Low-permeability Fiber-reinforcement Concrete of Composite Binder

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Abstract. The subject of this work is the low permeable concrete which is produced by a novel composite binder. The binder is produced through joint grinding of the Portland cement, fly ash, and limestone together with superplasticizer using a vario-planetary mill. Grinding of active mineral supplements allows crystallization of ash particles as a result of the binding of Ca(OH)₂ during hardening alite, which intensifies the clinker minerals hydration process; the presence of fine grains limestone also leads to the hydrocarboaluminates calcium formation. The highest strength has been measured when 45 wt.% of Portland cement is replaced with industrial waste. This higher strength of milled Portland cement is due to the increased formation of "needle-like" and "stem-like" crystals. In general, the reduction in capillary porosity of compositions modified by the technogenic waste more than 2 times should be noted for all specimens compared with reference specimen.

1. Introduction

Traditional concretes have insufficient properties of gas- and vapor- permeability. At the same time, it is necessary to improve the strength and deformability quality of composite to achieve fine-grained fiber-reinforced concrete. The fine-grained structure with high homogeneity is characterized by increase of the integrated strength between aggregate and cement paste, and decrease of effective stress in the contact area. Adhesion of sand component increases significantly with increase of contact area; these conditions are realized when creating the fine-grained concrete based on composite binders by using crushed granite from Wrangel deposit (Russian Far East) [5-6]. Thus, development of a concrete matrix dense structure with high gas-, water- and vapor- impermeability is desirable. Composite binders, obtained by co-grinding of Portland cement, superplasticizer, ash and limestone screenings waste have been proposed to achieve this goal. During the joint grinding of the components, the most effective mixing of the components takes place. Also, in addition to the mechanical activation of the composite binder, the processes of chemically activating are involved. [4-9] One of the ways to improve the properties of concrete, to reduce permeability parameters is the use of highly active additives of various compositions and genesis at micro- and nanosized levels, which contribute to the optimization of structure formation processes by initiating the formation of hydrated compounds. The efficiency of use of the active mineral additives of nanostructured silica-modifier composition has been proved [1-3]. The possibility of the permeability reduction of the concrete by mechanically grinding the composite binder’s components was also studied previously [4]. The pozzolanic reaction mechanism that SiO₂ of the pozzolanic material would react with portlandite and produce more CSH gel was research in papers. [19-21] This will reduce the pore size and volume of...
the cementitious matrices and then improve the durability and mechanical characteristics of the products. Grinding of the raw material various mills was investigated in number of papers [4, 7-9].

It was previously shown that although incorporating fly ash into self-compacting concrete resulted in higher volume of pores, fly ash exhibited a proper pozzolanic reaction suggesting a high pack effect. High packing effect was a proper arrangement of small particles which fill the voids and contribute to the increment of compressive strength [17]. Thus, the issues of increasing the impermeability of concrete with the use of impermeable aggregates and an impermeable binder (pozzolanic cements) have been studied previously [1, 6, 13, 16, 17, 18]. However, the protective properties (impermeability parameters) and efficiency of high-density impermeable concrete (HDIC) produced on the basis of composite binder were not considered before.

An assumption about the possibility of low-permeability concrete is obtained by varying the amount and type of additives, fineness of the composite binder components and hardening conditions [5-6]. The purpose of this work is to reduce porosity and increase strength characteristics of concrete by co-grinding of Portland cement, superplasticizer, fly ash and limestone crushing waste. The advantage of this system would a concrete with reduced carbon footprint and at the same time reduction of waste materials.

2. Results and Discussion

2.1. Sample preparation

To optimize the mix design throughout this study, various mixes have been prepared where CEM 1 42.5N content was varied between 30 to 100 wt.%, fly ash (FA) content between 0-50 wt.% and limestone crushing waste (LCW) between 0 to 20 wt.%; see Table 1. For simplicity water/solid mass ratio and the Pantarhit PC 160 superplasticizer amount was constant for all mixes with 0.3. Furthermore, the amount of superplasticizer was fixed to 0.3 wt.% based on the total solid concentration; CEM1 + FA + LCW. To achieve a sufficient mixing, all raw materials have been mixed by mass and placed in a Pulverisette-4 vario-planetary mill from Fritsch GmbH (Germany). The advantage of a planetary mill compared to a conventional ball mill or vibration mill is the energy-efficiency and at the same time the higher operation powers [7-10]. Un-treated, meaning un-milled CEM1 was used as reference sample.

| No  | sample name | Cement content, by weight [%] | Fly ash content, by weight [%] | Limestone content, by weight [%] |
|-----|-------------|------------------------------|-------------------------------|---------------------------------|
| Reference | 100 | 100 | – | – |
| 1 | 30/50/20 | 30 | 50 | 20 |
| 2 | 35/45/20 | 35 | 45 | 20 |
| 3 | 40/45/15 | 40 | 45 | 15 |
| 4 | 45/15/10 | 45 | 45 | 10 |
| 5 | 50/40/10 | 50 | 40 | 10 |
| 6 | 55/40/5 | 55 | 40 | 5 |

After all raw materials have been mixed in the vario-planetary mill for 1h, the required amount of water added and the paste further mixed for 6 minutes.

For each test, six specimens have been fabricated to ensure a statistical feasibility result.

2.2. Influence of cementitious binder particle size on compressive strength
Once the optimum superplasticizer was determined, the surface area of cementitious binder was altered by milling and measuring the surface area. Fig. 1a shows an almost linear relation of required time for achieve various specific surface area in the range of about 280 to 900 m$^2$/kg. This behavior has been expected because the application of energy is linear over time. However, of more importance is, that with this data the required milling time to reach a specific surface area can be calculated.

After milling cementitious binder together with 0.3 wt.% Pantarhit PC 160 and measuring the surface area, water was added and the compressive strength after 28 days curing measured. Results are shown in Fig. 1b. It can be seen that the highest compressive strength was obtained for a surface area of 550 to 600 m$^2$/kg. An increase of the surface area does not lead to further significant increase in strength and even a decrease is measured. This is due to accumulation of the fine particle because the limit of the superplasticizer was reached [4-6, 11]. This behavior was also observed by a change of the mix viscosity when the surface area of the particles was above 600 m$^2$/kg. It is expected that an increase of the superplasticizer amount will result in concrete with even higher compressive strength.

![Figure 1. Bond between compressive strength [MPa] of the cementitious stone samples and the composite binder surface area. Each point represents the average of six measurements.](image)

### 2.3. Influence of cementitious binder particle size on compressive strength

In order to optimize the mix design, by reduction of CEM I and replacing it with waste materials but at the same time increasing the mechanical properties six mixes have been prepared, as shown in Table 1. In each mix, CEM I, FA, LCW and superplasticizer were milled until a surface area of 550 m$^2$/kg was reached. The results are shown in Fig. 2a. As expected increases the compressive strength of the concrete sample with increasing CEM I content. However, of interest is that by plotting the CEM I concentration on the x-axis and the strength on the y-axis, a linear strength increase with an R$^2$ value of 0.99 is observed, see Fig. 4b. This indicates that in this case FA does not act as pozzolanic material. It can be concluded that FA and limestone performs more as an inert filler rather a reactive material. Due to this, it is expected that the inert filler material will fill fine pores and the final concrete will have a denser packing. Furthermore, samples have only been tested after a maximum curing time of 28
days, this means that a reaction of FA and/or limestone with CSH gel cannot be excluded for longer curing times. According to ternary phase diagrams, a reaction of FA and CSH to CASH gel can be expected when aluminum oxide is dissolved from FA [11].

Figure 2. a) The strength of composite binders, and b) variation of the compressive strength by CEM I concentration.

The influence of FA and LCW on the porosity is shown in Fig. 3. The presence of waste materials does not influence the porosity with the pore size between 1 and 100nm and is around 2%.

Figure 3. Influence of the composition on cement specimen’s porosity, a) NMR spectroscopy, b) powder diffractometry, c) Hg intrusion porosimetry.

Existence of a large quantity of hydrosilicate connections is confirmed by decreasing of the gel pores (<1-2 nm) in crystalline bunch in conjunction with modified composites on molecular level with its maximum reduction more than 5 times (from 8.2 to 1.6) [16-17]. Although the maximum strength is 77.3 MPa in the optimal composition of binder (55% CEM I, 40% FA, 5% LCW), the gel porosity of the composite fell almost in 2 times (from 8.2 to 4.4). In this case, high strength is influenced by the
complex actions: reduction of capillary porosity (compared with [52, 53]) due to the intensification of the processes of growth of primary crystals of hydrosilicate phases [18-19]; due to possible formation of secondary recrystallization and crystals creation; due to filling the space at the micro-, submicro- levels (50-100 nm and < 50 nm respectively) of structural organization composite with them and in conjunction with reduction technological porosity on 17% (from 1.2% to 1%) due to the formation of a dense packing of the grain structure at the macro level (10^2-10^3 nm), with the participation of spherical fine components of fly ash and limestone crushing screenings.

This expectation is confirmed by SEM images from pure milled CEM I and milled CEM I mixed with FA and limestone, as shown in Fig. 4. The additional amount of fine inert material fills voids at the micro level in the crystalline matrix of calcium hydrosilicates at the boundary of the contact area.

Furthermore, the highest strength has been measured when only 45 wt.% of CEM I is replaced with industrial waste. Although a higher strength can be achieved when pure milled CEM 1 is used, the obtained strength of the mixed system is already higher compared to “conventional” CEM 1. This higher strength of milled CEM 1 is due to the increased formation of "needle-like" and "stem-like" crystals. These needle-shaped crystals contributes to reinforcement of the composite structure on nano- and micro- levels, reduction of porosity and improvement of the composite complex strength [20-21].

3. Conclusion

To develop and optimize a new low permeable binder system and at the same time reduce existing waste, several materials have been mixed together. These materials can be divided into three groups: reactive/inert material and superplasticizer. To optimize the mix design throughout this study, various mixes have been prepared where CEM 1 content was varied between 30 to 100 wt.%, FA content between 0-50 wt.% and LCW between 0 to 20 wt.. To determine the “best” superplasticizer, the six most common commercially available superplasticizers in the Russia have been evaluated.
It can be seen that the highest compressive strength was obtained for a surface area of 550 to 600 m$^2$/kg. In order to optimize the mix design, by reduction of CEM I and replacing it with waste materials but at the same time increasing the mechanical properties six mixes have been prepared. This indicates that in this case FA does not act as pozzolanic material. It can be concluded that FA and limestone performs more as an inert filler rather a reactive material.

Although, DTA and XRD data show no difference between standard CEM 1 and CEM 1 mixed with waste materials, an influence of FA and LCW can be seen using porosity measurements. Existence of a large quantity of hydrosilicate connections is confirmed by decreasing of the gel pores (<1-2 nm) in crystalline bunch in conjunction with modified composites on molecular level with its maximum reduction more than 5 times (from 8.2 to 1.6).

The most important task of high-density impermeable concrete creating is the rational formation and optimization of the pore space structure. In general, the reduction in capillary porosity of compositions modified by the technogenic waste more than 2 times should be noted for all specimens compared with reference specimen.

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