Low-water demand cements – a reliable way of CO₂ emission reduction

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Abstract This paper presents results of performance comparison and common conclusions about low-water demand cements (LWDC) which were developed in USSR in 1980-ies. Using technology of this composite binders allows to dramatically decrease CO₂ emission without loss of performance. In current study different parameters of production have been studied such as types of admixtures, mineral fillers, workability parameters, e.g., milling ability with superplasticizers solutions as grinding agents and compressive strength. It is set that during first period of grinding any cement systems which contain water will perform lowered grinding ability, but after some time this parameter begins to grow and up to values, equal to systems without water. This fact makes possible to use, e.g. water solutions of PCE, and allows to decrease cost of LWDC in order to make it cost-effective.

1 Introduction

Worldwide engineering is not only 10% of GDP and 7% of employment but also 30% of CO₂ emission, 38% of energy and 40% of non-renewable materials consumption and 40% of industrial waste. Thus, main problem of modern engineering is its ecology orientation which has principles of efficient utilization of energy and materials.

It is clear that Portland cement industry, more precisely, klinker production, as base of structural concretes, do not respond to the principles circumscribed above because it causes about 7% of worldwide CO₂ emission. Wherein, it also has high level of conditional fuel – 215 kg/ton and...
energy consumption (119 kW/ton), and colossal volumes of limestone and clay consumption.

Concerning this facts, minimization of klinker consumption in cement concretes is one of the most important challenges because of its necessity of lowering of CO₂ emission.

Nowadays, one of the most efficient binder which respond to the requirement of low klinker content are low-water demand cement (LWDC). It was developed by USSR scientists and technologists in 1980-ies [1-8]. LWDC production based on non-kilning technology of joint or consequential grinding of cement, mineral filler (limestone, quartz sand, slag, fly ash etc.) and superplasticizer (SP). In this case mineral filler part can reach up to 70% without loss of strength.

Basing on literature dedicated to LWDC in recent years, it is possible to separate following fields of research and technological development:
- detalization of mechanism of mechanical-chemical interaction of SP with cement’ and mineral filler’ grains [9, 10];
- development and industry trials of mills acceptable for LWDC production [11, 12];
- evaluation of new types of anthropogenic mineral fillers and its mixes for production of different types of LWDC [13, 14].

Fields of research described above are unconditionally actual, but the main direction of LWDC development which will possibly make its properties significantly different is the way of SP’ selection and determination of interaction’ principles with mineral part. It is clear that character of it will directly affect efficiency of LWDC and concretes based on it.

On the other way, SP is also the barrier of wide LWDC’ utilization because of its high cost – it takes part in binder’s mass up to 3%. Basically it is closely connected with fact that dry SP is produced from its water-based solution and desiccation process increases cost of admixture from 2 to 4 times.

Basing on the facts written before, scope of research was study of high-concentrated water solutions of SPs as admixture for LWDC.

2 Materials and Methods

In this study, PCE type SPs concentrated water solutions were tried for LWDC because of their relative efficiency in case of low dosage, equal to 0,3-0,6% (in comparison with naphthalene-formaldehyde SPs – 1-3%). In
this case amount of entertaining water will be 3-5 times less. It is known from [15] that water amount in initial raw mix of components should not be more than 3% (by mass).

As a first goal of study, evaluation of grinding ability of CEM I 42,5 R with concentrated SP solutions was conducted. Nowadays they are produced only either in liquid or powder form; because of that first time powdered SP was dissolved up to its maximal concentration. After cement with both powdered and dissolved form of SP was ground and specific surface area was measured during it. As an addition, grinding ability of cement with pure water was evaluated in same way.

Grinding was conducted in laboratory vibratory ball mill with specific surface area up to 600 m²/kg.

**Specimens**

4 samples of materials were made for evaluation of possibility of grinding of OPC with liquid form of SPs:
- OPC;
- OPC with pure water (1% by mass of cement);
- OPC with powdered PCE SP (0,6% by mass of cement);
- OPC with 37,5% (by mass of solution) of SP (1,6% of cement mass which equal to 0,6% of SP dosage).

After that, standard (Haggermann’s cone) mortar (quartz sand and ground OPC) samples were made for evaluation of strength properties.

2 samples (A and B) were made for evaluation of efficiency depending on difference of PCEs.

### 3 Experimental results

Results of research of grinding ability are performed at Figure 1. Fig.1 shows that without SP (sample 1) grinding is slow and ineffective. In case of addition of water (sample 2) grinding significantly improves and value of specific surface area becomes higher 10-20% after same time of grinding.

Comparison between OPC with powdered and liquid form of SP shows that powdered one (sample 3) is initially ground faster than liquid (sample 4). Although the slow of grinding at first period, further development of process shows that grinding becomes equally effective up to specific surface area 560±20 m²/kg.
Thus, it could be concluded that production of LWDC is possible not just with powdered form of SP but also with its liquid form (water solution).

Reason of lowering of grinding ability at the first phase of grinding and limiting of specific surface area’ growth could be explained by viscosity of water solution of SP.

It correlates with results of evaluation of grinding ability of OPC with watered SPs which have no powdered form. Two samples of OPCs with specific surface area equal to 380 and 260 m²/kg were studied with two different PCE solutions (concentrations of SPs are 39 and 39.5%, consequently) with 0.6% dosage (by active dry mass). Results are performed at Figure 2a and 2b.

Figure 1. Kinetics of Portland cement grinding 1 – CEM I; 2 – CEM I with water; 3 – CEM I with powdered PCE; 4 – CEM I with liquid PCE.

Figure 2a. Kinetics of Portland cement grinding with water-based SPs solutions.
4 Discussion

As in first time of cement grinding (Fig. 1), there is a slow of grinding (see Fig. 1). Basing of results performed at Fig.2a and 2b it could be concluded that it is connected with not only viscosity of SP but also with chemical structure. It is clear that during further grinding SP, step by step, becomes distributed in the mass of OPC, and after that growth of specific surface area starts.

Table 1. Bending/compressive strength of ground binders, MPa.

| Hardening type | Ground OPC | OPC + dry SP (LWDC) | OPC + liquid SP (LWDC) |
|----------------|------------|---------------------|-----------------------|
| Standard, 24 hours | 2/12       | 5/23                | 6/35                  |
| Steam          | 6/42       | 7/72                | 7/74                  |

Figure 2b. Kinetics of Portland cement grinding with water-based SPs solutions.
curing, 7
+(4+6+2)=
19 h, t= 80
°C

| Standard, 28 days | 7/60 | 7/69 | 8/85 | 8/88 |
|-------------------|------|------|------|------|

It could be seen from Table 1 that LWDC based on liquid form of SP do not inferior (by strength measures) to its analogue based on dry form. The only one difference between them is that 1-day strength significant growth is 52% higher for LWDC based on liquid form admixture. It possibly could be explained by the following fact that during grinding process OPC grains could partially hydrate and become hard epitaxial substrate, which improves initial growth of strength by accelerated crystallization of CSH phase.

Basing on numerous trials, sufficient factors which define efficiency of LWDC with liquid SP were determined. SP should be used with concentration between 30 and 50% (by dry mass) and humidity of ready LWDC should be not more than 2%.

Using semi-industrial vibratory ball mill (see Figure 3) with bi-harmonic vibratory motions and capacity equal to 1 ton/hour (1,1 short ton/hour) 2 batches of LWDC with liquid form of SP were produced. Good results were obtained on binder itself and on concretes based on it.

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**Figure 3.** Mill equipment: top - overview of mill equipment, bottom – vibratory ball mill.

Due to using of water solutions of SP and limestone fillers high-active LWDCs were made. Using these binders heavy concrete mixes with low klinker consumption to compressive strength ratio were made – 2,8-2,9
This value is almost 4 times less than in case of conventional heavy concrete made on CEM I 42,5 R – 11,1 kg/MPa.

5 Conclusion

Thus, development of worldwide cement industry on the way of lowering of klinker consumption is being successfully implemented in low-water demand cements technology; this fact unconditionally will ensure wide implementation of these binders in concrete industry.

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