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Hydraulic Activity of Mineral Fillers of Manufacturing Origin Mixed with Cement

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***Abstract* – The paper presents the results of determining the degree of hydraulic activity of manufactured mineral filler (concrete broken material, demolition of buildings and structures, ceramic brick fights, ash and slag waste from thermal power stations (TPS), substandard raw materials mixed with cement used in high-quality concrete mixtures. The paper describes the strength of the compositions based on fine mineral fillers and calcium hydroxide. The paper studies an x-ray of a control sample of concrete broken material and the mineral composition of the latter. The hydraulic activity of the mineral filler from concrete broken material containing up to 20-25% of non-hydrated grains of cement used in the preparation of concrete from which this filler was obtained. It was experimentally proved which confirms the correctness of the choice of this raw material as a finely ground active microfiller for concrete.**

Keywords – manufactured raw materials; concrete broken material; broken bricks; ash and slag mix; substandard raw materials; quartz sand; mineral filler; concrete mix; activity of fine ground filler.

I. INTRODUCTION

In recent decades, various mineral fillers (MFs) have been increasingly introduced into concrete technology, providing the required parameters for remolding effort and final concrete strength [1–3].

Such materials (i.e., MF) are obtained, as a rule, by mechanical or mechano-chemical processing of natural or manufactured materials (ashes, ground slags, ash-and-slag mixtures, rocks, dust from stone sawing and stone processing, etc.) to obtain a uniform fine powder [4, 5]. In this way, they differ from the aggregate in that they have small particles (less than 0.16 mm, and more often even less), and from chemical modifiers in that they do not dissolve in water. Fine particles of the mineral filler occupy equal volumes in the intergranular space of a larger aggregate and thereby significantly compact the cement stone. In some cases, the use of MF saves a binder, so they are often called mineral additives [4, 6–8]. Depending on the effect on the properties of the concrete mix and concrete, mineral fillers are distinguished:

1) MF-thinners (ash, having dispersion almost like cement - 200 - 500MH m²/kg);

2) MF-seals (microsilica with dispersion of about 100 times less than the dispersion of cement - 20000–30000 MH m²/kg).

We consider the latter more effective additives, since they can occupy small voids between the particles of the binder, and, as a rule, have an increased reactivity [4, 9–12].

In addition, MFs can be active and inert [4]. Additives that are capable of reacting chemically with other components in the concrete mix are active fillers. As a rule, active MFs react with $Ca(OH)_2$, which are formed in the cement medium during its hydration [13, 14].

Inert MFs are those milled additives that, under normal temperature conditions, do not react with the clinker part. These MFs include ground quartz sand, powders from various rocks, etc.

Mineral natural additives obtained by grinding various rocks are also widely used in the technology of self-compacting concrete. The author [15] proves the effectiveness of volcanic ash as a fine filler for composite binders with an activity of 65–75 MPa.

MF from manufactured raw materials are : ash and slag mixtures, dust from screenings of crushing products of dismantling of buildings and structures (concrete broken material , brick breaking, etc.), silica fume, etc. have different mineralogical composition and dispersion, determining the effectiveness of their use. The description of the properties of the MF used and their influence on the properties of concrete mixtures we give further.

TABLE I. FINELY DISPERSED MINERAL ADDITIVE-FILLERS.

№ number	Filler name		Specific surface Ssp, m²/kg
	full	**contracted**	
1	Mineral filler of manufactured origin (MFMO) from concrete broken material (CBM)	MFMO from CBM	571
2	Mineral filler of manufactured origin (MFMO) from ceramic brick breaks (CBB)	MFMO from CBB	592
3	Mineral filler of manufactured origin from ash and slag mixture (ASM)	MFMO from ASM	560
4	Fine quartz sand mineral filler	MFMO from fine quartz sand	476

II. METHODS AND MATERIALS

In this work, we used locally available materials as dispersed mineral additives (fillers), namely, the dust-like fraction of the product of crushing concrete broken material (CBM) and ceramic brick breaks (CBB), ash- and- slag mixture (ASM) and fine quartz sand (Table 1).

As shown by numerous studies of scientific schools of professors Yu.M. Bazhenov, P.G. Komokhov, V.I. Solomatova, V.S. Lesovik, S.A.Yu. Murtazaev [16–25], the use of «inert» dispersed MF in concrete mixtures not only does not reduce the strength of the filled cement binder, but also in some cases even leads to its hardening.

III. RESULTS

To determine the effectiveness of the applied mineral fillers of manufactured origin (MFMO), we conducted studies of their hydraulic activity in a mixture with $Ca(OH)_2$ (i.e., lime). All MFMOs were ground in a laboratory vibration mill «MV-20-EX» to a specific surface of 450–600 m²/kg for 5 minutes, mixed with $Ca(OH)_2$ «ChDA» in the ratio MFMO: $Ca(OH)_2$ - 70 : 30 with the same W/C of 0.3. From the resulting pastes, control samples we made control samples: cubes with an edge of 2 cm, which should be kept in wet conditions, ensuring their protection against CO_2 access and carbonation of lime (Table 2).

As follows from the data of table 2, the samples on ground quartz sands had practically no strength, while the compressive strength of Rsc of samples with MFMO from concrete broken materials at the age of 90 days was over 3.5 MPa.

By facilitating the diffusion of Ca_2^+, OH^-, CO_3^- ions in the structure of $Ca(OH)_2$, $CaCO_3$, water molecules can activate both the surface layers of $Ca(OH)_2$ particles and the surface layers of sedimentary limestone particles. In this case, isomorphous mixtures are formed, which are represented by solid solutions between $Ca(OH)_2$ and $CaCO_3$. Of course, all this contributes to the strengthening of the composite structure of the material. However, the crystalline ordered structure of SiO_2, in which the interplanar distances are noticeably different, the amorphization process proceeds more difficult. This explains that particles of MF from quartz sand and CCB are less reactive compared to other MFMOs.

TABLE II. STRENGTH COMPOSITIONS BASED ON FINELY DISPERSED MINERAL FILLER OF MANUFACTURED ORIGIN (MFMO) AND CALCIUM HYDROXIDE.

№ number	Name MFMO	Ratio MFMO : $Ca(OH)_2$	Strength R^{90}, MPa
1	MFMO from concrete broken material(CBM)	70 : 30	3,85
2	MFMO from CBB		0,11
3	MFMO from ASM		1,21
4	MF from fine quartz sand		0,14

Thus, the disclosed values of the reaction and chemical activity of MFMO mixed with limestone, which is the main component of hydrated cement, confirm that the introduction of mineral fillers (especially MFMO from concrete broken materials) into concrete mixtures is an effective and economically viable step in optimizing the latter.

TABLE III. KINETICS OF CURING CEMENT COMPOSITIONS FILLED WITH VARIOUS MFMO

Num	Filler name	Strength Rsc, MPa, age, days, at ratio							
		MFMO : C = 70:30				MFMO : C = 30:70			
		1	3	7	28	1	3	7	28
1	MFMO from CBM	4.9	6.1	16.7	22.1	17.8	21.9	49.8	73.8
2	MFMO from CBB	4.0	5.0	16.5	19.4	14.8	18.0	42.3	66.9
3	MFMO from ASM	4.0	5.3	15.2	18.8	14.1	19.0	43.4	67.7
4	MF from fine quartz sand	4.2	5.5	16.0	19.5	15.0	20.2	44.0	68.8

This is confirmed by additional tests using the same method, with an assessment of their hydraulic activity mixed with cement (C), taken in the ratio of MFMO: C - 70:30 and 30:70 with a W/C ratio of 0.20 and 0.28 accordingly (Table 3). The strength of the binder composition MFMO: C = 70:30 at the age of 28 days was noted for compositions on MFMO from concrete broken material - 22.1 MPa. Composite with MFMO from CBM, ASM and quartz with the same ratio at the age of 28 days had approximately the same strength results - about 19 MPa. The daily strength of these compositions was about 4.0 MPa, when the same indicator for the composition on MFMO of concrete scrap is close to 5.0 MPa.

Such an active influence of the MFMO of concrete broken materials can be explained by the fact that its composition may contain incompletely non-hydrated cement particles, which was used in the manufacture of reinforced concrete products or structures, from which this type of mineral filler was obtained during their disposal.

Additional grinding of the dust fraction of the product of crushing concrete scrap allows you to re-engage these particles in the hardening process, which opens up the possibility of improving the physical and mechanical properties of concrete, saving costly and energy-intensive portland cement in their production and improving the efficiency of use of this manufactured raw materials.

The work of many scientists is devoted to the possibility of the presence of non-hydrated cement particles in concrete. So, the famous domestic scientists Yu.M. Bazhenov [4], V.S. Lesovik [6], S.A.Y. Murtazaev [7], S.S. Kaprielov [10] in their works experimentally prove that cement grains in the process of hydration in concrete will not fully utilize their potential, but only by 70-80% maximum. The remaining part of the cement grains, according to scientists, remains completely non-hydrated in a « blocked » form in the concrete composite structure, which can remain in such a «sleeping» mode for a long time, almost throughout the entire life of the concrete in the structures of buildings or structures.

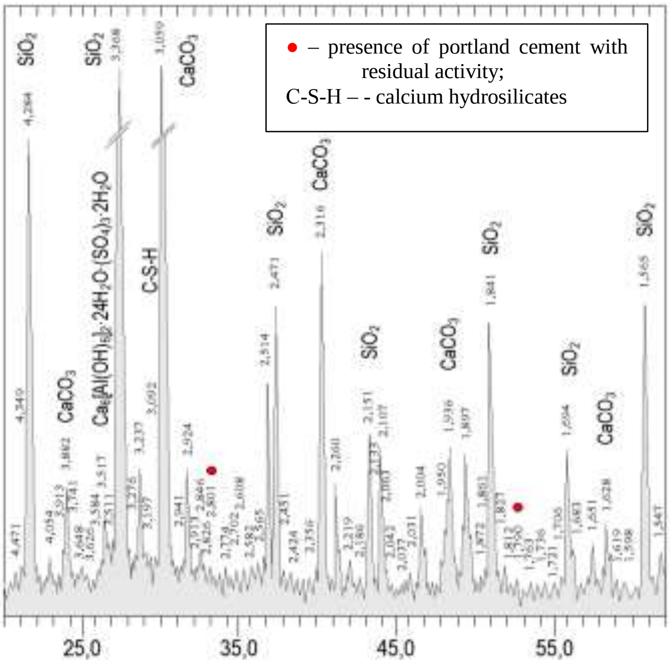

Fig. 1. Fragment of radiographs of MFMO from concrete broken materials, on which non-hydrated grains of cement are fixed in the composition .

The mineral composition of the screening crushing of concrete broken materials is shown in Table 4.

TABLE IV. THE MINERAL COMPOSITION OF THE SCREENING CRUSHING OF CONCRETE BROKEN MATERIALS

Mineral or cement hydration product	Amount, %	Interplanar spacing d, Å	Note
SiO_2	51.1	4.284; 3.368; ...; 1.841; ...	Quartz
$CaCO_3$	32.2	3.882; 3.059; 2.514; 2.316; ...	Calcite
μ-$CaCO_3$	1.4	3.584; 3.311; 2.774; ...; 2.042	Vaterite
$Ca_6[Al(OH)_6]_2 \cdot 24H_2O \cdot (SO_4)_3 \cdot 2H_2O$	0.9	3.913; 3.517; ...	Ettringite
Non-hydrated portland cement	3.5	2.780-2.732; 2.587; ...; 1.769; ...	–
xCaO·SiO_2·$y$$H_2O$; [C-S-H]	5.1	…; 3.092; 2.846; 1.872	Calcium Hydrosilicates
$2CaO \cdot Al_2O_3 \cdot 8H_2O$; [$C_2AH_8$]	0.6	…; 2.891; 2.565; ...	Dicalcium aluminate 8-water
$Ca_3Al_2(OH)_{12}$; [C_3AH_6]	2.3	…; 2.826; 2.321; 2.063; ...	Tricalcium aluminate hexahydrate
$3CaO \cdot Al_2O_3 \cdot 6H_2O$+ +$CaO \cdot Fe_2O_3 \cdot xH_2O$; [$C_3(AF)H_6$]	2.4	…; 2.451; 2.031; 1.530; ...	Four-calcium alumoferrite hexahydrate
Other inorganic ingredients	0.5	–	–

The study of the mineral composition of concrete broken material filler using X-ray analysis (Figure1) showed the presence of quartz in the amount of 51.0%, calcite (about 32.0%), calcium hydrosilicates (more than 5.5%), non-hydrated portland cement in the amount of 3, 5% by weight (Table 4).

IV. Conclusion

Thus, we defined the degree of hydraulic activity of MFMO mixed with cement used in high-quality concrete mixtures.

The hydraulic activity of MFMO from concrete broken materials containing up to 20-25% of non-hydrated grains of cement used in the preparation of concrete, from which the filler is obtained, has been experimentally proved, which will serve as the basis for its effective use in concrete technology as finely ground active mineral filler.

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