle laws, which drive construction materials’ producers to implement wide usage of by-products and wastes, especially in technology of mineral binders and ceramics, are adopted.
Technology of LWDC has quite good capacity of large-tonnage production wastes utilization [6-8]. This technology is safe for the environment, has lesser energy consumption and easier to implement in comparison with OPC production one. Using an LWDC technology makes it possible to decrease significantly CO$_2$ emission (up to 3-4 times), and utilize up to 70% of wastes such as fly ash per 1 ton of binder, also it could be built in “classic” technology of OPC without colossal investments and readjustments. LWDC technology could be rightfully assigned as one of the best available technologies for mineral binders’ production.

2. Materials and methods
In current work evaluation of composite LWDC was made with usage of three types of mineral fillers. First one is a dump ash obtained from TPP-10 (total amount of ash dumps of TPP of JSC “Irkutskenergo” is about 80 million ton and annual increase is about 1.7 million ton). According to data obtained by x-ray spectral analysis, this ash includes silica (20%), mullite (13%), albite (4%), aluminosilicate mineral (about 1%) and the rest is aluminosilicate glass phase.

Table 1. Properties of dump ash from TPP-10

| Property                  | True density (g/cm$^3$) | Bulk density (g/cm$^3$) | Voids content (%) | Specific surface area (cm$^2$/g) | pH of 10%-water solution |
|---------------------------|-------------------------|-------------------------|-------------------|----------------------------------|--------------------------|
| Value                     | 2.03                    | 0.76                    | 64%               | 1334                             | 9.6                      |

Second type of filler – marble from Sludjanskoy quarry (Irkutsk region), evaluated source is about 120 million ton.

Third type – micro silica MK-85 from LLC “Bratsk ferritic alloys plant”, produced according to TU-5743-048-02495332-96.

As a clinker containing part of LWDC, CEMII/A-F 32,5 R SC “Angarsk cement and mining plant”.

Table 2. Properties of cement

| Property                  | Standard consistency W/B (%) | Setting time (min) | Activity at 28-day age (MPa) |
|---------------------------|------------------------------|--------------------|------------------------------|
| Value                     | 2.03                         | 75                 | 180                          | 35                           |

Choice of current binder was made due to its low consumption in Irkutsk region in order of search of possibility of its modification and properties’ enhancement.

Choice of superplasticizer was made from most popular types of such ones in current region:
1. Polyplast Ligno – admixture based on modified lignosulfonates.
2. Polyplast SP-1 (naphthalene formaldehyde).
3. Polyplast PK (PCE).

Table 3. Properties of superplasticizers by comparison of standard consistency W/B and price values

| Type of admixture | Dosage (%) | Standard consistency W/B (%) | Price incl. VAT (RUR/kg) | Remarks |
|-------------------|------------|------------------------------|--------------------------|---------|
| Polyplast Ligno   | 1          | 25,5                         | 56                       | Significant retardation at 1-day age |
| Polyplast SP-1    | 1          | 24,5                         | 80                       | ---     |
| Polyplast PK      | 1          | 21,5                         | 360                      | ---     |

Basing on obtained values of standard consistency W/B and prices, it was decided to make an evaluation of composite LWDC with SP-1 admixture. Apparently, low water-reducing effect of Polyplast PK was obtained due to addition of lignosulfonate agent as intensifier of grinding, which has ceased PCE-based admixture’s efficiency.

Since the fillers used differ in hardness, the LWDC was obtained in a sequentially separate manner using a vibration-rod mill. This method consisted of preliminary joint grinding of cement, ash and superplasticizer and their subsequent grinding with marble with the addition of micro silica.
For a comprehensive assessment of the effect of fillers on the properties of composite LWDC and a reduction in the amount of experimental work, method of mathematical planning were used. It was a 2-level 3-factor experiment ($2^3$). Factors and range of variation are given in table 4, the planning matrix is tab. 5. In this case, the specific surface area of the LWDC ranged between 7000 and 7500 cm$^2$/g, depending on the content of silica fume in accordance with the conditions of regression analysis. The output parameter of the experiment is the compressive strength of hardened cement paste at the age of 3, 7 and 28 days of normal hardening and after thermal curing under standard isothermal conditions at a temperature of 80 °C (method GOST 310.4).

Table 4. Factors and range of variation

| Factors                                      | Level of factor | Range of variation |
|----------------------------------------------|-----------------|--------------------|
| $X_1$ (cement content in LWDC)               | -1              | 30                 |
|                                              | 0               | 50                 |
|                                              | +1              | 70                 |
| $X_2$ ratio micro silica: ash : marble, %    | 20/60/20        | 10/60/30           |
|                                              | 0/60/40         | 10                 |
| $X_3$ superplasticizer content by LWDC mass, %| 0,5             | 1                  |
|                                              | 1               | 1,5                |
|                                              | 0,5             | 0,5                |

Table 5. Planning matrix

| Number of composition | $X_0$ | $X_1$ | $X_2$ | $X_3$ |
|-----------------------|-------|-------|-------|-------|
| 1                     | +     | +     | -     | +     |
| 2                     | +     | -     | -     | +     |
| 3                     | +     | +     | +     | +     |
| 4                     | +     | -     | +     | +     |
| 5                     | +     | +     | -     | -     |
| 6                     | +     | -     | -     | -     |
| 7                     | +     | +     | +     | -     |
| 8                     | +     | -     | +     | -     |

Initially, the specific surface area and normal density of the LWDC were determined, adopted according to the planning matrix: and the compressive strength of cement stone at the age of 3, 7, 28 days of normal hardening (Table 6).

3. Results

In table 6 physical and mechanical properties of LWDC, determined by laboratory tests, are performed. Specific surface area of LWDC compositions were determined with PSH-12 in every case, according to variation of content during regression analysis, so as compressive strength of LWDC at age 3, 7, and 28 days of normal hardening and after thermal curing. Regression equations are obtained, which display influence of basic factors on output parameter – compressive strength at different ages. At table 7 values of basic criteria of evaluation of obtained model adequacy – Fischer and Student coefficients and dispersion of regression quotients.

Table 6. Technological, physical and mechanical properties of LWDC-based cement paste

| № composition | Specific surface area (cm$^2$/g) | Standard consistency W/B (%) | Compressive strength at age, MPa | Thermal curing |
|---------------|-----------------------------------|-----------------------------|---------------------------------|---------------|
|               |                                   | 3 days | 7 days  | 28 days |                          |
| 1             | 7120                              | 20,5   | 31,57   | 44,83   | 58,5 | 43,95 |
| 2             | 7573                              | 19,5   | 12,83   | 27,7    | 33,1 | 24,6 |
| 3             | 7558                              | 21     | 16,73   | 24      | 34   | 28,95 |
| 4             | 7550                              | 22     | 6,33    | 9,33    | 20,75 | 9,3  |
Table 7. Values of Fisher coefficients and variance of model adequacy

| Type of index | 3 days | 7 days | 28 days | Thermal curing |
|---------------|--------|--------|---------|----------------|
| $S^2_{ad}$    | 10     | 12     | 26,4    | 4,5            |
| $F_{obs}$     | 7,23   | 3,57   | 8,25    | 0,61           |
| $F_{table}$   | 9,12   | 9,12   | 9,12    | 9,12           |
| Model adequacy check |        | the model is adequate, because $F_{exp} < F_{tab}$ |
| Regression coefficient dispersion | 0,17   | 0,42   | 0,4     | 0,92           |
| Confidence interval | 0,41   | 0,94   | 2,17    | 2,17           |
| Student coefficient | 2,36   | 2,36   | 2,36    | 2,36           |

Based on the results of the work, the regression equations for composite LWDCs are obtained:
- 3 days of normal conditions hardening:
  \[ R_3 = 15,99 + 5,76x_1 - 4,65x_2 + 0,875x_3 \]  

- 7 days of normal conditions hardening:
  \[ R = 24,08 + 6,94x_1 - 7,64x_2 + 2,38x_3 \]  

- 28 days of normal conditions hardening:
  \[ R_{28} = 34,31 + 7,55x_1 - 7,53x_2 + 2,28x_3 \]  

- after thermal curing:
  \[ R_{prop} = R = 26,13 + 8,86x_1 - 6,59x_2 + 0,575x_3 \]  

4. Discussion
As follows from the table, 3, LWDC has a standard consistency W/B from 19.5 to 26.5% compared with cement CEM II A / Z 32.5B, whose’ one is 28%.
Analyzing the data obtained from the regression equations, it can concluded that a significant contribution is made by micro silica on the output parameter (strength of the LWDC stone) in the quantitative corresponding contribution of $X_1$ (type of binder) for all hardening ages (3, 7, 28 days). Moreover, the significance of the contribution increases (pozzolanic activity) by 7 days and remains almost unchanged till 28 days. An analysis of the kinetics of hardening of the studied composite LWDC indicates 50% of the set of strength at the age of 3 days, 80% of the set of strength at the age of 7 days and after thermal curing. Having considered the regression equation at the age of 28 days of normal hardening, it can be said about the sufficient strength of the LWDC-30, given in addition that the actual content of the clinker component in terms of the LWDC is no more than 124%.
Reliability of the presented results was justified by calculating the confidence interval, checking the model for adequacy taking into account the Fisher coefficients (Table 7).

5. Conclusion
Basing on the foregoing, it can be concluded that the introduction of the technology for the production of LWDC can undoubtedly make a significant contribution to the implementation of the national project “Ecology”, by implementing the federal program “Implementation of the best available technologies”, at least, on the scale of the Irkutsk region and regions where solid fuel is a fundamental type. Thus, LWDC, no doubt, predicts a reliable future and widespread distribution.
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