

New Composite Cement for Construction 3D Printers

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Abstract. A composite binder based on a mixture of fine fly ash with standard cement grade CEM I 42,5 was developed in accordance with the requirements of the concrete mixtures for molding products using of construction 3D printers. The influence of the ratio between ash and cement on the strength characteristics of the hardened binders was analyzed.

Introduction

In modern construction business are widely used innovative technologies in field of materials science and in the technology of manufacture of building materials and construction technology directly. In the construction industry and in other industries (automotive, mechanical engineering, and others.) expands the using of automation, including robotics. One of such innovations is the using of construction 3D printers.

It has long been 3D-press was not outlandish novelty, disturbing the public mind. Today they are widely used in engineering, medicine, arts and other fields. Over a rather short period of time that has passed since the first of 3D printers appeared, people have learned to type dishes, clothes, toys, parts for machines and the machines themselves, and even human tissue and organs. In the construction industry 3D-press has also found its application in the production of individual building structures and buildings and structures entirely.

Results and Discussion

As is well known construction 3D printers operates using extrusion technology, where each new layer of building material is extruded from the extruder over the previous layer. Such 3D-press allows to get unique items without concrete formwork, thereby significantly reducing the cost of human labor, and time of construction.

As new technology unlike all existing is formless, the efficiency of its application will primarily be predetermined by properties of the used concrete mix. Consequently its characteristics should be substantially different from those of traditional mixtures, products of which are formed in the rigid formwork. However, many characteristics of concrete mixes for building 3D printers are contradictory. Thus the concrete mix should have a high strength plastic, that is, hold its shape after extrusion, as well as high mobility to reduce the energy costs of mixing and supplying the prepared concrete mixture in an extruder, and also should have high adhesion to connect the individual layers. This can be achieved by analogy with forming bricks of clay mass with plastic manner by obtaining superplastic concrete structure with fine grain size due to a large content of fine mineral powders. Therefore, we have seen that concrete mixtures and concretes for construction 3D printers should be developed on the basis of powdered and powder-activated sandy concrete of a new generation by modifying them in order to obtain the desired properties of the concrete mix. Also, the concrete mixture should have accelerated structure formation, ie rapid transition from ductile into solidified with achieving the necessary strength, that can support the weight of the upper layers in the 3D-molding.

A distinctive feature of the new generation concrete is a significant content of the powdery material from dense rocks and fine-grained natural or crushed sand with fractions of 0-0,5 mm (0,16-0,63 mm). Dispersible powders of micrometric dimension level with specific surface $S_{sp} = 300-400 \text{ m}^2/\text{kg}$, in concrete reaches 40-120% by weight of cement, are facilitating to the formation in concrete mix of a significant volume of aggregation-stable, highly concentrated suspensions (30-60% by volume concrete mix) and provide a uniform structure, self-spreading and self-compacting mixtures under the influence of modern superplasticizers.

Thus, it is possible to create concrete for of construction 3D printers on the basis of powder and the fine-grained new generation concrete as possible satisfy the requirements for grain composition. However, due to the characteristics of the new technology this concrete must be subjected to modification of the composition to improve the plastic strength, adhesion and accelerating the early pattern formation. This can be achieved using special cements.

However, we have seen what is economically feasible to create binder for the new technology, based on Cement with no add-ons that match the type CEM I and class on the strength of not less than 42,5 per GOST 31108-2003 "Cements. Specifications" with the introduction of mineral additives in combination with chemicals.

Modern building materials industry in its production uses a great variety of chemical additives. They are plasticizers, stabilizers structure, hardening accelerators and retarders.

Fine mineral components obtained by milling of rocks (such as granite, basalt, quartz, etc.), industrial waste products (slag, ash, and others.) and specifically produced additives (micro-silica, white carbon, etc.). Have different functions. According to our classification [1, 2] all suitable highly dispersed mineral components are divided into 3 groups.

Rheologically active (latent reactive), well thinning with sufficient amount of water under the influence of superplasticizers of slurry individually or mixed with cement, while moderate and low water introduction stabilizing additives - forming a dense homogeneous plastic mineral mass. They may be reaction-inert (limestone, dolomite) or chemically weakly active with sustained, extended in time interaction with the cement hydration products (quartz or quartzite flour, granite, diabase, gabbro, basalt). They are the primary fine powder component of modern concrete.

Reactive active – not self-hardening during mixing with water, but interacting with the products of cement hydration to form additional cementitious compounds. Some of them have a mosaic particle's surface charge and have a rheological activity. Other, having a negative charge-rheology are not active, but in a mixture with cement in the charge of surface, form aggregation-stable suspension (micro-silica, dehydrated kaolin, volcanic ash, glass, lines, etc.).

Rheologically active and reactive, self-hardening with water. This class includes technogenic products (ash and slag), which are the most valuable components for a new generation concrete.

In order to reduce the cost of concrete is better to use highly dispersed mineral components (including those derived from other productions waste), to ensure the formation of a plastic mass and accelerate the nucleation. The preliminary studies have shown that the most suitable mineral component is finely dispersed alkaline fly ash produced by burning brown coal.

Economic efficiency from using the fly-ash due to several factors: the similarity of their chemical and mineral composition to the composition of cement clinker, high rheological properties under the influence of superplasticizers and hydraulic activity with the formation durable hardened stone, and the presence of large amounts of free lime contributes to the rapid thickening of the dough and set early strength. In addition, fly ash has a low cost, because for Energy enterprises it is a waste.

Fly ash is a finely divided, dry material, consisting, as a rule, of particles of up to 0,14 mm, ie sufficiently close to Portland cement dispersibility. It is formed from the combustion of solid fuels in CHP and captured by cyclones and electrostatic precipitators. Particles of ash - is spherical grains (50-60 micron size) containing within itself even smaller particle size of 1-10 microns. Therefore, if the granule is not destroyed, its interaction with water begins with surface of glassy granule.

Small granules remain intact as long as gidrotation of upper shell will ends. Only then will start the hydration of the finer granules. Therefore, when ashes are used in a natural, i.e. unmilled form, large granules' destruction practically does not occur.

The basic technology for preparing the particulate components is mechanochemical activation of fly ash. With the development of technology of grinding process it is required in factories, construction industry and quarries to grind raw materials into the specific surface area which is comparable or slightly higher than the dispersion of cement. This concerns not only to the dropout lithoclasty of rocks, but also the most valuable departure CHP – fly ash, although it has the physical condition of the powder. However, the specific surface area of the ash is insufficient ($S_{sp} = 150-200 \text{ m}^2/\text{kg}$) for using of the totality of all its positive properties with a substantial decrease in consumption of cement in concrete and accelerate its hardening [3].

The department "Technology of building materials and wood" Penza State University of Architecture and Construction developed composite concrete mixture [4]. The basis of these concrete mixes is composite cement, which is produced by intergrinding Portland cement with fly ash and hardening regulators. The using of mechanical-activated fly ash has substantially eliminate the use of a part of the concrete mix expensive pulverized quartz and to reduce the share of cement up to 20-40% by weight of the total binder, because ash has hydraulic activity and the formation of a solid rock during the hydration process.

In studying of the possibility of using fly ash, obtained by burning brown coal Kansk-Achinsk field with natural specific surface $S_{sp} = 150-200 \text{ m}^2/\text{kg}$ were found both positive and negative aspects. Manifestation hydration activity primarily belongs to the positive aspect, i.e. upon mixing with fly ash mixed with water and the end of the hydration process, the samples had some strength. The negative aspects include the unevenness of volume change upon hydration.

To determine the soundness standard procedure, used for cement, has been selected. This choice was due to the identity of the chemical and mineral composition of cement and studied fly ash and its hydration activity. In accordance with the test procedure, lozenges were made from the samples of fly ash with a natural specific surface of $S_{sp} = 150-200 \text{ m}^2/\text{kg}$ after the mechano-chemical activation process of grinding up to $S_{sp} = 450-500 \text{ m}^2/\text{kg}$.

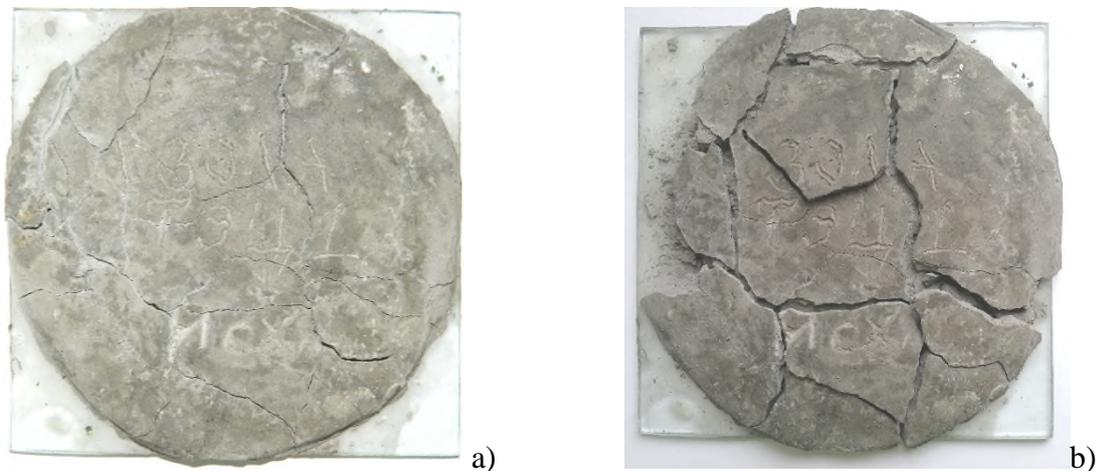


Fig. 1 Samples of binder, based on initial ashes after the test equability of volume change (a) and the subsequent storage in air (b).

As shown, the test for uniformity of volume changes of the sample surface was covered with a grid of cracks (Fig. 1, a), and after storage in air sample destroyed itself (Fig. 1, b).

It is caused by the fact that the test fly ash has a high content of free calcium oxide and magnesium CaO and MgO , which continue to interact with the water after solidification of the samples which ultimately leads to their destruction.

While test samples made from crushed fly ash showed no unevenness of volume change. This indicates that the milling ashes completely eliminates the development of stresses by quenching of free CaO and MgO , as a result of grinding to a high specific surface area burned MgO and CaO is quenched in the manufacturing process of the concrete mixture and curing the plastic to solidify it (Fig. 2).

During the research it was determined that the crushed ash has high reaction activity when interacting with the mixing water. Thus, ash dough obtained upon mixing pulverized fly ash and water, solidified rapidly and thickened. Mixtures of cement and ash, at various ratios to each other as quickly thickened, it is not possible to produce samples of the test materials with the required rheological properties. Therefore it needed to find an effective inhibitor of hardening of the ash and ash-cement binders. Using as a hardening retardant gypsum allowed to control the setting time of the composite cement-ash binder over a wide range [5].



Fig. 2 Samples of binder based on ash without gypsum (a) and with the addition of 3% gypsum (b) after the test equability of volume change

At the first stage of research of physical and mechanical properties of the samples were made from binder of fine ash (Table 1). As it shown, the slurry of ash binder is characterized by a relatively high mobility and good viability, due to administration of the grinding fly ash 7% by weight of gypsum. The strength of the samples after 28 days of normal hardening was 24 MPa.

Table 1. Physical and mechanical properties of the solidified ash binder based on the mill ground fly ash

Component Name	For 1 m ³ concrete mix, [kg]	Water - Fly Ash ratio	ρ , [kg/ m ³]	Strength after 28 days, [MPa]	Specific consumption of fly ash, [kg/MPa]
Ash + gypsum 7% from ash, $S_{sp} = 605$ [m ² /kg]	1663	0,232	2011	$R_{comp}=24$	69,3
SP Hidetal 9 1% by weight of ash	16,6			$R_{bend}=3,6$	
Water	385	Cone broke Hegermann 25 [cm]	Pot life of mix 1,5 hours		
Weight concrete mix	2048				

In the second phase samples were made of cement-ash binder (CAB) on the basis of the Krasnoyarsk Portland cement CEM I 42,5 and fly ashes (Table 2). The amount of ash was ranged from 20 to 70% by weight of binder. Tests were conducted at ages 2, 7, 28 days of normal hardening on samples 40×40×160 mm, made of cast, self-sealing slurries.

Table 2. The rheological and technological properties of cement-ash slurry and the physical and mechanical properties of hardened cement-ash binder.

Ratio cement: ash, [%]	Water - aggregate ratio	ρ , [kg/m ³]	Cone broke Hegemann, [sm]	Compressive strength, through days, [MPa]			Indicators	
				2	7	28	CAB _{sp} [kg/MPa]	C _{sp} , [kg/MPa]
20 : 80	0,209	2150	35	26	60,5	84	25,00	5,00
30 : 70	0,211	2205	37	48	75,6	114	18,42	5,53
40 : 60	0,215	2215	41	62,4	95,2	128	16,41	6,56
50 : 50	0,209	2240	35	80,8	100	140	15,00	7,50
60 : 40	0,214	2245	38	86,8	110	144	14,58	8,75
70 : 30	0,200	2241	36	102	112	143	14,67	10,28

Nomenclature:

CAB_{sp} – specific consumption Cement-Ash Binder

C_{sp} – specific consumption cement

Comparative analysis of the properties of the slurry and solidified cement- ash binders with different ratio cement: the ash is given in Table 2. Specific consumption of cement in the cement ash binder per unit compressive strength as a function of the percentage of cement varies from 5,00 to 10,28 kg/MPa. Due to the fact that the strength characteristics of the hardened binders 50, 60 and 70% of cement virtually identical, it makes no sense to increase the content above 50% cement. However, the maximum final amount of cement can be installed during concrete test.

The unusual behavior of ash in the reaction process of hardening cement-ash stone explained by several factors, one of which, in our opinion, is the reaction of lime with their own aluminosilicate glass ash. And the reaction process ash cement hydration products is possible. Confirmation of these assumptions given researches material composition of ash and cement-stone ash by X-ray analysis.

Conclusion

Such a high ash content is made possible thanks to the "awakening" of binding properties of ash by mechanical activation of cement-ash composite binder combined final grinding of Portland cement, ash and gypsum. Due to this it is implemented it's intense hardening in conjunction with hardening of Portland cement. Such a composition cement has a high rheological activity under the influence of superplasticizers, allowing preparation of plastic concrete. And the introduction of different amounts of gypsum can adjust setting time and curing the binder (start hardening from 5 to 40 min), and as a consequence the concrete mix, which allows to prepare sufficient plastic concrete mix which hardens rapidly after extrusion. Produced in this way concrete is a fine-grained with minimum porosity (4,2%) that it provides a high cold resistance, and its strength can be up to 100-120 MPa. In the case of using fiber strength may reach 150-200 MPa.

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