Refractory concretes with additives of fine-milled high-alumina industrial wastes

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Abstract. The paper is discussing the results of the study of alumina binder and refractory concrete with additives of fine-milled high-alumina industrial wastes. The siftings of the catalyst support of dehydrogenation of hydrocarbons and ferrochromic aluminothermal slag by Kliuchevskoi Ferroalloys Corp. were used as additives. Selecting ferrochromic slag as additive is based on the fact that its content of alumina and phase composition is the closest to the alumina (CAC) and high-alumina cement (HAC). The siftings of the catalyst support of dehydrogenation of hydrocarbons consist of alumina in the active form. These additives provide increased refractoriness of cement. The information on the composition of additives is given. Superplasticizers, based on PCE, were introduced into the binder to compensate the reduction of strength. As PCE additives were used Melflux 1641F, Melflux 2641F, Melflux 2651F and Glenium 51 by BASF Constraction Polymers. The effect of additives on hydration is shown. It is established that the superplasticizers take a retarding effect on the concrete setting process. The optimal quantities of high-alumina additives and superplasticizers have been identified. The basic properties of obtained binders and concrete were investigated. The temperature of application of the developed concrete is 1,400-1,600 ° C.

1. Introduction

At present, the most widely used heat-resistant concretes are based on alumina (CAC) and high-alumina cements (HAC). Alumina cement based concretes rapidly getting strength. However, the temperature of their application is significantly lower than that of HAC. In turn, more refractory concretes on the base of HAC acquire strength more slowly [1,2]. In this regard, questions of modifying the CAC in order to accelerate the hardening, increasing the strength parameters and fire resistance are very relevant.

There is a well-known domestic and foreign experience of modifying CAC with dispersed additives to increase refractoriness. Addition of fine-milled alumina, aluminum hydroxide and corundum improves fire resistance of the binder [3-5]. This direction currently is not widely developed as the addition of aluminum hydroxide and alumina increases shrinkage significantly and reduce strength. Salmanov et al. obtained concrete on the basis of CAC with corundum fine-milled additive and aggregates from titanium-alumina slag with a compressive strength above 30 MPa and application temperature up to 1500 ° C [6]. The addition of active alumina makes it possible to provide a more smooth set of strength and subsequently gives a significant growth due to sintering [4,5]. Such an astringent is considered as a variety of high-alumina cement. Before mentioned alumina and corundum additives are expensive technical products and aluminous slag require significant investment in grinding. In this connection, the problems of their replacement with more accessible industrial alumina-containing waste are still actual [7].

Of great interest are studies of the effect of additions of alumina-containing aluminothermal slag in CAC and HAC [7-9]. They reduce setting time and accelerate hardening due to the presence of $C_{12}A_7$. The spinel CA_6 and alkali-containing corundum $12Al_2O_3$*(Na, K)$_2$O present in significant amounts improve the refractory properties of the binder.

Wastes of chemical and petrochemical industry are characterized by high content of Al2O3 and have high dispersion. For example, aluminum chromium catalysts and siftings of the catalyst support of dehydrogenation of hydrocarbons. This makes them a valuable raw material for obtaining high-alumina binders [8].

The introduction of the above mentioned alumina containing additives inevitably increases the normal density of the binder, reduces compressive strength and increases shrinkage after heating. To increase the strength characteristics, it is advisable to use plasticizers. At present, superplasticizers based on naphthalene are widely used. Such as S-3 [3], and in particular on the basis of polycarboxylate esters (PCE) [7,10-15]. The most studied is the use of S-3. However, it gives a significant reduction in strength after heating [8]. Additives based on PCE are free of this drawback [7,10-14].

Thus, it is possible to single out the following promising directions for modifying CAC and HAC:

- the introduction of active aluminous additives, increasing the temperature of application of CAC, preventing the dumping of strength in the heating process;
- introduction of fine-milled additives of slags of aluminothermic productions, contributing to a more smooth set of strength of aluminous cements and increasing their refractoriness;
- additives of slag of aluminothermic productions in HAC accelerate the hardening in the early periods;
- the introduction of additives-superplasticizers based on PCE, providing the production of binders and concretes with low water content, normalizing the setting, increasing the strength parameters, reducing shrinkage.

2. Materials and methods

For current work aluminous cement GC-50 according to GOST 969 of Pashiysk Metallurgical-Cement Plant - the most common type of alumina cement in the Urals region was used.

As high-alumina cement, VC-75 cement was used according to TU 21-20-60-84 of the production of "IC AS Teplostroy" Ltd. (Chelyabinsk) with an Al2O3 content of not less than 75 %.

The binder was modified by adding of ferrochrome slag (SFC-A) according to TU 0798-060-00186482-2006 and its self- disintegrating variety SFC-S (produced by the Klyuchevsky Ferroalloy Plant, Sverdlovsk Region).

The main phases of the slag are spinel, CA and C12A7. The slag content was varied within the range of 20-40 % of the mass from the condition of ensuring the required strength and fire-resistance of the binder. The grinding of slag was carried out in a vibrating mill. The fineness of the slag grinding was 4200 cm^2/g. Also, an additive for screening of the catalyst support of dehydrogenation of hydrocarbons was used. They are produced by "Krona-SM" Ltd (Novosibirsk) according to TU 6-68-167-99. Siftings are a product of dehydration of aluminum hydroxide. They are obtained by thermal shock - heating in a gas stream with a temperature of 500-1200 ° C followed by rapid cooling to 60 ° C. Catalyst carrier siftings have a specific surface area up to 2500 cm^2.

As additives for superplasticizers, dry additives based on PCE - Melflux 1641F, Melflux 2651F and Melflux PP200F produced by BASF Constraction Polymers (Germany), most suitable for use in dry mixtures based on aluminous and high-alumina cements, were used. The superplasticizer was introduced in the dry state, before being quenched with water. Samples of cement bricks were prepared from a normal density test in accordance with GOST 310.3, hardening was carried out under normal conditions according to GOST 10180. The composition of the hydration products was studied by the methods of derivatography and X-ray phase analysis. The strength of the binder was determined both for alumina cement in accordance with the requirements of GOST 969 and GOST 310.4. Refractoriness is determined according to GOST 4069. The properties of refractory concrete were determined in accordance with GOST 20910.

3. Cement binders and heat-resistant concrete on the base of aluminous cement with addition of siftings of the catalyst support of dehydrogenation of hydrocarbons

The use of dispersed waste of alumina and chromium-aluminous composition in refractory binders is of great interest. They require relatively low costs for further grinding, and have high content of Al_2O_3, Cr_2O_3 that provides an increase in refractoriness [8,9].

Wasted aluminum chromium catalysts used in refractory binder and refractory concrete technology do not have hydraulic activity. In this regard, practically they are not used in concretes for CAC and HAC [8]. Alumina waste - siftings of the of the catalyst support of dehydrogenation of hydrocarbons have high chemical activity (Table 1). They are similar in properties to reactive alumina.

Table 1. Chemical composition of raw materials.

Materials	Oxide content, %							
	Al_2O_3	CaO	Cr_2O_3	SiO_2	TiO_2	FeO+ Fe_2O_3	MgO	Na_2O
Cement GC 50	48,5	38,9	–	10,3	1	–	0,4	–
Cement VC-75	74,4	20,9	0,9	1,2	–	0,5	1,5	0,7
Ferrochrome slag (SFC-A)	51,8	22,4	2,7	1,6	–	0,5	15,1	
Ferrochrome slag self-decomposed (SFC-S)	27,8	31,6	7,5	8,1	–	0,5	17,0	–
sifting of the catalyst support of dehydrogenation of hydrocarbons *	not less than 80,0	–	–	0,04	–	0,03	–	0,03

The introduction of milled siftings of the catalyst support of dehydrogenation of hydrocarbons into the aluminous cement of GC 50 grade allowed, while maintaining a high rate of strengthening during the first 3 days, to increase the content of the aluminum hydroxide gel in the cement stone. In this case, the phase composition of the cement stone is close to the material obtained with HAC. As a result, the refractoriness of the binder is significantly increased, as application temperature of the heat-resistant concretes based on it. Resetting the strength by heating at 800-1000 C typical for aluminous cement is significantly reduced.

High alumina binder is patented by the following composition, % [8]:

- Alumina cement, class GC 50 55-90
- siftings of the of the catalyst support of dehydrogenation of hydrocarbons, specific surface area 4000 sm^2/g 10-45

The binder was obtained on the basis of alumina cement grade GC 50 (Pashiysky Cement and Metallurgical Plant, Perm Region) according to GOST 969 (Table 1) and additions of catalyst siftings within the above properties with the following basic properties:

- Compressive strength at the age of 3 days 25-40 МПа
- Residual strength after heating up to 1000 °C 50-60 %
- Refractoriness 1500-1680 °C

The technical specifications of "High alumina binder" TU 5746-01-48284834-2005 were developed for the binder. Comparative properties of the heat-resistant concrete on the obtained binder, fireclay and corundum aggregates are given in Table 2.

Table 2. The main properties of heat-resistant concrete based on the high-alumina cement with additives.

Property	Aggregates			
	Fire-clay		Corundum	
The content of the addition of alumina siftings of the catalyst, % by weight	0	20-40	0	20-40
Average density after drying, kg/m^3	1950	1980- 2000	2650	2680- 700
The compressive strength in 3 days, MPa, not less than	30	20-25	35	23-30
Compressive strength after heating up to 1000 ºC, MPa	17	12-14	16	12-15
Temperature shrinkage at the application temperature, %	0,4	0,6-0,8	0,4	0,6-0,8
Residual strength at 800 ºC, %	40	57-67	40	35-30
Resistance to thermal shock at 800 ° C, water thermal cycles, at least	15	10-15	15	10
Refractoriness, ºC, not less than	1470	1590-1620	1570	1640-1690
Maximum temperature applications, ºC	1300	1400- 1500	1400	1500-1600

The developed high-alumina binder makes it possible to obtain concretes with a temperature of application not inferior to concretes on HAC and similar aggregates.

4. High-alumina refractory concrete with additives of self-disintegrating slag of aluminothermic ferrochromium production and screening of the catalyst support of dehydrogenation of hydrocarbons

The issue of improving the characteristics of HAC and concretes based on it with aluminous additives is no less actual than modification of aluminous cement. Since the strength properties and the hardening rate of the HAC are lower than the CAC, and the addition of sifting of the catalyst support of dehydrogenation of hydrocarbons increases the refractoriness, it somewhat reduces the compressive strength, it should be applied in conjunction with more active, calcium-rich aluminates, industrial wastes.

Such additives include wasted synthetic slag and a series of slags of aluminothermic production as well as ferrotitanium slag, ferrochromium slag SFC-A (Table 1) according to TU 0798-060-00186482-2006 and its decaying variety SFC-S. The latter contains a lot of CaO and, correspondingly, in addition to the aluminomagnesium spinel, there are calcium aluminates in a significant amount [7,9]. It is known that the introduction of spent refining steel synthetic slag in the CAC within 40 % ensures an increase in the curing speed in the early periods and a reduction in the cost [16,18]. The slag contained 25 % of $C_{12}A_7$ and 20 % of CA, providing a fast set of strength in 1-3 days of hardening. The same minerals contain, at higher refractory properties, some slags of the aluminothermic production, with the lowest processing costs being with the use of the self- disintegrating variety slag SFC-S. The main phases of the slag of SFC-S are alumina-magnesium spinel, CA and C12A7, as well as β-C2S and γ-C2S. Slags of aluminothermic smelting of ferrochrome have astringent properties, and after extraction of spinel on their basis, alumina cement can be obtained [17]. The binder of pure SFC-S after milling has an activity of 15-17 MPa to 7 days of hardening. The costs of milling of such a slag are small, because as a result of the decomposition it is a dispersed powder. The greatest activity is achieved with fineness of grinding withing 4200-4500 cm^2/g.

VC-75 high-alumina cement differs from HAC according to GOST 969 by a slightly slower strength growth in the first 7 days. When introducing SFC-S in the HAC, a fast-hardening binder is obtained. It is established that the optimal dosages of this slag are 25-30 % of the mass of the binder. The slag of the current output contains significant amounts of $C_{12}A_7$, which causes short period of setting - the beginning of setting in 3-4 minutes.

To adjust the setting time of the binder obtained, surfactant additives of various types were used, based on lignosulfonates (LST), a naphthalene base and on the basis of PSE [7,13,14,19,20]. It was found that the addition of LST is ineffective, and S-3 in an amount of up to 0,4 % allows to get the binder with the beginning of in 25-35 minutes at a normal density of 27,5 %. However, it was found that in the concretes with HAC superplasticizer S-3 gives a decrease in strength when heated [7]. Therefore, the impact of common PCE has been studied, which is well adsorbed on a surface of aluminate [11-15]. Dry superplasticizers Melflux 1641F, 2641F, 2651F, as well as liquid additive Glenium 51 produced by BASF were used.

The addition of Melflux 1641F in an amount of 0,2-0,6 % gives a strong water-reducing effect (a normal consistency of 18 %), with the beginning of setting, as with addition of S-3, in 35 min.

2641F and 2651F are somewhat more effective, and PP200F has an excessively pronounced effect of slowing down the setting and hardening processes. The use of Glenium 51 additive is most expedient in dosages of 0,2-0,4 %, while the binder has a start of setting not earlier than 40 minutes. Thus, cement with a setting time close to alumina cements by GOST 969 was obtained. The developed binder let obtain concretes with a compressive strength of 40-55 MPa.

To increase the fire resistance, the catalyst waste was injected into the binder composition, and in order to increase the strength, the amount of additives of the superplasticizers mentioned above was increased by 0,05-0,1 %. When using light concrete mixtures, the strength is 20-25 MPa. The use of hard mixtures provides a compressive strength of 35 MPa without plasticizers and at least 80 MPa with PCE. (Table 3).

The phase composition of the hydration products in cement stone differs from the HAC binder. The siftings of the catalyst support of dehydrogenation of hydrocarbons are hydrated to hydrargillite (gibbsite), so the amplitude of peaks of alumina hydrates on X-ray diffraction patterns increases high.

At the same time, the reflection intensity is relatively small, since the hydrates are poorly crystallized. X-ray diffraction patterns show intense reflections of γ-C2S contained by self-decaying slag of SFC-S, as well as the $4CaO*3Al_2O_3*CrO_3$. The presence of the latter is of great scientific interest and explains the low strength of the astringent from pure SFC-S slag. The binding of considerable amount of CaO to the inert compound significantly impairs the binding properties of chromium oxide (it is believed that calcium oxides in C_2S bind intensively in decomposing slags of various species of SiO_2, so the binder has low strength). It should be noted that the formation of chromium in such an inert compound as $4CaO*3Al_2O_3*CrO_3$ suggests that the slag is safe from the point of view of environmental requirements.

Table 3. Properties of refractory concrete with VC-75 binder with the addition of SFC-S and aggregate from slag of metallic chromium.

Property	Additive			
	SFC-S		SFC-S and siftings of the catalyst support of dehydrogenation of hydrocarbons	
Additive (Melflux 2641F), %	0	0,4	0	0,25
Average density after drying, kg/m^3	2700	2800	2600	2650
Compressive strength after steaming, MPa	40	55	35	80
Residual strength at 800 ºC, %	42	58	38	54
Resistance to thermal shock at 800 ° C, water thermal cycles, at least	14	16	12	14
Refractoriness, ºC, not less than	1600	1600	1600	1600
Maximum temperature applications, ºC	1700	1700	1770	1770

5. Conclusion

Thus, the combination of an active high-alumina additive in the form of siftings of the catalyst support of dehydrogenation of hydrocarbons with PCE, as well as sifting of the catalyst carrier with self-decomposed slag of the aluminothermic smelting of ferrochrome made it possible to obtain concretes with high strength and refractory properties.

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