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Features of Formation of the Phase Composition and Structure Sulfoferrite Clinker Based On sulfate Containing Secondary Raw.

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ABSTRACT

Synthesized sulfoferrite clinker based on ferrite and sulfate-containing recycled, used as an expanding agent in the manufacture of special types of cement. The features of mineralization in sulfoferrite clinker from waste, the mechanism of formation of the cubic system phase. It was determined that under the influence of impurities introduced manmade materials, occurs the formation of solid solutions with belite dicalcium ferrite, which leads to the formation of single phase cubic structure. Phase of the cubic system, synthesized in the clinker -based man-made materials, forms and infinite silicate system. In the presence of impurities is formed in a solid solution of dicalcium ferrite belite and anhydrite, belite introduction into anhydrite, dicalcium ferrite and increases the structural defect of minerals and thus catalyzing the diffusion processes, it is necessary for the formation of calcium sulfoferrita. The microstructure sulfoferritnogo clinker, formed under the influence of impurities. By determining the elemental composition of the resulting crystal phase, limits sulfoferrita calcium compounds, namely basicity relative to anhydrite, at different temperatures.

Keywords: sulfoferrite clinker, sulfoferrite calcium, cubic phase, solid solution, secondary raw materials, ferrite containing waste, sulfate containing waste.

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INTRODUCTION

Sulfoferrite clinker is calcine the raw material mixture consisting of a carbonate component, gypsum, and iron component, and is used as an expanding additive in the production of composite dimensionally stable and expanding cements [1]. The mineralogical composition of clinker sulfoferrite represented mainly by two phases: the main - sulfoferrite calcium $x\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot n\text{CaSO}_4$, is a solid solution of dicalcium ferrite anhydrite and silicate represented Belita C_2S [2-4]. Sulfoferrite calcium when mixed with water is able to grow in volume and the produced during hydration of calcium hydrosulfoferrit having ettringit needle structure reinforces the structure of cement stone, increasing its strength. Bleaches, in turn, is not capable of expansion and deformation is inert phase [5]. However, since almost all raw materials containing SiO_2 in the structure, complete absence of belite clinker in sulfoferrite impossible but sulfoferrite phase should dominate. Adding sulfo-ferritic clinker in an amount of 4-12% by ordinary cement allow to create on its basis dimensionally stable composite cements [6].

As the in present time goes actively developing of saving technologies contribute to increasing use as raw materials for cement production of alternative raw materials [7-9], we investigated the obtaining sulfoferrite clinker based on technogenic materials. Proceeding from the fact that virtually any secondary raw materials contains many impurities, the main purpose of job was to study the effect of impurities contained in the waste, on the synthesis sulfoferrite clinker.

THE MAIN PART

Sulfoferrite clinker (SFC) were synthesized based on chalk and secondary raw materials - ferrite and sulfate waste from ferrovanadium production, chemical compositions shown in Table 1. By waste were replaced society used pyrite cinders, whose use is restricted due to their scarcity and dihydrate gypsum. Glandular phase composition of waste was introduced hematite and gypsum dihydrate, sulfate waste - dihydrate gypsum [10].

Table 1: Chemical composition of raw materials used for synthesis of sulfoferrite clinker

Raw component	Oxide content, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	Other *
Chalk	2,68	0,61	0,22	53,74	0,26	0,01	0,15	—
Glandular waste	14,1	3,35	39,8	10,5	1,52	14,2	—	16,32
Sulfate waste	0,39	0,39	2,84	28,90	2,25	36,70	—	11,18

* Cr_2O_3 , TiO_2 , MnO_2 , V_2O_5

Calculation of the raw material mixture for the production of sulfoferrite clinker produced by glandular and sulfate modules and characterizing the resulting SFC mineralogical composition, namely basicity sulfoferrite calcium and its percentage with respect to belite [2, 11].

The raw material mixture was calculated to receive 60% of a highly basic calcium sulfoferrite $\text{C}_2\text{F}\cdot\text{CaSO}_4$ and 30% belite C_2S . In a mixture containing huddled impurity oxides in an amount of 7,83% ($\text{Cr}_2\text{O}_3 = 1,22$; $\text{TiO}_2 = 2,70$; $\text{MnO}_2 = 2,76$; $\text{V}_2\text{O}_5 = 1,15$).

Maximum firing temperature sulfoferrite clinker based on man-made materials became the temperature to 1350°C . Sintering is done with isothermal holding that prevented sublimation sulfates, starting at a given temperature.

To determine the effect of impurities contained in the waste to mineralization in sulfoferrite clinker as a reference clinker synthesized from chemically pure components taken in the same stoichiometric ratios as clinker based on recycled materials. Sulfoferrite clinkers were synthesized under the same conditions.

The phase structure of the obtained spec clinker was investigated by X-ray analysis on the instrument ARL X'TRA.

Sulfoferrite clinker based on the pure components was presented sulfoferrite calcium and Belita (Fig.

1a), which confirms the literature data [2, 3]. Moreover, slight absorption anhydrite dicalcium ferrite at 1350°C took place, which is indicated by a change in intensity of the phase glandular analytical lines ($d = 2,68; 2,72; 2,80; 3,68; 2,61 \text{ \AA}$).

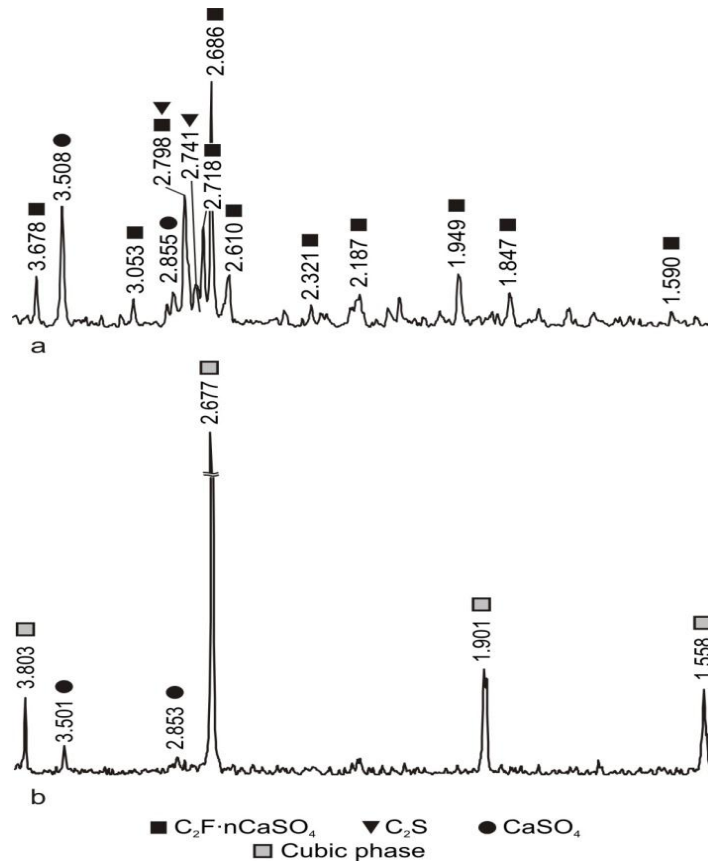


Figure 1: Features mineral in CFC by impurities: a - SFC based on chemically pure components, b - NFC-based man-made materials

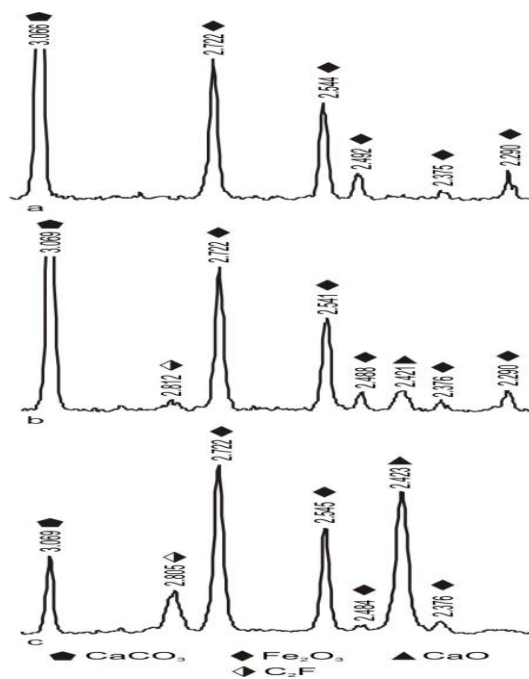


Figure 2: Formation C_2F system $CaCO_3-Fe_2O_3$: a - t firing = 700°C; b - t firing = 750°C; c - t firing = 800°C

Thus in this clinker is present in a large amount is not metabolized anhydrite ($d = 3,50; 2,85 \text{ \AA}$).

Sulfoferrite clinker based on man-made materials are also designed to receive sulfoferrite calcium and Belita was presented single phase (Fig. 1b), which had a perovskite structure ($d = 2,70; 1,91; 1,57 \text{ \AA}$), which crystallizes in cubic system with the unit cell parameter $3,905 \text{ \AA}$. Cubic phase was obtained unit cell parameters $3,800 \text{ \AA}$, which characterizes some of its distortion compared with the crystal lattice perovskite.

Anhydrite in the clinker at the same temperature and aging present in much smaller amount in comparison with the clinker based on the pure components.

Based on the fact that the phase structure of clinker based technogenic materials differed sharply from the phase structure of clinker on the basis of pure components to study the laws of phase formation in the synthesis of SFC based on secondary raw materials made a series of isothermal sintering in the temperature range $600\text{-}1500^\circ\text{C}$ in steps of 50°C .

The decomposition of calcium carbonate in the raw material mixture starts at 700°C . The released calcium oxide reacts with available iron oxide to the mixture. This reaction, like many solid-phase reaction can proceed in steps, or the formation of the final phase may take place without the occurrence of the intermediates [12]. Mineralization in the system $\text{CaO-Fe}_2\text{O}_3$, calculated for a highly basic calcium ferrite C_2F , hitherto not well studied, and data on the formation of minerals of this system is contradictory. According to one of the primary phase of the system is highly basic CF, which reacts with calcium oxide goes into C_2F [2], on the other - C_2F formation occurs without the formation of an intermediate phase [3].

Primary phase of the X-ray diffraction study of a mixture of clinker, calculated for a SC-based waste has not been possible to establish, as hematite, ferrite one calcium and dicalcium ferrite have similar diffraction reflection. Therefore, mineralization in the system $\text{CaO-Fe}_2\text{O}_3$ studied on pure components - CaCO_3 and Fe_2O_3 - using high X-ray analysis (Fig. 2). Shooting was performed in the temperature range $600\text{-}1350^\circ\text{C}$ with steps of 50°C without crystallization of the material. Found that when the first portion of CaO, released during decomposition CaCO_3 in raw mixture is formed dicalcium ferrite, identified by the characteristic reflection $d = 2,80 \text{ \AA}$ [13] (Fig. 2b). With increasing temperature, the intensity of the peak $d = 2,80 \text{ \AA}$, C_2F -owned, growing, thus continuing C_2F mineral formation (Fig. 2, c).

Thus, in a mixture calculated to obtain a ferrite highly, basic calcium C_2F formation is not an intermediate phase CF, therefore, a primary phase is C_2F . Theoretical studies of the possible reaction $2\text{CaO} + \text{Fe}_2\text{O}_3 = \text{C}_2\text{F}$ made using thermodynamic calculations. Since the calculation of the Gibbs energy was carried out at temperatures above the phase transition temperatures of the reactants, the enthalpies and entropies of reactions were calculated separately for each interval between the temperatures of phase transformations, including intervals of 25°C (298K) to the temperature of the first phase transformation from the last phase transformation to the final temperature [14]. To 927°C (1200K), the reference data used for the reaction system in $\text{CaCO}_3\text{-Fe}_2\text{O}_3$, over 927°C (1200K), - the data for the reaction in the system $\text{CaO-Fe}_2\text{O}_3$. When calculating the thermodynamic quantities used and the coefficients of the heat capacity of the reference tables compiled Babushkin V. I. [15] and Kireev V. A. [16]. Thermodynamic calculations showed that at temperatures above 800°C is possible in principle to the formation of a highly basic C_2F system. Moreover, with increasing reaction temperature increases the probability of transmission as indicated by the decrease in the Gibbs energy values (see Table 2).

Table 2: The values of the Gibbs energy for the synthesis reaction of the mineral C_2F at different temperatures

Synthesis reaction of C_2F	ΔG^0_t , kJ / mol at T, $^\circ\text{C}$								
	700	800	900	1000	1100	1200	1300	1400	1500
$2\text{CaCO}_3 + \text{Fe}_2\text{O}_3 = \text{C}_2\text{F} + 2\text{CO}_2$	15,9	-8,1	—	—	—	—	—	—	—
$2\text{CaO} + \text{Fe}_2\text{O}_3 = \text{C}_2\text{F}$	—	—	-30,8	-52,8	-74,2	-95,0	-115,4	-135,3	-145,1

After the end of the formation of clinker C_2F -based recycled materials at a temperature of 1000°C the latter is represented dicalcium ferrite, belite and anhydrite. However, already upon reaching 1100°C to sinter

belite was not detected, and clinker phase was submitted cubic system ($d = 2,70; 1,91; 1,57 \text{ \AA}$) and anhydrite. At higher temperatures gradually assimilated received CaSO_4 phase analytical lines which are shifted to smaller angles.

Reducing the intensity of the analytical lines anhydrite associated with its implementation in the resulting phase, but not from the sublimation. The fact of possible decomposition of anhydrite at a given temperature and volatilization of its degradation products, which is also characterized by a decrease in the intensity of the analytical lines CaSO_4 , not mounted, because the clinker out CaO_{fr} free calcium oxide released by the decay of CaSO_4 .

By modeling mixtures of chemically pure components with the addition of each impurity oxide alone and their various combinations found that such a cubic structure is formed under the joint influence of three impurity oxides - Cr_2O_3 , TiO_2 , MnO_2 .

Under the influence of these impurities is the introduction in two belite-calcium ferrite, as determined by the study of $\text{C}_2\text{F-C}_2\text{S-Cr}_2\text{O}_3\text{-TiO}_2\text{-MnO}_2$. This causes reorientation of the lattice of the crystal and formation of dicalcium ferrite cubic phase. Sulphate phase does not participate in the formation of crystals of the cubic system, however, appears intensifier implementation process Belita in dicalcium ferrite, as evidenced by the presence of the analytical lines of C_2S in Sulfate-Free system where its full implementation difficult.

In turn, the introduction of a belite in dicalcium ferrite provides virtually complete absorption anhydrite in the clinker, based on a significant increase in waste due to defects in the structure of dicalcium ferrite as opposed to on the basis of pure clinker components, in which anhydrite in large amount present in the free form.

Formation of the microstructure sulfoferrite clinker synthesized on the basis of manmade materials, was studied by energy dispersive analysis.

Clinker based on recycled materials, designed to obtain ferrite and silicate phases, was presented a crystal phase is uniformly distributed over the entire surface of the section. Crystals obtained phase based on the elemental composition contained not only the ions of iron, calcium, sulfur, but also all the silicon and the impurity elements, which is XRD data confirms the introduction of belite phase of dicalcium ferrite structure. The intermediate phase current represented clinker anhydrite, but its composition as well as resulting in a single phase composition, includes in an amount of belite 0.5-0.7 moles per 1 mole of impurity elements, and CaSO_4 . Thus, in the presence of impurities are occurs distributed belite between the sulfate and glandular phases, and in structure of ferrite embedded anhydrite, already containing in their structure belite.

Microscopic studies comparing samples of this clinker baked at three temperatures - 1250, 1300 and 1350°C showed that the crystals obtained phases at various temperatures have the same qualitative composition. The intermediate clinkers presented anhydrite with imbedded silicate phase and some trace elements (Table 3). Moreover, in the anhydrite mainly implemented vanadium oxide (Table 3), whereas the glandular phase in the composition is present in small amounts along with the oxides of chromium, manganese, and titanium.

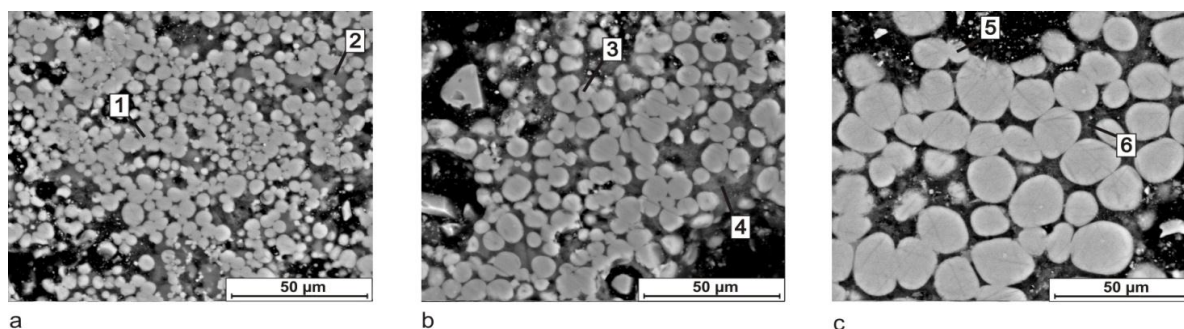


Figure 3: Electron micrographs sulfoferrite clinker synthesized based on man-made material, at a magnification of 2000:
a – t firing = 1250 ° C; b - t firing = 1300 ° C; c - t firing = 1350 ° C

Table 3: The crystal composition (%) in the measuring points indicated in Fig. 3

Measuring point	The oxide composition of the crystals,%									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	TiO ₂	Cr ₂ O ₃	MnO	V ₂ O ₅
1	43,56	11,24	3,34	26,67	3,42	1,05	3,86	1,92	3,71	1,23
2	46,06	12,81	1,79	—	31,55	1,25	0,92	—	0,86	4,76
3	42,76	6,62	2,26	28,93	6,19	0,56	6,13	—	5,79	0,75
4	48,35	11,76	1,23	—	33,02	0,35	—	1,01	—	4,28
5	41,70	11,03	2,20	21,09	9,89	1,16	3,35	1,45	3,78	1,23
6	49,74	12,02	—	—	32,73	0,22	—	1,14	—	4,15

In clinker based on man-made materials with increasing temperature coarsening crystals obtained phase (Fig. 3), due to their bonus re crystallization and fewer intermediate phase represented by anhydrite, due to the gradual assimilation of its calcium ferrite.

At a temperature of 1250°C. The composition of the phase limit in terms of pure calcium sulfoferrite was $C_2F \cdot 0,25CaSO_4$, at 1300°C - $C_2F \cdot 0,65CaSO_4$, at 1350°C - $C_2F \cdot 0,91CaSO_4$. Thus, with increasing temperature an increasing absorption provided glandular anhydrite phase that is substantially completed when reached the maximum firing temperature.

CONCLUSION

In sulfoferrite clinker based on recycled materials under the influence of introduced impurities formed different phase structure and microstructure unlike clinker based on the pure components. In the presence of impurities is the formation of single phase cubic structure in the clinker, calculated to produce calcium sulfoferrite orthorhombic and belite.

Findings

- In clinker based on recycled raw materials, designed to obtain a ferrite and silicate phases, actually formed one cubic phase structure.
- The process of assimilation of anhydrite in the clinker-based man-made materials is practically completed by 1350°C, whereas in the clinker on the basis of the pure components of its full implementation difficult.
- The process of formation of phase C_2F going one-step, without forming an intermediate compound low basic CF.
- Phase of cubic symmetry in the NFC-based man-made materials formed under the joint influence of three impurity oxides - Cr₂O₃, TiO₂, MnO₂.
- In the presence of impurity phases occur in the introduction of the silicate lattice dicalcium ferrite.
- The intermediate phase of clinker represented anhydrite with ethyl introduced it whitens together with impurities.

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