Combined cements with non-shrinking properties using sulfoferrite clinker

I N Borisov¹, A A Grebeniuk¹, V I Dyukareva²

¹Department of Technology of Cement and Composite Materials, Belgorod State Technological University named after V.G. Shukhov, 46, Kostyukov Street, Belgorod 308012, Russia
²Department of Higher mathematics, Belgorod State Technological University named after V.G. Shukhov, 46, Kostyukov Street, Belgorod 308012, Russia

E-mail: alexander.grebeniuk@mail.ru

Abstract. The increase of stackable waste products quantity demands taking measures is directed towards its decrease. This waste products usage in cement production which is one of the most consumptive branches of production, based on material and expenditure of energy, is one of the possible decisions. The usage of recycled resources in special sorts of cement production in contrast with its application in the Portland cement production is poorly understood and requires the increase of scientific knowledge with the purpose of total control over a technological process. The appropriate roasting conditions and whole technology ensuring is possible by careful updating and control of raw mixes. There is a potential that the most components are added the most qualitative final product will be in condition of necessary control. Two calculated modules (ferrite and sulfate) are usually used in the production, which guarantees an optimal technology of relatively clean raw materials production. The production of high-quality sulfoferrite clinker, having fair quantities of silicon oxide, is complicated since collateral compounds are formed during roast. As a result, the formation of calcium sulphate solid solution in calcium ferrite is put off until higher temperatures are reached, and after that it becomes improbable in view of both anhydrite crystals’ extension and sublimation’s strengthening.

1. Introduction

Strengthening of productive and agriculture complexes and growth of consumer’s activity of the society bring huge benefit to both a region development and a whole country. Despite weighty and obvious positive moments there are negative ones what are connected to problems’ decision of lots of technogenic and domestic waste usage what makes both spoil area’s aesthetic appearance and damage to ecology.

Some kinds of domestic waste achieved widespread use as recycled resource components on the other productions [1,2]. Such kind of use solves the problems of waste recovery to allow to economize both raw material resources and finance. Furthermore, it doesn’t damage the final product quality by rational use. You may experience inability of all named qualities of secondary materials because of impenetrable difficulties arose in production line. That happens in case of unwanted components’ presence in technogenic waste what makes next usage of secondary materials impossible.
Premix use in cement production is caused by demand to get high quality cement the achievement of what is possible in condition of careful correction and control of raw materials’ chemical composition. Three module characteristics may be used for qualitative Portland cement preparation according to different Russian Federation demands. This usage guarantees necessary mineralogical composition what ensures strength bundle on every maturing phase and optimal amount of melt and its viscosity during clinker roast are the conditions by reason of technological process production difficulty [3]. When manufacturing special cement types especially sulfoferrite ones’ there are no rich opportunities of necessary chemical composition support at the implementation of adulterated components. These module characteristics help to produce qualitative sulfoferrite clinker only from relatively pure raw materials. The miry components’ usage causes difficulties both at the calculation of sulfoferrite clinker and at the next technological processes. So technological aspects of sulfoferrite clinker production from technogenic waste with some part of impurity element are described in the article [4]. Solid solution with dicalcium ferrite phases of larnite and anhydrite is a synthesis result from contained manganese oxide, chromium and titanium.

2. Methodology and equipment
The list of methods and appliances was used to study sulfoferrite clinker synthesis and cement stone properties got from mixed cement. The sulfoferrite clinker synthesis carried out on stove with carborundum rods as heating spirals. The ethyl glycerate and ion-exchange methods were used to determine substance of free calcium oxide and general quantity of Sulphur oxide (IV). The establishment of mineralogical contest of raw materials and sulfoferrite clinker synthesis were made with the help of X-ray photography analysis of roentgenogram what was given by ARL X’TRA Thermo Fisher Scientific. ARL 9900 WorkStation was used to determine chemical composition of raw materials components by X-ray fluorescence method. TESCAN MIRA 3 LMU was used to make an examination of synthesis examples microstructure. The particle size was studied by ANALYSETTE 22 NanoTec plus. The heat emission during Portland cement aquation and sulfoferrite clinker has been determined by ToniCal Trio for 7 days. Linear expansion and compressive strength of sample was defined by plant for linear expansion fixation with digital indicator and hydraulic press.

3. Main part
Chalk, scoria, ferrite waste and gypsum stone were used as raw materials for sulfoferrite clinker’s synthesis. Table 1 contains chemical composition of named components. The data presented above show that silicon oxide content in ferrite is not able to produce minerals. The table 1 shows big amount of aluminum oxide substance in used ferrite waste. Aluminum oxide cannot produce minerals during hydration of what the cement stone expands.

| Component       | Chemical composition of materials, % |
|-----------------|-------------------------------------|
|                 | CaO   | SiO₂  | Al₂O₃ | Fe₂O₃ | SO₃  | MgO  | R₂O  | Loss on ignition | Σ     |
| Chalk           | 54,62 | 1,90  | 0,37  | 0,20  | 0,04 | 0,22 | 0,07 | 42,58            | 100,00 |
| Residues        | 10,89 | 2,58  | 0,84  | 75,62 | 0,68 | 2,62 | 1,61 | 5,07             | 100,00 |
| Ferrite waste   | 15,43 | 24,92 | 4,04  | 40,56 | 0,75 | 2,37 | 1,21 | 10,56            | 100,00 |
| Gypsum stone    | 34,68 | 1,90  | 0,66  | 0,30  | 38,98| 0,62 | 0,14 | 22,72            | 100,00 |

X-ray phase analysis of raw materials was made to determine the order of necessary minerals in sulfoferrite clinker production and beginning of its reaction temperature (Figure 1). Mineralogical composition of raw materials contains of: calcite, beta-quartz and ferriferous enstatite composition for chalk; wustite, magnetite, pure iron also little admixture calcite and beta-quartz composition for
scoria; haematite, beta-quartz, wollastonite, clinoenstatite, akermanite composition for ferrite waste; gypsum, calcite – for gypsum stone.

Figure 1. Mineralogical composition of used raw materials: a) chalk; b) scoria; c) ferrite waste; d) gypsum stone.

There two calculated modules of calculation of raw mixes to produce sulfoferrite clinker [5]: ferrite (Ferrite module) and sulfate (Sulphate module) what adjusts calcium sulfoferrite composition. It’s necessary to adjust level of silicon oxide content in raw mix since there are significant amount of silicon what produces calcium silicate during synthesis what is unable to expand. We bring in sulfoferrite axial mode (Silicoferrite module) for this purpose [6] what adjusts correlation between phases of sulfoferrite and calcium silicate. Owning to tree calculated modules we have an ability to calculate quadripartite raw mix without extra blending what was used to count three-component raw mix. The used calculated module’s formulas are:

- Ferrite module $F_{M} = \frac{C - 1.867S - 0.549A - 0.7S}{F}$
- Sulphate module $S_{M} = \frac{S - 0.261A}{F}$
- Silicoferrite module $SF_{M} = \frac{S}{F}$

Raw mixes for highly basic sulfoferrite clinker’s synthesis were calculated with the help of: 1) two calculated modules (ferrite and sulphate) to produce tree-component raw mixes: in one case scoria is ferrous component (3 K (I)), in another case ferrite waste (3 K (II)) is used; 2) tree calculated modules – quadripartite raw mixes with different correlation of SiO2/Fe2O3 production. Thus, values SFM 0,15; 0,27 и 0,55 correspond to designations 4 K (I), 4 K (II) и 4 K (III). Value of ferrite and sulfate modules equal to 0,7 and 0,5 what is directed to obtainment of dicalcium sulfoferrite C2F∙CaSO4. Table 2 shows counted chemical composition of raw mixes.

Production of inert calcium silicosulphate compound 2C2S-CaSO4 in the range of 900-1230\(^\circ\)C during raw mix roasting directed to obtainment of sulfoferrite clinker. This reaction is undesirable because 2C2S-CaSO4 doesn’t have both the ability to expand and bind [7]. The correction of raw mix
composition for silicon oxide is able to decrease an amount of calcium silicysulphate at the intermediate reaction step without substantial technologic tactics. Figure 2 shows calculated mineralogical composition at temperature between 900–1230°C [8] during sulfoferrite clinker’s synthesis depending on silicoferrite module’s value. The figure shows that there no larnite phase in sulfoferrite clinker’s composition before the value reaches silicoferrite module is µ0.75 because it interacts with anhydrite and produces 2C2S-CaSO4. There will be phases of calcium silicysulphate, larnite, dicalcium ferrite in sulfoferrite clinker’s composition if silicoferrite module’s value is 0.75. There won’t be anhydrite solid solution in calcium ferrite because it will be used to bind larnite.

Table 2. Chemical composition of raw mixes.

| Designations | Sulfoferrite clinker’s chemical composition, % | Module characteristics |
|--------------|--------------------------------------------|------------------------|
|              | CaO  | SiO2  | Al2O3 | Fe2O3 | SO3  | MgO  | R2O  | The rest | F_M | S_M | SF_M |
| 3 K (I)      | 33.29| 1.58  | 0.46  | 28.58 | 14.41| 1.11 | 0.71 | 0.19     |     |     |      |
| 3 K (II)     | 36.95| 10.36 | 1.72  | 15.57 | 8.24 | 1.03 | 0.54 | 0.15     | 0   | 0   |      |
| 4 K (I)      | 34.22| 3.79  | 0.78  | 25.30 | 12.85| 1.09 | 0.66 | 0.18     | 0.7 | 0.5 | 0.15 |
| 4 K (II)     | 35.12| 5.96  | 1.09  | 22.08 | 11.33| 1.07 | 0.62 | 0.17     | 0.27|     |      |
| 4 K (III)    | 36.54| 9.37  | 1.58  | 17.04 | 8.93 | 1.04 | 0.56 | 0.15     | 0.55|     |      |

Figure 2. Dependence of mineralogical composition of sulfoferrite clinker’s change between 900-1230°C depending on silicoferrite module

Gypsum dehydration and it produces defect structure as a result of intence water outlet is primary reaction from the fusion reaction. The next stage is oxidation of iron and ferric oxide (FeO and Fe3O4) to the highest oxidation level – Fe2O3 at the temperatures near 600°C. This reaction leads to the cluster of energy express what promotes to the intensification of the next reactions (the Hadvall effect) [9]. Carbonate dissociation begins at the 750-800°C, as a result of combined effect of alkali and sulphates in raw mixes on the decomposition process [10,11]. Calcium oxide is produced in the process of the reaction also instantly reacts with Fe2O3 and its result is production of calcium ferrite of variable basicity of nCaO•mFe2O3. Larnite traces are fixed on roentgenogram at 850°C. Next step is production of calcium silicysulphate as the result of the reaction of C2S and CaSO4. Reaction of interaction between larnite and anhydrite is priority from the kinetics’ point of view comparing to CaSO4 solid solution production in calcium ferrite. Production speed of calcium sulfoferite increases only at 1100°C. Calcium silicysulphate decomposition in larnite and anhydrite happens at 1230°C. The SO2 efficiency upon anhydrite decomposition effects on the next C2F-CaSO4 production because stoichiometric correlation between calcium ferrite and anhydrite is broken and as a result there is surplus of free calcium oxide. The control of fulness formation minerals and anhydrite dissociation was valued at the CaO_f in SO3 parts at temperatures of 700 – 1300°C and 900 – 1300°C (Figure 3). The fraction of free oxide in the reaction process has some dependence. Hence CaO_f quantity decreases from composition of 3 K (II) to composition 3 K (I). Quantity of CaO_f in synthesized
sulfoferrite clinker strictly depends on C₃S quantity in mineralogical composition of every sample. Maximum quantity of unconsolidated CaO in every sample are observed at temperature 850°C. Later on the part of free calcium oxide lowers what shows the origin of reaction of sulfoferrite clinker’s mineral production. Composition 3 K (II) has a long period of CaO assimilation what associates slowing down of the calcium oxide and ferric oxide reaction because of low energy express quantity and structure defects since there was no iron on intermediate levels of oxidation in raw mix. Equal character of SO₃ composition curves shows the outlet of SO₂ from sulfoferrite clinker (Figure 3) that doesn’t depend on raw mix compound but only depends on temperature (with condition of identical firing sphere). The roentgenogram of roasted samples (Figure 4) shows the production of dicalcium sulfoferrite in all synthesized sulfoferrite clinker’s compositions because there is some apex shifting of dicalcium ferrite C₂F (от 2,685 Å до 2,675 Å) and decrease of anhydrite apex.

**Figure 3.** Kinetics of roasting of sulfoferrite clinker’s composition: a) part of stress-free calcium oxide; b) part of lost sulfur oxide (VI)

**Figure 4.** Mineralogical composition of synthesized sulfoferrite and Portland cement.

Peculiarities of synthesized samples’ microstructure at roasting temperature (1280°C) (Figure 5) were studied. In this way there is the increase of crystals of all phases distribution’s variability due to
the larnite phases decrease in samples. Grouped larnite crystals reach proportion 20 µm. There are thin anhydrite blades in grouped larnite having stayed after decomposition of calcium silicosulphate. Since anhydrite taking part in calcium silicosulphate composition stays between larnite crystals and doesn’t contact with dicalcium ferrite crystals it doesn’t take part in reactions of solid solutions composition with calcium ferrite.

![Figure 5](image_url)

**Figure 5.** Microstructure of synthesized sulfoferrite clinker samples at 1280°С.

After the roasting of sulfoferrite clinker it was also crushed in metallic mill to specific surface area of 460 m²/kg. Its value was chosen based on literature [12]. Used specific surface for production of compound Portland cements was 310 m²/kg. Granulometric analysis was made to determine used fractional composition of cement compounds in detail. Figure 6 contains produced distribution of particle size.
Figure 6. Fractional composition of used Portland cement and synthesized sulfoferrite clinker.

Fractional composition of used Portland cement (PC) is poly fractional and mono modal particle distribution predominating particles sizes from 7,5 to 75 µm. The grounded sulfoferrite clinker compositions have poly modal allocating whereby particles’ fraction sized from 0,1 to 1 µm is released. In this way there are two more high apex properties for three-component and 4 K (I), 4 K (III) compositions besides early mentioned range of distribution and for 4 K (II) – only one. Middle distributions of particles sizes for sulfoferrite clinker are: 3 K (I) – from 3 to 50 µm; 3 K (II) – from 1 to 45 µm; 4 K (I) – from 1 to 35 µm; 4 K (II) – from 0,9 to 50 µm и 4 K (III) – from 1 to 100 µm. All obtained curves can be described with the help of Rosin–Rammler and A.N. Kholgomorova’s distribution law. The systems with poly modal particles distribution are able to produce more solid structures comparing to mono modal distribution [13] what contributes to production of more solid cement stone with improved strength index and water passage through cement stone etc.
The heat generation during Portland cement hydration and all sulfoferrite clinker compositions has been studied for 7 days (Figure 7). The figure shows the most abundant supply of heat what was isolated at the early stages for Portland cement. The most differential change of abundant supply of heat among sulfoferrite clinker are in 4 K (I) и 3 K (I) compositions what have apexes of the hardening beginning starting with 40-th hours after blocking for 4 K (I) and with 48-th hours after blocking for 3 K (I). The 3 K (II) and 4 K (III) compositions have the most differential heat changes comparing with the other compositions at the early stages. The 4 K (III) composition has the least heat effect comparing with the other compositions. Due to the data of the heat generation and literature [14] we can summarize that 4 K (I) и 3 K (I) compositions can have some hydraulic activity comparing with the other compositions but the main part of hydration will take place after 40 hours of hardening that means after the cement stone’s frame formation what can lead to its destruction. Hence it’s advantageous to use these sulfoferrite clinker’s composition (with named values of specific surface, mechanical gradation and mineralogical composition) as contract components for cement stone.

Combined cements were composed by Portland cement and sulfoferrite clinker’s averaging as a different percentage. The sulfoferrite clinker’s concentrations were chosen for research: 1, 2, 4, 6, 8, and 10%. The averaging has been making for 6 hours in porcelain mill. Rubber plugs were used as averaging solids and it expelled possibility of abnormality of binders’ fractional composition. The samples’ formation was made in forms for little samples: little creeks samples sized 1,0х1,0х6,0 sm. and cube samples sized 1,41х1,41х1,41 sm. Water-cement relation for all composite binders was 26,67%. Samples with moisture of 90% sustained the first day of hardening. The forms were demolded and took out after first hardening and concrete strength development. The prism samples with named sizes were used to study linear expansion. Initial parameters of these sizes were measured with the help of linear expansion metering indicator with digital display what helps to register size change with a precision to 0,001mm. Gaging of linear expansion were made at age of 2, 3, 4, 5, 7, 10, 12, 14, 17, 20, 22, 24, and 28 days. Figure 8 shows the results of blend compositions’ linear expansion.

All blend compositions with sulfoferrite clinker’s concentration higher than 1% showed the increase of linear sizes. The change of sizes with the 3 K (I) и 4 K (I) sulfoferrite clinker’s use was the most intensive. At the age of 8 days the increase of linear expansion of these components was more than 70 % from maximum value for these compositions. It was 50% growth from the maximum value using 4 K (III) at age of 8 days. The composite cements with 3 K (II) admixture addition differs from mineralogy analogous 4 K (III) composition by the linear expansion value (more than double). This big difference can be caused by variety of synthesis process. The contained 4 K (II) compositions after the increase of its sizes during 17 days, shrink to the age of 20 days. Then linear expansions stayed stable. Blend compositions with 1 % sulfoferrite clinker’s addition at early ages insignificantly increase its sizes that is connected to cement stone soaking caused by significant growth of colloidal
mass. Hydrated minerals crystallize and cement stone compress after increasing. 1% of expanding additive is not enough for getting shrink-resistant formula.

![Figure 8. Linear expansion change of composite cements prism samples.]

Estimation of hydraulicity of procured composite binding materials was made with the help of test for cement stone compression at ages of 2, 7 and 28 days. Compression strength was calculated as arithmetic mean of four samples. Figure 9 contains the results of the test.

Blended cements have the most compressive attributes and they have 3 K (I), 4 K (I) and 4 K (II) as second component the quantity of which was limited to 4%. Ceiling of 3 K (II) and 4 K (III) was limited to 6%. The named above concentrations have compression roll-off what is connected to stiffening in cement stone structure and this leads to its destruction. Sulfoferrite clinker’s structure in small quantities leads to cement stone’s compression what increases the samples’ strength of compression.

At early ages of hardening the products of hydration are represented mostly by Portlandite Ca(OH)$_2$, ettringite C$_3$A·3C$_3$S·H$_{32}$ and low-basic hydrated calcium silicate C$_x$S$_y$H$_z$. Sulfoferrite calcium hydrating in binding cements happens after according to heat generation curves. The strength is based on both hydrated phases produced by Portland cement minerals and water interacting, and hydrate of sulfoferrite clinker’s minerals and tree-sulphate form of calcium hydroferrite C$_3$F·3C$_3$S·H$_{32}$
forming as a result. Low-basic forms of calcium hydrosilicate $C_xS_yH_z$ become high-basic at early stages of hardening. Also, $C_3F\cdot3CS\cdotH_2$ crystallization increases and in these ways the structure of cement stone compresses to certain bound. There are extra stresses in cement stone in case limit is exceeded what negatively effects on its strength.

![Compression strength of mixed cements](image)

**Figure 9.** Compression strength of mixed cements.

4. Conclusion
1. The presence raw mixtures when producing sulfoferrite clinker of silicon oxide have negative influence on production technology because the formed larnite not only have some abilities to expand but also draws to oneself calcium salphate. That is necessary to produce solid solution with dicalcium ferrite.
2. Mineralogical composition of synthesized sulfoferrite clinker influences on produced sulfoferrite cements’ properties. In this way samples having different mineralogical composition can have various grinding kinetics what can be marginally observed for different particle size distribution sulfoferrite clinker. We can conclude that expanding additive usage with Portland cement must be strictly monitored upon the results of heat generation of sulfoferrite clinker research.

3. The linear expansion and strength of compression indexes show their dependence upon quantity of sulfoferrite calcium phases in case of usage all types of synthesized sulfoferrite clinkers and presented C₂S. The quantity increase of expanding additive insertion leads to linear expanding increase and then crossing optimal quantity of insertion what leads to cement stone strength’ falling because of appeared body stress. The strength characteristics and linear expansion of sulfoferrite cements and the results of heat generation of synthesized sulfoferrite clinker prove the ability of widespread use in shrink-resistant and self-stressing cement technology.

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Acknowledgments

The article was prepared within development program of the Flagship Regional University on the basis of Belgorod State Technological University named after V.G. Shoukhov, using equipment of High Technology Center at BSTU named after V.G. Shoukhov.