Chapter

Peculiarities of Portland Cement Clinker Synthesis in the Presence of a Significant Amount of SO_3 in a Raw Mix

Oleg Sheshukov and Michael Mikheenkov

Abstract

Due to the depletion of the raw material base and a technogenic materials addition into a raw mix for the Portland cement clinker synthesis, sulfur and its oxides amount in a raw mix increases. According to literature the Portland cement clinker synthesis in the presence of a sulfur oxides significant amount is difficult. As the content of SO_3 in the raw mix increases the amount of C_2S increases while C_3S and C_3A amount decrease. With an equal total content of C_2S and C_3S in the clinker their ratio C_3S/C_2S decreases with an increased content of SO_3. These factors lead to a deterioration in the Portland cement clinker quality. The clinker formation reactions thermodynamic analysis and some experimental studies allow determining reasons for the Portland cement clinker quality deterioration. It was found that the presence significant amount of a SO_3 in the raw mix the synthesis in solid phase of low-basic $C_4A_3\overline{S}$ (ye'elimite) is the thermodynamically preferred rather than high-basic C_3A and C_4AF. As a result, excess and crystallized free lime inhibits the C_3S synthesis through the liquid phase. The experimental studies result helped to develop a methodology for calculating the composition of a raw mix from materials with significant amount of SO_3. It allows to reduce the SO_3 negative effect on the Portland cement clinker synthesis and to obtain high-quality Portland cement.

Keywords: high-sulfate raw material, Portland cement clinker, alite, belite, brownmillerite, ye'elimite, calculation procedure

1. Introduction

Sulfur and its oxides in the form of sulfate and sulfide minerals appear in the raw mixture of Portland cement clinker with the main raw materials for the preparation of clinker, namely clay and carbonate rock as well as additives and fuel. The technogenic origin additives of the metallurgical and heat-power industry, namely slags, fly ashes and oil cokes have especially high concentration of sulfur compounds [1–3]. According to [4] sulfur with calcium oxide forms calcium sulfate $CaSO_4$ under conditions of oxidative burning. Depending on the burning temperature the latter with the alkaline components of the raw mix forms alkaline metal sulfates or with clinker minerals forms sulfospurrit $2(C_2S)C\overline{S}$ and ye'elimite $C_4A_3\overline{S}$ and participates in the alkali-sulfate cycle of the furnace.

When the SO_3 content in the clinker is less than 2.0% it has a positive effect on the synthesis of Portland cement clinker since the alkali metal sulfates formed in its presence are effective melts that reduce the temperature of appearance of the liquid phase and its viscosity providing accelerated synthesis of clinker minerals [5, 6].

The positive role of SO_3 in clinker is also evident when using a raw mixture with a significant content of alkalis. When the molar ratio of $SO_3/(Na_2O + K_2O)$ is close to 1, the excess alkali is removed from the raw material mixture due to the removal of alkali metal sulfates during heating [4, 6].

If the SO_3 content in the clinker exceeds 2.0%, there are negative phenomena associated with both the quality of Portland cement clinker and its production technology.

According to [7, 8] when the content of SO_3 in the raw mixture increases the amount of C_2S increases, C_3S decreases and when the total content of these phases in the clinker is equal, their C_3S/C_2S ratio decreases.

Since alite (C_3S) is the most active and refractory component of Portland cement clinker the alite reduction leads to a decrease of the clinker refractoriness and activity. A decrease of the clinker refractoriness appears in the formation of rings in the furnace and incrustation in the calcinators cyclones and a decrease in activity shows in the drop in the strength of Portland cement.

It was found [9, 10] that not only the C_3S content but also C_3A content decrease in high-sulfate clinker. The reason for the decrease in the C_3A content in high-sulfate clinker is the isomorphic substitution of silicon for aluminum in silicate phases.

The reasons for the decrease of alite (C_3S) content in Portland cement clinker with an increase of SO_3 content in it are not found in the literature.

The main purpose of this study is to determine the reasons for the SO_3 negative impact on the Portland cement clinker synthesis and to develop a method to prevent it.

To achieve this goal, it is needed to:

- analyze literary sources;
- perform thermodynamic calculations;
- conduct experimental research;
- determine the reasons for the SO_3 negative influence on the Portland cement clinker synthesis;
- develop methods to prevent that negative impact.

2. Materials and experiment methods

Raw mixtures were burnt to produce Portland cement clinker with following modular characteristics: LSF = 0.92, n = 2.3 and p = 1.69. For the preparation of Portland cement clinker a raw mix based on limestone, clay, quartz sand and natural gypsum was used. When preparing the raw mix the composition was modeled by the introduction of gypsum into the raw mix with raw components in the ratio: raw mix/gypsum = 95/5%, to achieve SO_3 in the raw mix of more than 2.0%. The raw mix was homogenized in a laboratory mill by joint grinding of raw components and gypsum for 30 minutes. The homogeneous mixture was moistened and pressed at a pressure of 50 MPa.

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	LOI	Total
Limestone ($CaCO_3$)	56.35	0.04	0.06	0.04	0.03	0.37	42.8	99.69
Clay	1.21	50.70	19.90	11.80	0	1.40	14.81	99.90
Quartz sand	0.03	98.80	0.45	0.03	0	0	0.13	99.40
Natural gypsum	32.02	0.80	0.45	0.23	44.50	0	22.0	100.0
Clinker without gypsum	67.17	22.19	6.08	3.59	0.035	0.85	0	99.99
Clinker with gypsum	65.25	21.12	5.80	3.42	2.26	0.80	1.1	99.99

Table 1.
The chemical composition of raw materials and clinker, mass %.

The samples were burnt at temperatures from 1100 to 1300 °C. The synthesized clinker was crushed to a residue on the sieve No. 008 no more than 5.0% and the sugar-glycerate method was used to determine the content of CaO_{free} in it. The phase composition of fully synthesized clinkers was determined by chemical and x-ray methods. Qualitative x-ray phase analysis was performed using an XRD-7000 diffractometer (Shimadzu). Quantitative x-ray phase analysis was performed using a STADI-P diffractometer (STOE, Germany). The shooting was made under CuKα-radiation (40 kV, 30 mA), with graphite monochromator, in the range of scattering angles 2Θ = 10–70 deg., with a step of 0.02 deg. and an excerpt of 2 s. The results were analyzed using the PDF-2 database (Release 2008 RDB 2.0804). Thermal analysis (TA) of hydration products was performed using the DSC method (differential scanning calorimetry) on the STA 449 F3 Jupiter thermal analyzer (Netzsch-Geratebau GmbH). The temperature varied from room temperature (approximately 20°C) to 800°C at a heating rate of 10°C/min. The samples of the hydration products prepared by a grinding of synthesized clinker and on their basis cement paste prepared. The size of cement pastes were 20 x 20 x 20 mm, which were prepared under the condition of water: cement ratio of 0.4. After preparation, all samples were placed in box with water at temperature of 20°C. In a box samples were maintained 28 day before full hydration. Chemical analysis of cement was performed in accordance with the requirements of Russian Standard 5382–91. For reception of micro-photos the optical microscope Olympus GX-51 (Japan) was used. Samples of clinker was polished and their surface was etching by Nital [11]. After this procedure alite was painted in green-violet color, and belite in light brown color.

The chemical composition of raw materials and clinker is shown in **Table 1**.

3. Experimental results and discussion

The results of qualitative phase analysis of clinker based on a raw mix with the addition of 5% gypsum are shown in **Figure 1**.

Figure 2 shows a micrograph of clinker.

The content of free lime in a clinker based on a raw mix with the addition of 5% gypsum is shown in **Table 2**.

Analysis of the data presented in **Figures 1** and **2** and **Table 2** shows that the introduction of 5% gypsum into the raw mix suppresses the alite formation and contributes to the formation of a significant amount of free lime in the clinker. The diffraction peaks which are typical for free lime are present in a clinker based on a raw mix with the addition of 5% gypsum burnt at a temperature of 1300°C and the diffraction peaks which are typical for alite are not fixed at this temperature.

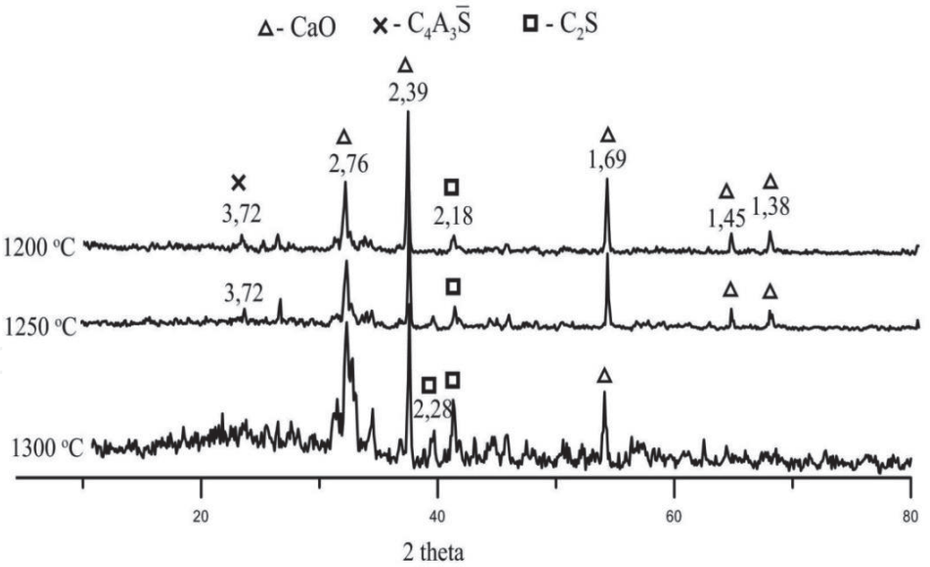

Figure 1.
The results of qualitative phase analysis of clinker based on a raw mix with the addition of 5% gypsum.

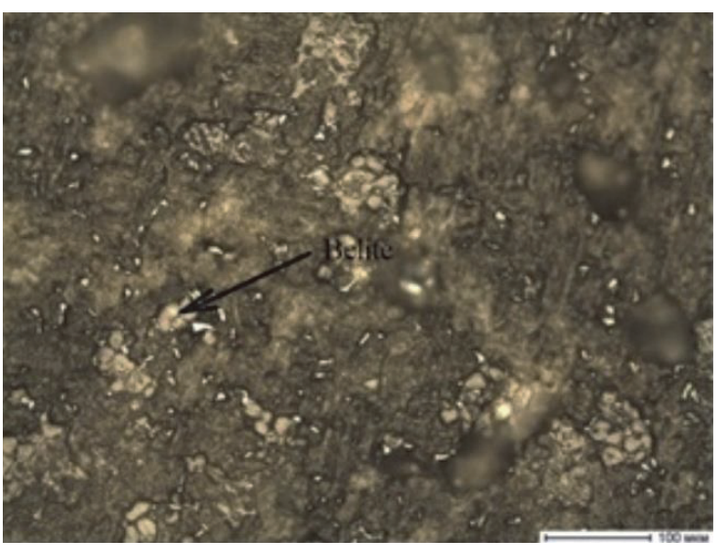

Figure 2.
A micrograph of clinker based on a raw mix with the addition of 5% gypsum.

Material	The content of free lime in a clinker, mass %, at the burning temperature, °C		
	1100	1200	1300
Clinker based on a raw mix with the addition of 5% gypsum	14.0	13.84	11.6

Table 2.
The content of free lime in a clinker.

Clinker completely melts when it is heated to a temperature of 1350°C. Analysis of the melt heated to a temperature of 1600°C indicates that alite is formed during this overheating but there is 6.2% free lime in the clinker.

The reason for suppressing the alite formation in a high-sulfate clinker is likely the formation of a well-crystallized CaO_{free} which is not soluble in the liquid phase, does not interact with C_2S and does not form C_3S. The absence of alite in the clinker

reduces its refractoriness and contributes to the appearance of a melt at temperatures below the temperatures of Portland cement clinker synthesis.

The formation of a significant amount of free lime in the clinker during the decomposition of gypsum is unlikely because with the stoichiometric ratio of CaO and SO_3 in gypsum anhydrite, respectively 41.19% and 58.81%, 2.06% of CaO_{free} can be formed from the decomposition of 5.0% of gypsum and according to the data presented in **Table 2**, more than 11% of CaO_{free} is formed at a temperature of 1300°C.

To determine the reasons for the appearance of a significant amount of free lime in a high-sulfate clinker a thermodynamic analysis of the reactions of C_3A and C_4AF formation was performed according to the data of [12] as well the reactions of $C_4A_3\,\overline{S}$ formation presented in [13]. The analysis results are presented in **Table 3**.

According to the data presented in **Table 4**, the synthesis of C_3A and C_4AF in a low-sulfate clinker is thermodynamically possible from the simple minerals, namely CaO, Al_2O_3 and Fe_2O_3 (reactions No. 1–2). In a high-sulfate clinker, reaction of the formation of ye'elimite $C_4A_3\overline{S}$ (reaction No. 3) is thermodynamically preferable since the free Gibbs energy of it is more negative than that of reactions No. 1 and 2.

There are different opinions about the formation mechanism of ye'elimite $C_4A_3\overline{S}$ in clinker during heating. According to [13] the synthesis of ye'elimite due to an excess of lime at the time of its formation begins with the formation of mayenite according to the scheme $C_{12}A_7 \rightarrow CA \rightarrow C_3A_3C\overline{S}$. According to our data [14] in the pressed raw mix due to its higher reaction ability the synthesis of ye'elimite proceeds according to the scheme $CA_2 \rightarrow CA \rightarrow C_2A_2 \rightarrow C_3A_3 \rightarrow C_3A_3C\,\overline{S}$ with the formation of calcium monoaluminate (CA) at temperatures about 700°C and its presence throughout the burning temperature range up to 1300°C. In the presence of calcium monoaluminate the formation of C_3A and C_4AF is thermodynamically impossible (reactions No. 4–6). Based on these studies the authors of [12] concluded that in the presence of calcium monoaluminate C_3A and C_4AF are formed not in solid-phase synthesis but from a melt.

Therefore if the calculation of the raw mix is carried out according to the usual scheme for the formation of C_3A and C_4AF minerals in a high-sulfate clinker, and in fact in a high-sulfate clinker low-base aluminates and calcium ferrites are formed before the melt appears, then due to the difference in the lime content in these minerals, free lime can be formed in the clinker by reactions:

$$3CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3 + 2CaO, \quad (1)$$

$$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow CaO \cdot Al_2O_3 + CaO \cdot Fe_2O_3 + 2CaO. \quad (2)$$

No.	Reactions	The value of ΔG_o, kJ/mol at temperature, K				
		298	1023	1200	1400	1500
1	$3CaO + Al_2O_3 = 3CaO{\cdot}Al_2O_3$	−17.0	−41.8	−47.0	−52.9	−55.7
2	$4CaO + Al_2O_3 + Fe_2O_3 = 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	−49.3	−64.9	−64.1	−60.83	−58.1
3	$3CaO + 3Al_2O_3 + CaSO_4 = 3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$	−99.1	−445.1	−583.6	−758.9	−853.5
4	$CaO{\cdot}Al_2O_3 + 2CaO = 3CaO{\cdot}Al_2O_3$	+33.7	+32.3	+31.7	+33.26	+34.4
5	$CaO{\cdot}Al_2O_3 + CaO + 2CaO{\cdot}Fe_2O_3 = 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	+10.4	+39.7	+49.0	+60.3	+66.2
6	$CaO{\cdot}Al_2O_3 + 2CaO + CaO{\cdot}Fe_2O_3 = 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	+42.4	+72.1	+79.77	+79.8	+83.7

Table 3.
Thermodynamic analysis of formation reactions C_3A and C_4AF according to data of [12] and formation reaction $C_4A_3\,\overline{S}$ according to data of [13].

Free lime begins to accumulate in the clinker from the decomposition beginning temperature of calcium carbonate to the appearance of the liquid phase due to the difference in the lime content in the tricalcium aluminate C_3A accepted in calculation and actually formed calcium monoaluminate CA. Totally because of gypsum decomposition and the difference between the limes content in the calcium aluminates, well-crystallized free lime in an amount of about 5% can be formed in the clinker from the decomposition beginning temperature of calcium carbonate until the appearance of the liquid phase, and this amount is sufficient to suppress the alite formation when the liquid phase appears.

Since the alite formation in clinker is suppressed and only belite is formed, so due to the difference in the lime content in these minerals the total content of free lime at the synthesis completion temperatures is already about 11%. When the melt temperature rises up to 1600 °C a small amount of alite is formed but the CaO_{free} however does not dissolve and is remained in an amount of about 6%.

To prevent the formation of CaO_{free} in high-sulfate clinker it is proposed to calculate the raw mix of Portland cement clinker in accordance with our patent [15] in two stages. At the first stage the calculation of calcium monoaluminate $CaO{\cdot}Al_2O_3$ synthesis in a high-sulphate clinker is made, meanwhile during burning intermediate metastable phase – ye'elimite $C_4A_3\,\overline{S}$ will form in a high-sulphate clinker. It decays when the liquid phase appears.

Since the formation of high-base phases is thermodynamically more likely when a liquid phase occurs, and C_3A and C_4AF can only be formed from low-base phases if free lime is present by reactions:

$$CaO \cdot Al_2O_3 + 2CaO \rightarrow 3CaO \cdot Al_2O_3, \tag{3}$$

$$CaO \cdot Al_2O_3 + CaO \cdot Fe_2O_3 + 2CaO \rightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3. \tag{4}$$

At a burning temperature of about 1300°C in the absence of CaO_{free} its source can only be the reaction of converting alite to belite and the decomposition of calcium sulfate by reactions:

$$3CaO \cdot SiO_2 \rightarrow 2CaO \cdot SiO_2 + CaO, \tag{5}$$

$$2CaSO_4 \rightarrow 2CaO + 2SO_2\uparrow + O_2\uparrow. \tag{6}$$

Since it is possible to convert alite to belite in a high-sulphate clinker by reaction 5, the calculation of the raw mix at the first stage is made for the formation of the maximum amount of alite in it which is possible at SC = 1. The calculation of the saturation coefficient of the raw mix by lime at the first stage is made using the well-known formula of Kinda V.A. [16] with SC = 1 for the formation of CA in the clinker (the coefficient for Al_2O_3 is 0.55):

$$SC = \frac{CaO - 0,55Al_2O_3 - 0,35Fe_2O_3 - 0,7SO_3}{2,8SiO_2}. \tag{7}$$

At a conclusion of this formula are used molar parities CaO, Al_2O_3, Fe_2O_3 and SiO_2 at formation in clinker the basic clinker minerals C_3S, C_2S, C_3A and C_4AF.

English analogue of the formula given is the formula for calculation LSF [17]:

$$LSF = \frac{CaO}{2,8SiO_2 + 1,2Al_2O_3 + 0,65Fe_2O_3}. \tag{8}$$

Factors in the given formula are taken from phase diagram $CaO\text{-}Al_2O_3\text{-}SiO_2$ and $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Fe_2O_3$ at optimum relationship oxides providing absence free lime in clinker. If to use Kinda V.A's design procedure [16], that the formula (8) becomes full analogue of the formula (7):

$$LSF = \frac{CaO}{2,8SiO_2 + 1,65Al_2O_3 + 0,35Fe_2O_3 + 0,7SO_3}. \quad (9)$$

For calculation degree of saturation (DS) of clinker metastable minerals by sulphate in the presence of gypsum Atakuziev T.A.'s formula [18] is used considering that sulfatization C_2S, CA in clinker is possible. Taking into account the given updating the formula DS calculation looks as follows:

$$DS = \frac{SO_3 - 0,261Al_2O_3}{0,667SiO_2}. \quad (10)$$

At DS = 0 $C_3A_3C\,\overline{S}$ will be formed in the raw mix and at DS = 1 sulfosporite $2(C_2S)C\,\overline{S}$ will also be formed.

At the second stage the calculation of the synthesis of alite Portland cement with the required modular characteristics is made. It is assumed that when the liquid phase appears the gypsum is completely decomposed by the reaction 6 and the chemical composition of the clinker formed after gypsum decomposition is considered to be the chemical composition of one of the raw mix components. Other components of the raw mix are limestone and a corrective additive – quartz sand. At the second stage the saturation coefficient (LSF) is calculated using the formula (9) but only for the synthesis of tricalcium aluminate $3CaO{\cdot}Al_2O_3$ in the clinker (the coefficient for Al_2O_3 is 1.65).

4. Example of calculation of high-sulphate raw material mixture No. 1

At the first stage on the basis of raw components the chemical composition of which is shown in **Table 1** the raw mix of high-sulphate clinker is calculated for the synthesis of calcium monoaluminate in it according to the formulas (9) and (10) with the modular characteristics LSF = 1 and DS = 0. At DS = 0 calcium sulfoaluminate $C_3A_3C\,\overline{S}$ can be formed in the raw mix based on calcium monoaluminate.

Table 4 shows the calculated composition of the raw mix and the chemical composition of clinkers before and after the gypsum decomposition.

At the second stage a typical Portland cement clinker with modular characteristics LSF = 0.92, n = 2.3, p = 1.7 is calculated on the basis of clinker after decomposition of gypsum as one of the components of the raw mix and corrective additives: limestone and quartz sand.

The calculated composition of the raw mix for obtaining Portland cement clinker and it's chemical composition is shown in **Table 5**.

Finally the composition of the raw mix is calculated by multiplying the quantity of raw components of the clinker shown in **Table 4** by the quantity of clinker shown in **Table 5**, and is summed up with the quantity of raw components shown in **Table 5**:

$$CaCO_3 = (71.31x0.633) + 30.7 = 75.8\%; \quad (11)$$

$$Clay = 25.71x0.633 = 16.3\%; \quad (12)$$

Clinker	Raw mix composition			Chemical composition of clinker, mass %					
	Lime-stone	Clay	Gyp-sum	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Total
Clinkers before the gypsum decomposition	71.31	25.71	2.98	64.66	20.39	8.06	4.79	2.1	100
Clinkers after the gypsum decomposition	71.31	25.71	2.98	66.05	20.83	8.23	4.89	0	100

Table 4.
The calculated composition of the raw mix and the chemical composition of clinkers before and after the gypsum decomposition.

Clinker	Raw mix composition			Chemical composition of clinker, mass %					
	Lime-stone	The first stage clinker	SiO_2	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Total
Portland cement clinker	30.7	63.3	6.0	68.2	22.1	6.1	3.6	0	100

Table 5.
The calculated composition of the raw mix for obtaining alite Portland cement clinker and its chemical composition.

$$SiO_2 = 6.0\%; \tag{13}$$

$$\text{Gypsum} = 2,98x0,633 = 1,97\%. \tag{14}$$

The actual gypsum content after the introduction of corrective additives will decrease by:

$$\text{Gypsum} = 2.98 - 1,97 = 1.01\%. \tag{15}$$

Then the quantity of corrective additives is calculated. The quantity of corrective additives is equal to the difference between the quantity of raw components calculated using the formulas (11)–(14) and the quantity of raw components calculated at the first stage and shown in **Table 4**.

The quantity of corrective additives is equal to:

$$CaCO_3 = 75.8 - 71.31 = 4.49\%; \tag{16}$$

$$\text{Clay} = 16.3 - 25.71 = -9.4\%; \tag{17}$$

$$SiO_2 = 6.0 - 0 = 6.0\%. \tag{18}$$

A negative value for the clay amount means that it should be reduced.

Figure 3 shows the data of qualitative phase analysis of clinker prepared in accordance with correction calculation No. 1 and burnt at temperatures of 1150, 1200, 1250 and 1300°C.

X-ray analysis indicates the absence of CaO_{free} in a clinker prepared in accordance with corrective calculations No. 1, at a burning temperature of 1200°C or higher. Stable alite in such clinker is formed already at the burning temperature of 1250°C as evidenced by the appearance of diffraction maxima with d = 1.76 Å and d = 3.04 Å which are typical for alite at this temperature. The change in the intensity of the diffraction maxima of the main phases of the clinker prepared in accordance with the correction calculation No. 1 and burnt at temperatures of 1150, 1200, 1250 and 1300°C is shown in **Figure 4**.

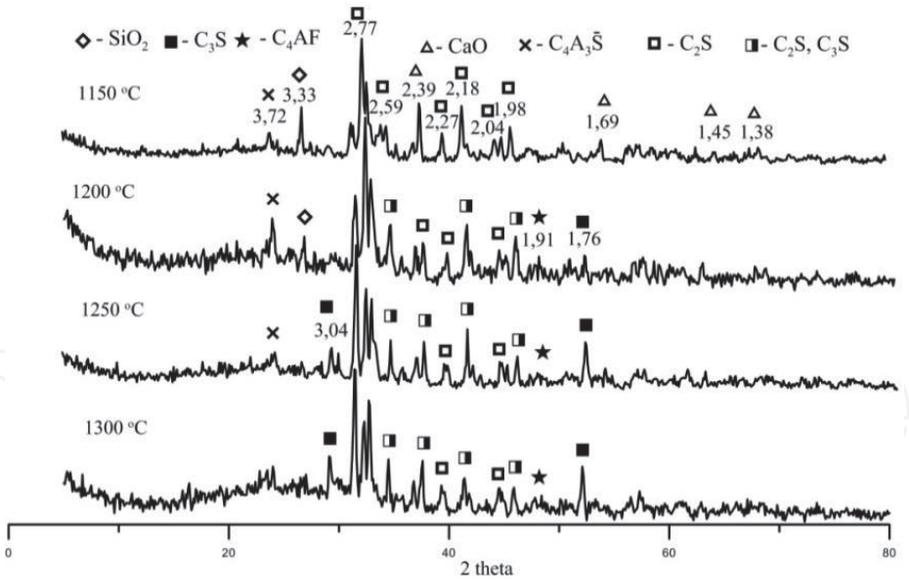

Figure 3.
The data of qualitative phase analysis of clinker prepared in accordance with correction calculation No. 1 and burnt at temperatures of 1150, 1200, 1250 and 1300°C.

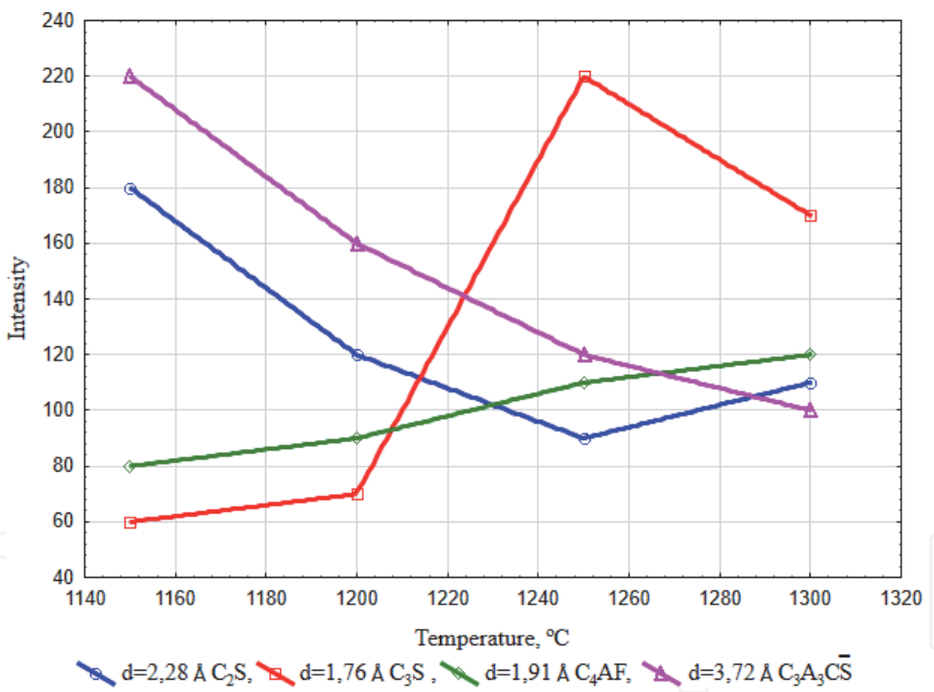

Figure 4.
The change in the intensity of the diffraction maxima of the main phases of the clinker prepared in accordance with the correction calculation No. 1 and burnt at temperatures of 1150, 1200, 1250 and 1300°C.

Diffraction peak with d = 1.76 Å which is typical for C_3S, increases up to a temperature of 1250°C and decreases starting from a temperature of 1250°C. The diffraction peak with d = 2.28 Å which is typical for C_2S on the contrary decreases to a temperature of 1250°C and increases at temperatures above of 1250°C which indicates the transformation of alite part into belite according to Eq. (5). The intensity of the diffraction maximum with d = 3.72 Å which is typical for $C_3A_3C\bar{S}$, decreases above the temperature of 1150°C, which indicates the decomposition of $CaSO_4$ in accordance with the reaction (6) and decay as a result.

To determine the actual phase composition of the clinker prepared in accordance with the correction calculation No. 1 and synthesized at a temperature of 1300°C a quantitative x-ray phase analysis was performed and it is shown in **Figure 5**.

Table 6 shows the phase composition of clinker synthesized in accordance with correction calculation No. 1 based on quantitative phase analysis.

On the basis of clinker prepared in accordance with corrective calculation No. 1 and synthesized at a temperature of 1300°C Portland cement was prepared by joint grinding of clinker with gypsum dihydrate (**Figure 6**). The cement activity was

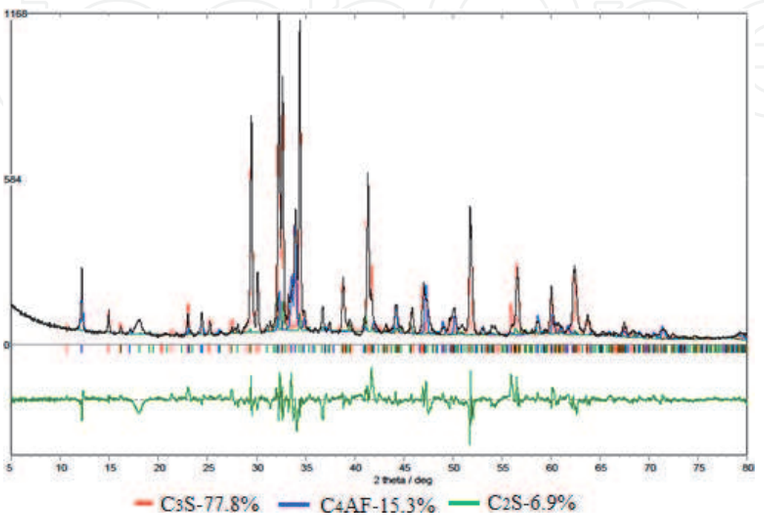

Figure 5.
The phase analysis data of clinker synthesized on the basis of raw mix in accordance with correction calculation No. 1.

Name of mineral phase	Guantity in clinker, mas. %
Three calcium silicate (alite) C_3S	77.8
Two calcium silicate (belit) C_2S	6.9
Brownmillerit C_4AF	15.3

Table 6.
The phase composition of clinker synthesized in accordance with correction calculation No. 1.

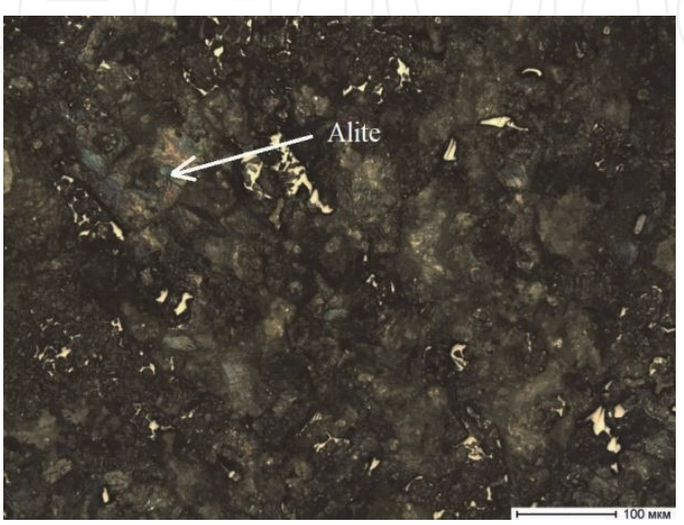

Figure 6.
A micrograph of clinker synthesized in accordance with correction calculation No. 1.

Clinker type	Composition, %		SO_3, %	S*, m2/kg	R008, %	ND, %	Setting time, hour-minute	
	Clinker	Gypsum					Initial	Final
Clinker No. 1	96	4	3.96	348	12.7	25.2	2–50	4–15

**S – Blaine's specific surface; R008 – residue on the sieve No. 008; ND – normal density.*

Table 7.
The physical and mechanical properties of Portland cement.

Clinker type	Compressive strength, MPa, after, days			
	2	7	14	28
Clinker No. 1	21.8	31.1	42.5	67.3

Table 8.
Portland cement compressive strength.

determined on cubes with a size of 2x2x2 cm prepared from cement paste of normal density. The physical and mechanical properties of cement are shown in **Tables 7** and **8**.

5. Example of calculation of high-sulphate raw material mixture No. 2

At the first stage on the basis of raw components the chemical composition of which is shown in **Table 2** the raw mix of high-sulphate clinker is calculated for the synthesis of calcium monoaluminate in it according to the formulas (9) and (10) with the modular characteristics LSF = 1 and DS = 1. At DS = 1 calcium sulfoaluminate $C_3A_3C\,\overline{S}$ can be formed in the raw mix based on calcium monoaluminate and sulfospurrit $2(C_2S)C\,\overline{S}$ can be formed in the raw mix based on belite.

Table 9 shows the calculated composition of the raw mix and the chemical composition of clinkers before and after the gypsum decomposition.

At the second stage a alite Portland cement clinker with modular characteristics LSF = 0.92, n = 2.3, p = 1.7 is calculated on the basis of clinker after decomposition of gypsum as one of the components of the raw mix and corrective additives: limestone and quartz sand.

The calculated composition of the raw mix for obtaining alite Portland cement clinker and its chemical composition is shown in **Table 10**.

Finally the composition of the raw mix is calculated by multiplying the quantity of raw components of the clinker shown in **Table 9** by the quantity of clinker

Clinker	Raw mix composition			Chemical composition of clinker, mass %					
	Lime-stone	Clay	Gypsum	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Total
Clinkers before the gypsum decomposition	59.8	21.3	18.9	60.3	16.5	6.6	3.9	12.7	100
Clinkers after the gypsum decomposition	59.8	21.3	18.0	69.1	18.9	7.5	4.5	0	100

Table 9.
The calculated composition of the raw mix and the chemical composition of clinkers before and after the gypsum decomposition.

Clinker	Raw mix composition		Chemical composition of clinker, mass %						
	Lime-stone	The first stage clinker	SiO_2	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	$\sum$
Portland cement clinker	20.8	72.9	6.4	68.3	22.1	6.0	3.6	0	100

Table 10.
The calculated composition of the raw mix for obtaining alite Portland cement clinker and its chemical composition.

shown in **Table 10**, and is summed up with the quantity of raw components shown in **Table 10**:

$$CaCO_3 = (59,8x0,729) + 20,8 = 64,3\%; \quad (19)$$

$$Clay = 21,3x0,729 = 15,5\%; \quad (20)$$

$$SiO_2 = 6,4\%; \quad (21)$$

$$Gypsum = (18,9x0,729) = 13,8\%. \quad (22)$$

Then the quantity of corrective additives is calculated. The quantity of corrective additives is equal to the difference between the quantity of raw components calculated using the formulas (19) and (20) and the quantity of raw components calculated at the first stage and shown in **Table 9**.

The quantity of corrective additives is equal to:

$$CaCO_3 = 64,3 - 59,8, \ = 4,4\%; \quad (23)$$

$$Clay = 15,5 - 21,3 = -5,8\%; \quad (24)$$

$$SiO_2 = 6,4 - 0 = 6,4\%; \quad (25)$$

A negative value for the clay amount means that it should be reduced the same as in the calculation example No. 1.

The actual gypsum content after the introduction of corrective additives will decrease by:

$$CaSO_4 = 18,9 - 13,8 = 5,1. \quad (26)$$

Figure 7 shows the data of qualitative x-ray phase analysis of clinker prepared in accordance with calculation mentioned above and burnt at temperatures of 1100, 1200, 1300 and 1350°C.

X-ray analysis indicates the absence of CaO_{free} in a clinker prepared in accordance with corrective calculations No. 2 at a burning temperature above 1300°C. Stable alite C_3S is formed at the burning temperature of 1350°C as evidenced by the appearance of diffraction maxima with d = 1.76 Å and d = 3.04 Å which are typical for alite at this temperature.

The intensity of the diffraction maximum with d = 3.72 Å which is typical for $C_3A_3C\overline{S}$ increases to a temperature of 1300°C but above this temperature it is not fixed which indicates the decomposition of $CaSO_4$ in accordance with the reaction (No. 6) and decay as a result.

According to the qualitative phase analysis data a significant amount of gypsum is released up to the burning temperature of 1300°C which is fixed by the diffraction maximum with d = 3.47 Å. Gypsum remains are fixed even at a temperature of 1350°C.

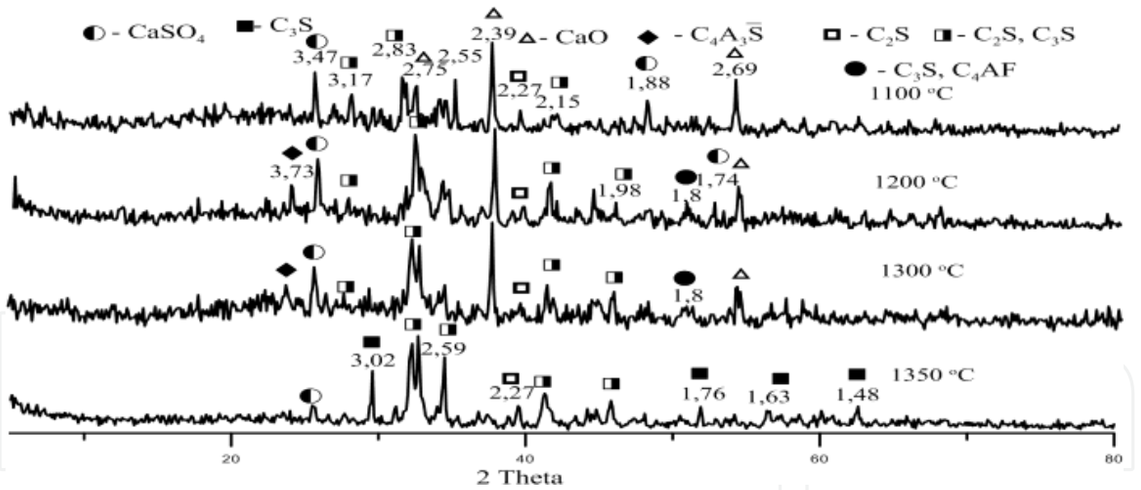

Figure 7.
The data of qualitative phase analysis of clinker prepared in accordance with calculation No. 2 and burnt at temperatures of 1100, 1200, 1300 and 1350°C.

To determine the actual phase composition of the clinker prepared in accordance with the correction calculation No. 2 and synthesized at a temperature of 1350°C a quantitative x-ray phase analysis was performed. Its results shown in **Figure 8**.

Table 11 summarizes the results of quantitative x-ray phase analysis of synthesized clinker.

The test results show that in accordance with corrective calculation No. 2 a significant amount of C_3S is retained when preparing clinker based on a high-sulphate raw mix that initially contains 12.7% SO_3 (**Figure 9**).

On the basis of clinker prepared at temperature of 1350°C Portland cement was prepared by joint grinding of clinker with natural gypsum. The cement activity was determined on cubes with a size of 2x2x2 cm prepared from cement paste of normal density.

The physical and mechanical properties of cement are shown in **Tables 12** and **13**.

Examples data of corrective calculations show that using the proposed calculation method it is possible to save a significant amount of C_3S in a clinker synthesized on the basis of a high-sulphate raw mix.

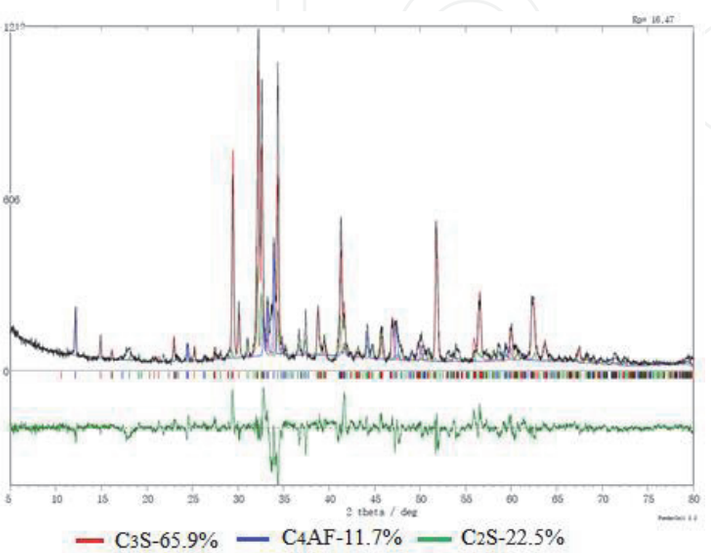

Figure 8.
The phase analysis data of clinker synthesized on the basis of raw mix in accordance with correction calculation No. 2.

Name of mineral phase	Guantity in clinker, mas. %
Three calcium silicate (alite) C_3S	65.9
Two calcium silicate (belit) C_2S	22.5
Brownmillerit C_4AF	11.7

Table 11.
The phase composition of clinker synthesized in accordance with correction calculation No. 2.

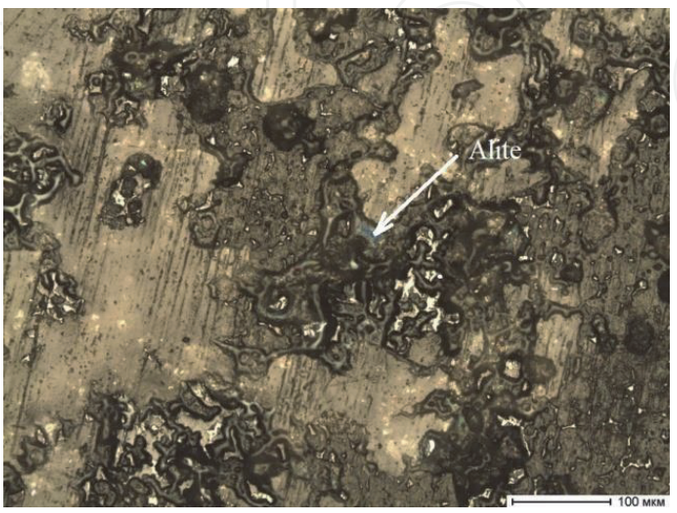

Figure 9.
A micrograph of clinker synthesized in accordance with correction calculation No. 2.

Clinker type	Composition, %		SO_3, %	S*, m2/kg	R008, %	ND, %	Setting time, hour-minute	
	Clinker	Gypsum					Initial	Final
Clinker No. 2	100	0	12.7	378	3.1	28.3	1–50	2–15

**S – Blaine's specific surface; R008 – residue on the sieve No. 008; ND – normal density.*

Table 12.
The physical and mechanical properties of Portland cement.

Clinker type	Compressive strength, MPa, after, days			
	2	7	14	28
Clinker No. 2	10.1	14.7	20.0	44.7

Table 13.
Portland cement compressive strength.

The quantity of corrective additives depends on the modular characteristics of the synthesized clinker. When limiting the modular characteristics of Portland cement clinker LSF = 0.92–0.98; n = 2.0–3.0; p = 1.7–4.0 the minimum amount of additives equal to 4.0% is introduced with the minimum values of modular characteristics, i.e. LSF = 0.92; n = 2.0; p = 1.7; and with the minimum amount of gypsum introduced, i.e. DS =0. The maximum amount of corrective additives equal to 23.0% is introduced with the maximum values of modular characteristics, i.e. LSF = 0.98; n = 3.0; p = 4.0 and with the maximum amount of gypsum introduced, i.e. DS =1.

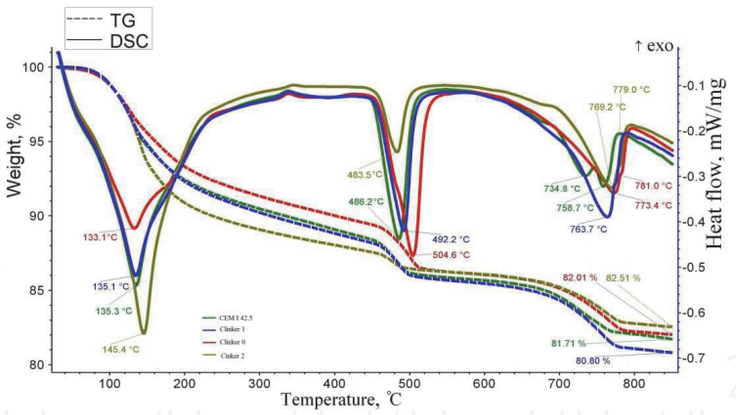

Figure 10.
Results of comparative thermal analysis (TA) of hydration products.

Clinker type	The value of the endo effect, J/g	Mass loss, %
Clinker 0	148.2	17.9
Clinker 1	167.0	19.2
Clinker 2	180.5	17.5
CEM I 42.5	155.0	18.3

Table 14.
Values of the first endo-effect and the total mass loss of samples.

The quantity of clay removed from the raw mix correlates with the amount of mix additives put in the raw mix, i.e. with the same modular characteristics of the clinker the minimum quantity of clay removed corresponds to a minimum quantity of additives and the maximum quantity of clay removed corresponds to the maximum quantity of additives.

At the final stage of investigation comparative thermal analysis (TA) of hydration products was conducted. Results of tests are resulted on **Figure 10**.

The **Table 14** shows the values of the first endo-effect and the total mass loss of samples.

At hydration alite attaches 5 molecules of water, but belite only 2. Due to this difference, the clinker 0 has smallest first endo effect.

6. Conclusion

The present study revealed that the SO_3 negative impact on the Portland cement clinker synthesis, resulted in a C_3S content reduction and the C_2S and C3A content increasing in the final product. It leads to lowering clinker fire resistance and cement quality due to the thermodynamic preference of the ye'elimite $C_4A_3\,\bar{S}$ synthesis in the presence SO_3 and, consequently, the presence of low-basic calcium monoaluminate CA in the synthesized clinker. In the presence of calcium monoaluminate, solid-phase synthesis of high-base C_3A and C_4AF is thermodynamically impossible. As a result, free lime accumulates in the synthesized clinker, which prevents the liquid-phase synthesis of C_3S.

A method for elimination of the SO_3 negative impact on the Portland cement quality by calculating the raw material mixture composition with a significant amount of SO_3 has been developed and patented.

Abbreviations

The following abbreviations are used in this manuscript:

C_3S	$3CaO \cdot SiO_2$;
C_2S	$2CaO \cdot SiO_2$;
C_3A	$3CaO \cdot Al_2O_3$;
C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$;
$C_3A_3C\bar{S}$	$3CaO \cdot 3Al_2O_3 \cdot CaSO_4$;
$2(C_2S)C\bar{S}$	$2(2CaO \cdot SiO_2) \cdot CaSO_4$;
$C_{12}A_7$	$12CaO \cdot 7Al_2O_3$;
CaO_{free}	free CaO;
SC	Saturation Coefficient;
LSF	Lime Saturation Factor;
DS	Degree of Saturation by Sulfate;
LOI	Loss On Ignition.

Author details

Oleg Sheshukov* and Michael Mikheenkov
Ural Federal University Named after the First President of Russia B.N. Yeltsin, Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russian Federation

*Address all correspondence to: o.j.sheshukov@urfu.ru

References

[1] Factors el Mar Cortada Mut, Linda Kaare Norskov, Peter Glarborg, Kim Dam-Johansen Sulphur release from alternative fuel firing / Maria del Mar Cortada Mut & other//Global Cement Magazine 9 (2014) p. 36–41.

[2] Július Strigáč Effect of Selected Alternative Fuels and Raw Materials on the Cement Clinker Quality/ Strigáč Július // Journal Of Civil Engineering Vol. 10, Issue 2, 2015 p. 81–92.

[3] Ying-Liang Chen, Juu-En Chang , Ming-Sheng Ko Reusing Desulfurization Slag in Cement Clinker Production and the Influence on the Formation of Clinker Phases/ Chen Ying-Liang & other// Sustainability 9, 1585 (2017) p.1–14.

[4] Javed I. Bhatty.; Role of Minor Elements in Cement Manufacture and Use, Portland Cement Association, Skokie, Illinois 1995, p.24–25.

[5] M. Yamashita, H. Tanaka Low Temperature Burnt Portland Cement Clinker Using Mineralizer/ Yamashita M., Tanaka H. // Cement Science and Concrete Technology № 65 (2011) p. 82–87.

[6] H.F.W. Taylor, Cement Chemistry, Academic Press, London, 1990.

[7] Sayed Horcoss Influence of the clinker SO_3 on the cement characteristics / Horcoss Sayed, Ltief Roger, RizkToufic//Cement And Concrete Research 41 (2011). p. 913–919. Available from: http://www.sciencedirect.com/science/article/pii/S0008884611001268

[8] Mieke De Schepper, Philip Van den Heede, Eleni C. Arvaniti, Klaartje De Buysser Sulfates in Completely Recyclable Concrete and the effect of $CaSO_4$ on the clinker mineralogy/ Schepper De & other //Construction and Building Materials 137 (2017) p. 300–306.

[9] Sayed Horkoss, Roger Lteif, and Toufic Rizk Calculation of the C_3A Percentage in High Sulfur Clinker / Horcoss Sayed & other // International Journal of Analytical Chemistry Volume 2010, Article ID 102146, p. 1–5.

[10] Laure Pelletier-Chaignat, Frank Winnefeld, Barbara Lothenbach, Gwenn Le Saout Influence of the calcium sulphate source on the hydration mechanism of Portland cement–calcium sulphoaluminate clinker–calcium sulphate binders/ Pelletier-Chaignat Laure & other // Cement & Concrete Composites 33 (2011) p. 551–561.

[11] Donald H. Campbell. Microscopical Examination and Interpretation of Portland Cement and Clinker Second Edition/ Published by:Portland Cement Association – USA, 1999. 214 p.

[12] Babushkin, V.I., Matveev G.M., Mchedlov-Petrosjan, O.M. Thermodynamics Of Silicates - M: Stroyizdat, 1986.408 p.

[13] Kuznezova T.V. Aluminate and sulfoaluminate cements/ - M.: Stroyizdat, 1986., 208 p.

[14] Michael A. Miheenkov Compacting as a way of reception sulfated hydraulic binders/Vestnik MGSU.- – 2011. – № 1 . – p. 131–142

[15] Patent 2527430 Russian Federation: MPK C04B 7/36. Method for Correcting Composition of Portland Cement Clincer Based on Highe-Sulphate Crude Mixture. Author: Michael A. Miheenkov., Patent Holder: Michael A. Miheenkov. – 2013112990/03; Date of declare. 22.03.2013 ; Date of publication. 27.08.2014. Bulletin. № 24.

[16] Kind V.A. Chemical characteristics of Portland cement/ L.-M. Gosstroyizdat, 1932..

[17] Walter H. Duda Cement.; Data-Book /Internationale Verfahrenstechniken der Zementindustrie 2., Auflage Bauverlag GmbH Wfmbaden and Berlin, 1981, 484 p.

[18] Atakuziev, T.A. Sulfomineral cements on a basis of phosphogypsum/ T.A.Atakuziev, F.M.Mirzoev.: "FAN", 1979. – 152 p.