

# Study of the reasons for blocking $C_3S$ formation in the presence of $SO_3$ and finding ways to overcome blockages

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**ABSTRACT:** The results of thermodynamic analysis influence of clinker  $SO_3$  on synthesis of  $C_3S$ , the technique of calculation of raw mix on formation in high sulfur clinker intermediate metastable phases are presented.

**Keywords:** High sulfur clinker, alit,  $C_3S$ , metastable phases.  
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## I. The Summary

In connection with growth of cost of the basic hydrocarbon fuel resources, manufacturers of Portland cement began to use the alternative energy sources containing significant amount of  $SO_3$  for its manufacture. At presence in raw materials of significant amount  $SO_3$ , activity of Portland cement on the basis of such raw mix considerably decreases. It is caused by maintenance reduction in is high-sulfur clinker by alit  $C_3S$ . In present paper the reasons of suppression of formation alit in is high-sulfur clinker are considered and ways of increase of the maintenance to it alit at the expense of formation are offered at synthesis clinker intermediate metastable phases.

## II. Introduction

Sulfur and its oxides in the form of sulfate and sulfide minerals can get to structure of a raw mix for manufacture of Portland cement clinker as together with the basic raw materials for clinker preparation - clay and lime stone, and with additives and fuel. The maintenance of sulfurous connections in additives of a man-caused origin of the metallurgical and heat power industry - slag, fuel, fly ash and fuel in the form of petro-coke is especially high. On data [1,2], in the conditions of oxidizing roasting sulfur forms with calcium oxides anhydrite of sulfate of calcium  $CaSO_4$  which depending on roasting temperature forms sulfates of alkaline metals with alkaline components of a raw mix, with clinker's minerals sulphospurrite  $2(C_2S)C_3\bar{S}$  and ye'elimit  $C_4A_3\bar{S}$  and participates in a alkali - sulfur cycle of the furnace.

At maintenance  $SO_3$  in clinker less than 2,0 % it makes positive impact on synthesis of Portland cement clinker as the sulfates of alkaline metals formed at its presence are effective fluxing agent, reducing temperature of occurrence of a liquid phase and it's viscosity, providing the accelerated synthesis clinker's minerals[3].

Positive role of  $SO_3$  in clinker also is shown at use of a raw mix with the considerable maintenance of alkalis. With mole parity  $SO_3/(Na_2O+K_2O)$  close to 1, removal of sulfates of alkali from a raw mix at the expense of ablation of sulfates of alkaline metals is provided at heating.

In excess of the specified limits clinker's  $SO_3$  observed the negative effects associated with Portland cement clinker quality and with the technology of its production. According to[1,4], at maintenance increase in the raw mix  $SO_3$ , quantity  $C_2S$  increases,  $C_3S$  decreases, and at the equal total maintenance of the given phases in clinker, their parity  $C_3S/C_2S$  decreases. As alit  $C_3S$  is not only the most active mineral of clinker, defining durability of Portland cement clinker, but also it's most refractory phase, decrease in maintenance clinker's  $C_3S$  leads to decrease in its fire resistance and activity of Portland cement.

In the paper [5] established that the reason for the decline of  $C_3A$  in high-sulfur clinker is isomorphic substitution of aluminum silicate phases of silicon and based on the research are invited to adjust the formula R.H. Bogue calculation of  $C_3A$  in high-sulfur clinker.

Reasons for the decline of  $C_3S$  in clinker with increasing content of clinker's  $SO_3$  in references are absent.

## III. Material and Methods

The raw mixes calculated under modular characteristics on reception Portland cement clinker with modular characteristics  $LSF=0,92$ ,  $SR=2,3$  and  $AR=1,69$  were exposed to roasting. For preparation Portland cement clinker the raw mix on basis of lime stone, clay, quartz sand and natural gypsum was used. At preparation of a raw mix the case when gypsum gets to a raw mix together with raw components was modelled. Natural gypsum was entered into the raw mix prepared according to calculation in the ratio, a raw mix – 95 %, gypsum – 5 %, for achievement of maintenance  $SO_3$  in a raw mix more than 2,0 %. The raw mix dried and homogenizing in a laboratory mill by a joint grinding of raw components and gypsum within 30 minutes. Homogenizing mix before calcination was pressed at 50 MPa.

The pressed samples subjected to roasting at temperatures from 1100 to 1300°C. Completely synthesised clinker crushed to the rest on a sieve 008 no more than 5 % (Blaine 450) and by the chemical analysis defined the maintenance in them free lime and clinker's oxides [6]. At completely synthesised clinker chemical and x-ray ways defined phase structure. Qualitative x-ray phases analysis spent on device DRON-3. Quantitative x-ray phases analysis carried out on diffractometer STADI-P (STOE, Germany).

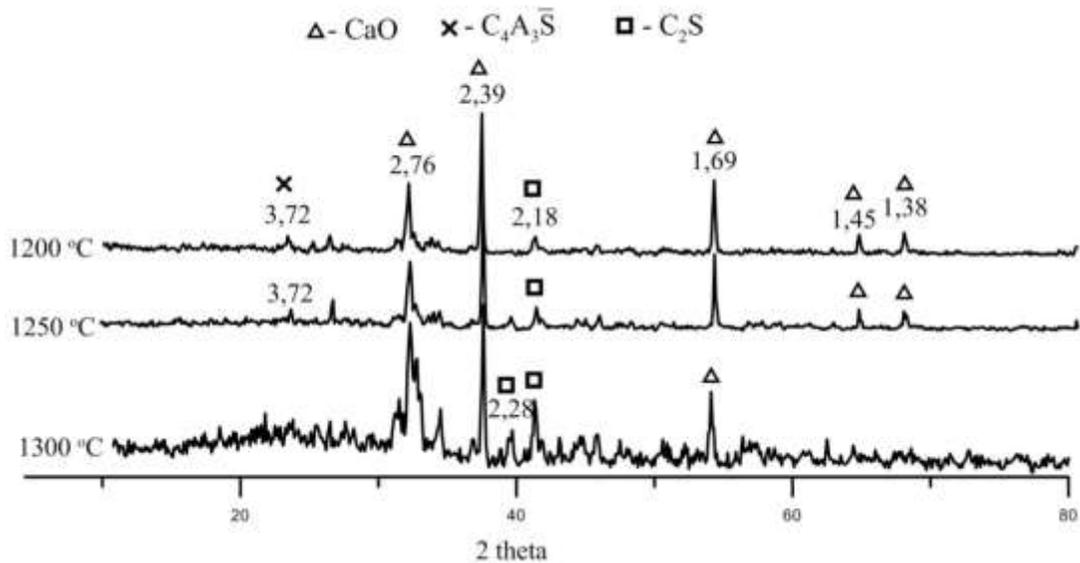
Thermogravimetric researches spent on scanning calorimeter STA 449 F3 Jupiter (Netzsch-Geratebau GmbH) by the methods of DIN 51004:1994. The chemical compound of raw components and clinker is presented in Table 1.

| Component   | CaO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> | MgO  | P <sub>2</sub> O <sub>3</sub> | LOI   | The sum |
|---|-------|------------------|--------------------------------|--------------------------------|-----------------|------|-------------------------------|-------|---------|
| Lime stone(CaCO <sub>3</sub> )                      | 56,35 | 0,040            | 0,06                           | 0,04                           | 0,03            | 0,37 | 0,014                         | 42,80 | 99,70   |
| Clay  | 1,21  | 50,70            | 19,90                          | 11,80                          | 0               | 1,40 | 0,17                          | 14,81 | 99,90   |
| Quartz sand   | 0,03  | 98,80            | 0,45                           | 0,03                           | 0               | 0    | 0                             | 0,13  | 99,40   |
| Natural gypsum                                      | 32,02 | 0,80             | 0,45                           | 0,23                           | 44,50           | 0    | 0                             | 22,0  | 100,0   |
| Clinker without taking into account gypsum's oxides | 67,17 | 22,19            | 6,08                           | 3,59                           | 0,035           | 0,85 | 0,067                         | 0     | 99,99   |
| Clinker with the account gypsum's oxides            | 65,25 | 21,12            | 5,80                           | 3,42                           | 2,26            | 0,80 | 0,064                         | 1,1   | 99,99   |

**Table 1:**The Chemical compound of a raw mix, mas. %

#### IV. Results

Results qualitative x-ray analysis of the investigated mixes are presented in Figure 1.



**Figure 1:** Results qualitative x-ray analysis of clinker with the additive 5 % of gypsum

The maintenance of free lime in high-sulfur clinker is presented in Table 2.

| Thematerialname | Maintenance of free lime in clinker, mas. %, at temperature of roasting, °C |       |      |
|-----------------|---|-------|------|
|                 | 1100  | 1200  | 1300 |
| Rawmix          | 14,0  | 13,84 | 11,6 |

**Table 2:** The maintenance of free lime in high-sulfur clinker

Results of tests testify, that introduction in a raw mix of gypsum of 5 % suppresses alito-formation and promotes formation in clinker a significant amount of free lime. Diffractonal maxima, characteristic for free lime, are present in clinker, calcinated at temperature 1300 °C, and diffractonal maxima, characteristic for C<sub>3</sub>S, at this temperature are not fixed. At heating of all clinkers up to temperature 1350 °C they completely melting. The analysis of meltin's products, heated up to temperature of 1600 °C, testifies, that C<sub>3</sub>S at such overheat is formed, but in clinker there are 6,2 % free lime.

#### V. Discussion

The reason of suppression of formation a C<sub>3</sub>S in is high-sulfur clinker most likely is formation of free lime, which has a stable crystallization structure, is not dissolved in a liquid phase, does not co-operate with C<sub>2</sub>S and does not form C<sub>3</sub>S. Absence heat-resistant

C<sub>3</sub>S in clinker leads to decrease in its fire resistance and fusion at temperatures, below usual temperatures of synthesis of Portland cement clinker.

The assumption of that superfluous free lime in clinker is formed owing to decomposition of the gypsum entered into a raw mix, it is erroneous. As show given tab. 1, maintenance free CaO in clinker, containing gypsum it is, less, than in clinker without gypsum, besides, a significant amount free lime to exhaust in is high-sulfurclinker it is formed at temperatures when gypsum does not decay yet (tab. 2).

For finding-out of the reasons of occurrence of a significant amount of free lime in high-sulfur clinker, the thermodynamic analysis of reactions of formation C<sub>3</sub>A and C<sub>4</sub>AF according to data of works has been carried out [7,8]. Results of the analysis are presented inTable3.

| №<br>п/п | Reaction   | Gibbs energyΔG, kJ/mol at temperature, K |        |        |        |        |
|----------|--|--|--------|--------|--------|--------|
|          |  | 298                                      | 1023   | 1200   | 1400   | 1500   |
| 1        | 3CaO+Al <sub>2</sub> O <sub>3</sub> =3CaO·Al <sub>2</sub> O <sub>3</sub>   | -17,0                                    | -41,8  | -47,0  | -52,9  | -55,7  |
| 2        | 4CaO+Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> =4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>         | -49,3                                    | -64,9  | -64,1  | -60,83 | -58,1  |
| 3        | 3CaO+3Al <sub>2</sub> O <sub>3</sub> +CaSO <sub>4</sub> =3CaO·3Al <sub>2</sub> O <sub>3</sub> ·CaSO <sub>4</sub>                                 | -99,1                                    | -445,1 | -583,6 | -758,9 | -853,5 |
| 4        | CaO·Al <sub>2</sub> O <sub>3</sub> +2CaO=3CaO·Al <sub>2</sub> O <sub>3</sub>   | +33,7                                    | +32,3  | +31,7  | +33,26 | +34,4  |
| 5        | CaO·Al <sub>2</sub> O <sub>3</sub> +CaO+2CaO·Fe <sub>2</sub> O <sub>3</sub> =4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> | +10,4                                    | +39,7  | +49,0  | +60,3  | +66,2  |
| 6        | CaO·Al <sub>2</sub> O <sub>3</sub> +2CaO+CaO·Fe <sub>2</sub> O <sub>3</sub> =4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> | +42,45                                   | +72,1  | +79,77 | +79,8  | +83,7  |

**Table 3:** The thermodynamic analysis of reactions of formation C<sub>3</sub>A and C<sub>4</sub>AF according to works [7,8]

According to the resulted data in is low-sulfur clinker synthesis C<sub>3</sub>A and C<sub>4</sub>AF thermodynamic is possible from simple minerals CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> (reaction 1-2). In is high- sulfur clinker hermodynamic course of reaction of 3 formations ye'elimit C<sub>4</sub>A<sub>3</sub> $\bar{S}$  is more preferable. Concerning the formation mechanism ye'elimit in clinker at heating there are different opinions. According to work [8] synthesis ye'elimit, begins with formation of mayenite under scheme C<sub>12</sub>A<sub>7</sub> → CA → C<sub>3</sub>A<sub>3</sub>C $\bar{S}$ . According to data of our paper [9] in the pressed raw mix proceeds under scheme CA<sub>2</sub> → CA → (CA)<sub>2</sub> → (CA)<sub>3</sub> → C<sub>3</sub>A<sub>3</sub>C $\bar{S}$  with formation at occurrence temperatures to exhaust monoaluminate of calcium CA and its presence at all temperature interval of roasting to temperature of 1300°C. In the presence of monoaluminate of calcium formation C<sub>3</sub>A and C<sub>4</sub>AF thermodynamically is impossible (reactions 4-6). On the basis of the given researches authors [7] have drawn a conclusion, that in the presence of monoaluminate of calcium C<sub>3</sub>A and C<sub>4</sub>AF are formed from melt. Hence, if calculation of a raw mix is conducted on formation in is high-sulfur clinker minerals C<sub>3</sub>A and C<sub>4</sub>AF, and actually in such clinker before occurrence of a liquid phase are formed CA and CF, such process can lead to occurrence free lime under schemes:

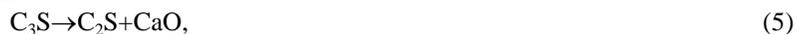


Formed free lime in the course of heating has a stable crystallization structure, it is not dissolved in liquid phase and suppresses formation C<sub>3</sub>S at the initial stage of its formation. Quantity free lime, formed in clinker at the expense of a difference of its maintenance in C<sub>3</sub>A and CA it is insignificant, and makes only 3 %, but it is probable this quantity enough for formation suppression C<sub>3</sub>S at the initial stage and creations of conditions for formation in clinker a significant amount free lime. As C<sub>3</sub>S in clinker it is not formed, and it is formed C<sub>2</sub>S, at the expense of a maintenance difference lime in the given minerals, the total maintenance free lime at temperatures of end of synthesis makes already about 11,0 %. At a considerable overheat melt to 1600 °C C<sub>3</sub>S all the same it is formed, but free lime it is so a stable crystallization structure, that is not dissolved in melt even at such overheat and remains in quantity about 6,0 %.

For prevention of formation free lime, suppressing formations C<sub>3</sub>S in SO<sub>3</sub> presence, it is offered to settle an invoice the raw mix on synthesis in Portland cement clinker intermediate metastable phases existing in a solid phase, but breaking up at occurrence of a liquid phase. As at occurrence of a liquid phase thermodynamically is possible there is a formation C<sub>3</sub>A and C<sub>4</sub>AF phases, they can be formed from CA and CF only in the presence of free lime under schemes:



In the conditions of temperatures of roasting of 1300°C, in the absence of free lime its source may become the only transformation of C<sub>3</sub>S and disintegration of calcium sulfate by schem:



If at structure designing Portland cement it is in advance known, that  $C_3S$  can decay, it is expedient to form in clinker its maximum quantity that it is possible to reach only at  $LSF=1$ .

For calculation of factor of saturation in Russia used Kind V.A. formula [10]

$$KSk = \frac{CaO - (1,65Al_2O_3 + 0,35Fe_2O_3)}{2,8SiO_2} \quad (7)$$

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

English analogue of the given formula is the formula for calculation Lime Saturation Factor [11]

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

Lime Saturation Factors in the given formula are taken from phase diagram  $CaO-Al_2O_3-SiO_2$  and  $CaO-Al_2O_3-SiO_2-Fe_2O_3$  at optimum relationship oxides, providing absence free lime in clinker. If to use Kinda V.A's design procedure [10], that the formula (8) becomes full analogue of the formula (7)

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

As calculation on formation in high-sulfur clinker  $C_3A$  and  $C_4AF$  leads to formation in it of a significant amount of free lime, the given formulas have been corrected for formation in clinker metastable phases

$$KSk = \frac{CaO - 0,55Al_2O_3 - 0,35Fe_2O_3 - 0,7SO_3 - 1,18P_2O_5}{2,8SiO_2} \quad (10)$$

$$LSF = \frac{CaO - 1,18P_2O_5 - 0,7SO_3}{2,8SiO_2 + 0,55Al_2O_3 + 0,35Fe_2O_3} \quad (11)$$

The given formula for calculation of factor of saturation is received with the account, that at roasting of a raw mix in the presence of gypsum, in clinker minerals  $C_3S$ ,  $C_2S$ , and metastable phases  $CA$  and  $CF$  are formed. Value  $1,18P_2O_5$  is considered, if in quality mineralizer is used phosphogypsum. At synthesis ferrite of calcium  $C_2F$  use value  $0,7Fe_2O_3$ .

For calculation of degree of saturation of metastable clinker's minerals by sulphate in the presence of gypsum used Atakuziev T.A.'s formula [12] with the account, that in clinker is possible sulfatization  $C_2S$ ,  $CA$ ,  $CF$  and  $C_2F$ . Taking into account the given updating, the formula of calculation of degree of saturation looks as follows

$$DS = \frac{SO - 0,261Al_2O_3 - 0,167Fe_2O_3}{0,667SiO_2} \quad (12)$$

In a case when it is synthesized  $C_2F$ , at  $Fe_2O_3$  the factor 0,5 and when it is not supposed sulfatization of ferrite of calcium, values  $0,167 Fe_2O_3$  is used and  $0,5 Fe_2O_3$  into the formula are not entered.

When synthesized  $C_2F$ ,  $Fe_2O_3$  is the coefficient 0,5, and when ferrites is not sulfatized, the coefficients 0,167 and 0,5 in formula are not entered.

For check of possibility of the formation of  $C_3S$  in is high-sulfur clinker, synthesis of clinker through metastable phases  $C_4A_3\bar{S}$ ,  $CF$ ,  $C_2F$ ,  $3(CF)C\bar{S}$ ,  $C_2FC\bar{S}$  and  $2(C_2S)C\bar{S}$  was carried out.

Calculation of a raw mix from the components which chemical compound is presented to table 1 on synthesis in products of roasting of silicate phase  $C_3S$  ( $KSk=1$ ), intermediate metastable aluminate phase  $C_4A_3\bar{S}$  and intermediate metastable ferrit phases  $CF$ ,  $C_2F$ ,  $3(CF)C\bar{S}$  and  $C_2FC\bar{S}$  was made. Settlement structures of raw mixes and a chemical compound clinkers, it is presented in Table4.

| The name of clinker | Structure of a raw mix, mas. % |       |        | Chemical compound of clinker, mas. % |                  |                                |                                |                 |
|---------------------|--------------------------------|-------|--------|--------------------------------------|------------------|--------------------------------|--------------------------------|-----------------|
|                     | LS*                            | Clay  | Gypsum | CaO                                  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> |
| Clinker № 1         | 71,42                          | 25,6  | 2,97   | 64,98                                | 20,41            | 8,03                           | 4,76                           | 2,1             |
| Clinker № 2         | 70,65                          | 25,28 | 4,07   | 64,39                                | 20,14            | 7,92                           | 4,69                           | 2,85            |
| Clinker № 3         | 71,96                          | 25,13 | 2,92   | 65,27                                | 20,07            | 7,9                            | 4,68                           | 2,03            |
| Clinker № 4         | 69,73                          | 24,2  | 6,07   | 64,38                                | 19,33            | 7,6                            | 4,49                           | 4,22            |

\* - lime stone

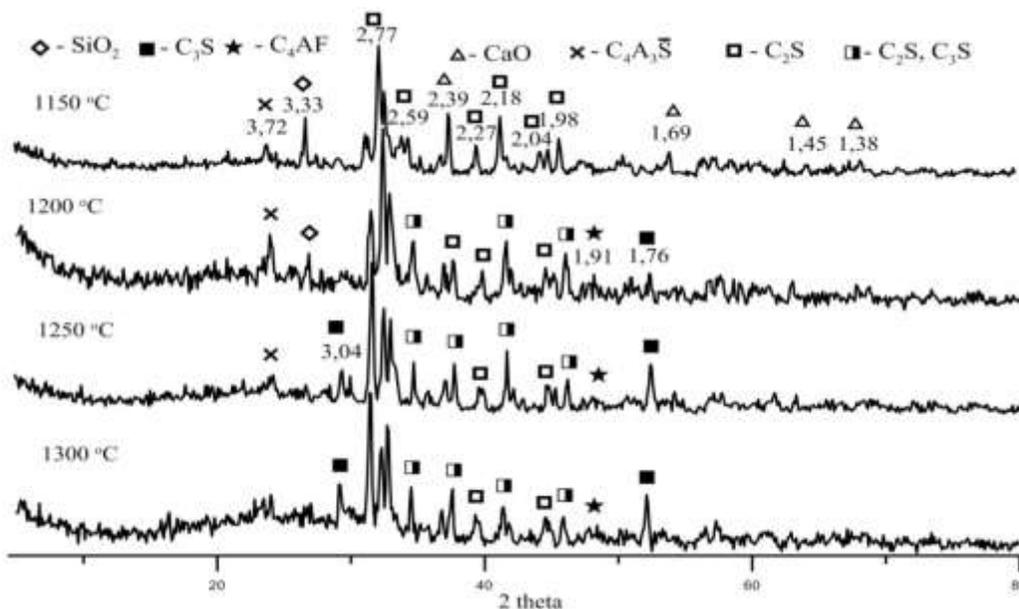
**Table 4:** Structure of raw mixes and clinkers of synthesised cements

Modular characteristics for all clinkers have made  $KSk = 1$ ,  $DS = 0$ ,  $SR = 1,6$  and  $AR = 1,69$ . The settlement intermediate phase clinker's structure is presented in Table. 5.

| The name of clinker | $C_3S$ | $C_4A_3\bar{S}$ | CF   | $3(CF)C_2\bar{S}$ | $C_2F$ | $C_2FC_2\bar{S}$ | The sum |
|---------------------|--------|-----------------|------|-------------------|--------|------------------|---------|
| Clinker № 1         | 76,23  | 16,94           | 6,81 | -                 | -      | -                | 99,98   |
| Clinker № 2         | 75,18  | 16,68           | -    | 8,15              | -      | -                | 100,01  |
| Clinker № 3         | 74,9   | 16,65           | -    | -                 | 8,43   | -                | 99,98   |
| Clinker № 4         | 73,75  | 15,92           | -    | -                 | -      | 10,43            | 100,1   |

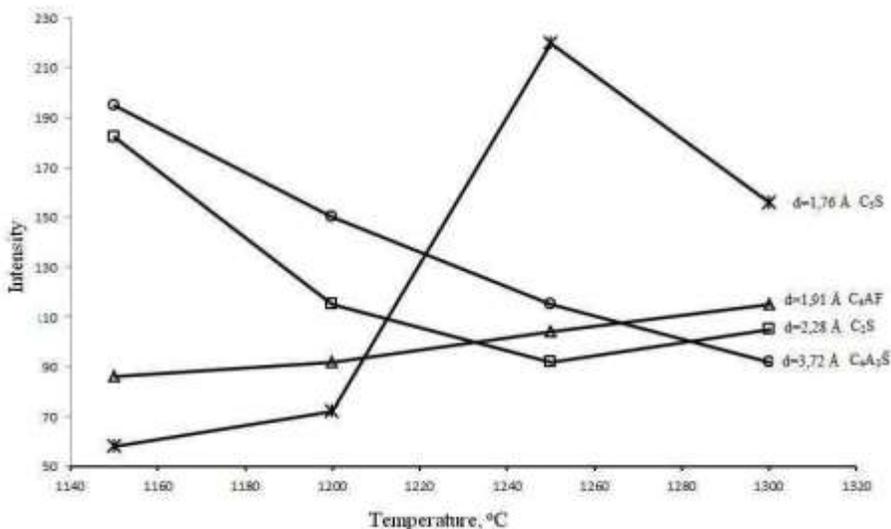
**Table 5:** Settlement intermediate phase structure of clinkers

The raw mixes prepared according to calculation subjected to homogenization in a laboratory mill by a joint grinding within 30 minutes. Homogenization mixes pressed at 50MPa. Roasting of all mixes was spent at temperatures 1150, 1200, 1250 and 1300 °C. Roasting products investigated x-ray methods. Results qualitative x-ray the analysis clinker № 1 calcinated at temperatures 1150, 1200, 1250 and 1300 °C are presented in Figure 2.



**Figure 2:** Results qualitative x-ray analysis of clinker № 1, calcinated at temperatures from 1150 to 1300 °C

Change of intensity diffractonal maxima of the basic phases clinker № 1 depending on roasting temperature, is presented in Figure 3.



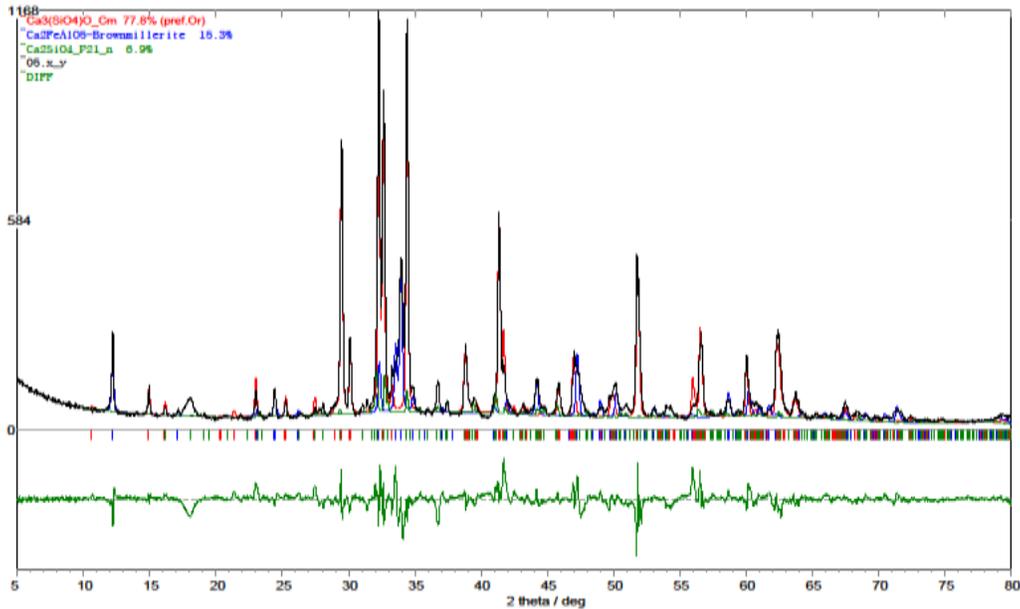
**Figure 3:** Intensity change diffractonal maxima of the basic phases of clinker № 1 depending on roasting temperature

Data qualitative x-ray testify, that in clinker, calculated on synthesis in the presence of gypsum of intermediate metastable phases, free lime at temperature of roasting of 1200 °C and above, no find. Diffractonal maximum with  $d=1,76\text{Å}$ , characteristic for  $C_3S$ , to temperature of 1250 °C increases, and since temperature of 1250 °C, decreases. Diffractonal maximum with  $d=2,28\text{Å}$ , characteristic for  $C_2S$ , on the contrary, to temperature of 1250 °C decreases, and above this temperature – increases, that testifies to part

transformation  $C_3S$  in  $C_2S$ . With increase in temperature of roasting intensity diffractional maximum with  $d=1,91 \text{ \AA}$  increases, characteristic for brownmillerite  $C_4AF$ . Intermediate metastable phase  $C_4A_3\bar{S}$  ( $d=3,72 \text{ \AA}$ ), with increase in temperature of roasting breaks up, to what reduction of its intensity of the basic diffractional a maximum after temperature of  $1150 \text{ }^\circ\text{C}$  testifies.

Similar results are received at roasting of the raw mixes calculated on reception in clinkers as intermediate metastable ferrit  $3(CF)C\bar{S}$ ,  $C_2F$ ,  $C_2FC\bar{S}$  and aluminate  $C_4A_3\bar{S}$  phases.

For definition of actual structure of clinkers, synthesised at temperature  $1300^\circ\text{C}$ , has been spent quantitative x-ray the analysis. Results quantitative x-ray the analysis for clinker № 1 are presented on Figure 4.



**Figure 4:** Results of quantitative x-ray the analysis for clinker № 1

In Table 6 presents summary results of quantitative x-ray the analysis synthesised clinkers.

| The name of phases     | Amount of phases, mas. %, in |           |           |           |
|------------------------|------------------------------|-----------|-----------|-----------|
|                        | clinker 1                    | clinker 2 | clinker 3 | clinker 4 |
| Alite $C_3S$           | 77,8                         | 70,8      | 72,2      | 46,1      |
| Brownmillerite $C_4AF$ | 15,3                         | 19,6      | 14,6      | 14,2      |
| Belite $C_2S$          | 6,9                          | 9,6       | 13,2      | 39,7      |

**Table 6:** Summary results quantitative x-ray synthesised clinkers

Results quantitative x-ray the analysis testify, that in clinkers on the basis of the corrected raw mix really there is a significant amount of alit (except clinker № 4). In synthesized clinkers presence of  $C_3A$  is not fixed, and absolutely are absent sulfated phases. X-ray ways of identification of phase structure badly define light oxides, in particular sulphates. Definition of the maintenance of sulphates in synthesisedclinkers a weight method has shown, that in them contains from 0,5 to 2,75 mas. %  $SO_3$  that means, that from 40 to 75 mas. % of the sulphates entered into a raw mix disappears, and remained in clinker sulphates, possibly, are connected in sulfated phases or are in alit in the form of a solid solution.

Results qualitative, quantitative x-ray and data of the chemical analysis synthesized clinkers have allowed establishing, that at synthesis of cements with intermediate metastable phases at a finishing stage difficult physical and chemical processes proceed.

At temperatures of roasting to  $1200^\circ\text{C}$ , in the conditions of absence of a liquid phase, synthesis proceeds with formation of intermediate metastable minerals and their quantities, defined settlement by. As soon as at the temperature close to temperature of  $1200^\circ\text{C}$ , in system there is a liquid phase, thermodynamically it becomes more preferable formation through liquid phase  $C_4AF$ , and  $C_3A$  which start to be formed in the liquid environment, involving in reaction already generated in conditions of solid-phase synthesis intermediate metastable aluminate and ferrit minerals, causing their decomposition.

Lime, necessary for synthesis of  $C_4AF$ , and  $C_3A$  from metastable low lime aluminates and calcium ferrites, arrives from partial transformation alit in belit and also gypsum decomposition under schemes 5 and 6. After partial transformation of alit in belit, actual KSk (LSF) synthesized clinkers 1-4 it is equal accordingly 0,965; 0,949; 0,935 and 0,823. The sulphate liberated at decomposition of intermediate phases, either disappears, or enters reaction with alit with formation of a solid solution. Thus, remained in clinker sulphate can be connected residual  $C_4A_3\bar{S}$  or silicate phases.

Absence in clinkers  $C_3A$  in is high-sulfur clinker is possibly connected with isomorphic replacement Si in silicate phases by the Al, that will be coordinated with data of paper [4]. Owing to aluminium occurrence in silicate phases, the maintenance of alit also raises.

On the basis of received at temperature 1300°C clinkers, 4 cements by a joint grinding clinker with natural gypsum have been prepared. As in synthesized clinker sulphates already contain, the quantity of natural gypsum at a grinding was added from calculation, that maintenance SO<sub>3</sub> in Portland cement would not exceed admissible standard documents of quantity - 4,0 %. Activity of cement was defined on cubes with a size 2x2x2 the sm, prepared of the cement test of normal density.

Results of definition of physico-mechanical properties of cements are presented in Table 7 and Table 8.

| Type of clinkers | Material structure |        | SO <sub>3</sub> , % | S, m <sup>2</sup> /kg | R <sub>008</sub> , % | ND, % | Terms of cementation, hour-minute |      |
|------------------|--------------------|--------|---------------------|-----------------------|----------------------|-------|-----------------------------------|------|
|                  | clinker            | gypsum |                     |                       |                      |       | begin                             | end  |
| Clinker № 1      | 96                 | 4      | 3,96                | 348                   | 12,7                 | 25,2  | 2-50                              | 4-15 |
| Clinker № 2      | 97,5               | 2,5    | 4,0                 | 368                   | 12,0                 | 29,3  | 2-15                              | 3-15 |
| Clinker № 3      | 96                 | 4      | 3,86                | 353                   | 7,8                  | 25,0  | 2-35                              | 4-05 |
| Clinker № 4      | 100                | 0      | 4,22                | 344                   | 10,7                 | 30,1  | 2-00                              | 3-05 |

\*S – a specific surface; R<sub>008</sub> – the rest on a sieve № 008; W/C – a water-cement parity; ND – normal density

**Table 7:** Results of tests of Portland cement

| Type of clinkers | Strength at compression, MPa, through, days |      |      |      |
|------------------|---|------|------|------|
|                  | 2   | 7    | 14   | 28   |
| Clinker № 1      | 21,8  | 31,1 | 42,5 | 67,3 |
| Clinker № 2      | 22,5  | 33,2 | 44,7 | 70,0 |
| Clinker № 3      | 25,2  | 37,3 | 46,4 | 72,5 |
| Clinker № 4      | 30,8  | 46,3 | 54,1 | 73,7 |

**Table 8:** Results of tests of Portland cement

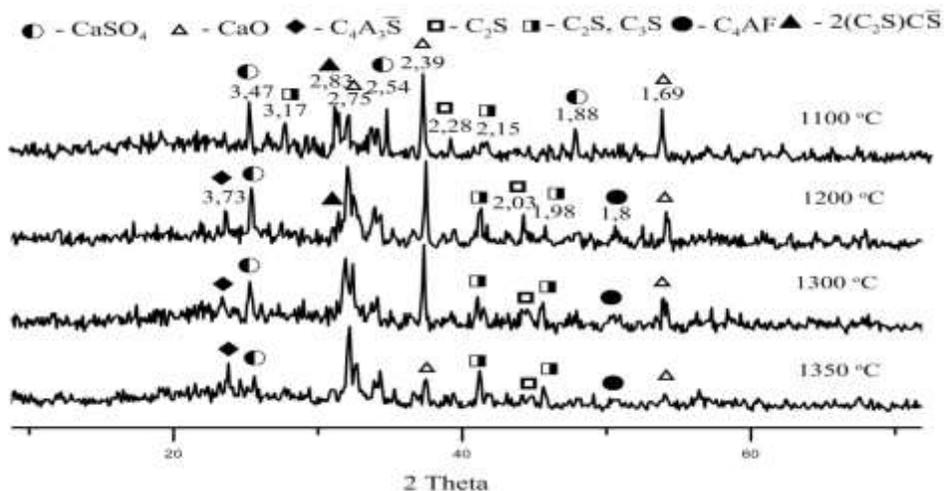
The results of calculating the raw mix for synthesis phase C<sub>3</sub>S (KSk=1) through metastable phases C<sub>4</sub>A<sub>3</sub>S̄ and 2(C<sub>2</sub>S)C̄S̄ presented in Table 9.

| The name of clinker   | Structure of a raw mix, mas. % |      |        | Chemical compound of clinker, mas. % |                  |                                |                                |                 |
|---|--------------------------------|------|--------|--------------------------------------|------------------|--------------------------------|--------------------------------|-----------------|
|   | LS*                            | Clay | Gypsum | CaO                                  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> |
| Clinker with metastable phases C <sub>4</sub> A <sub>3</sub> S̄ and 2(C <sub>2</sub> S)C̄S̄ | 59,9                           | 21,2 | 18,9   | 60,2                                 | 16,4             | 6,5                            | 3,8                            | 12,6            |

\* - lime stone

**Table 9:** Structure of raw mixes and clinkers of synthesised cements

Results of qualitative x-ray the analysis clinker with metastable phases C<sub>4</sub>A<sub>3</sub>S̄ and 2(C<sub>2</sub>S)C̄S̄ calcinated at temperatures 1100,1200, 1300 и 1350 °C are presented in Figure 5.



**Figure 5:** Results of qualitative x-ray analysis of clinker with metastable phases C<sub>4</sub>A<sub>3</sub>S̄ and 2(C<sub>2</sub>S)C̄S̄ calcinated at temperatures 1100,1200, 1300 и 1350 °C

Results quantitative x-ray the analysis testify hat, in accordance with the calculation in the clinker, the metastable aluminate phase of  $C_4A_3\bar{S}$  is formed, identifiable from its main diffraction peak with  $d = 3.73\text{\AA}$ , reaching its maximum intensity at  $1350\text{ }^\circ\text{C}$  and the metastable silicate phase of sulfospuritrit  $2(C_2S)C\bar{S}$ , identified by its main diffraction maximum with  $d = 2.83\text{\AA}$ , reaching a maximum intensity at a temperature of  $1100\text{ }^\circ\text{C}$ , and decaying at a temperature above  $1200\text{ }^\circ\text{C}$ .

According quantitative x-ray data, it can be concluded that after the disintegration of sulfosporrite  $2(C_2S)C\bar{S}$ , a significant amount of gypsum is formed in the clinker, identified by the main diffraction maximum with  $d = 3.47\text{ \AA}$  and free lime identified by diffraction maxima with  $d = 2.39\text{ \AA}$  and  $d = 1.69\text{ \AA}$ , which persist even at a temperature of  $1350\text{ }^\circ\text{C}$ . The formation of  $C_3S$  (alite) in the clinker is not detected.

Based on the results of the tests, it follows that alit formation is suppressed as a result of the formation of a significant amount of free lime from the decomposition of sulfosulpurite and gypsum, which means that in the case of the formation of a metastable silicate phase in the clinker, it is not enough to stabilize the ality formation, in the clinker of calcium monoaluminate, as it shown above, but it is still necessary to take measures to prevent the formation of a significant amount of free lime, formed after the decomposition of the metastable silicate phase.

To bind a significant amount of free lime, formed after the disintegration of sulfosulpurite, it is proposed to perform a two-stage calculation of the composition of the raw mixture for the formation of conventional Portland cement clinker.

At the first stage, the raw meal is calculated for the formation of metastable aluminate and silicate phases in it by the formulas and methods described above. At the second stage of the calculation it is assumed that when the melt appears, the metastable phases and all the gypsum decomposes according to the reaction 6. The chemical oxide composition, formed under such conditions, is taken as one of the components of the raw mixture. Other components of the raw mix are correcting additives, represented by limestone and quartz sand. At the second stage, the calculation is carried out according to the usual generally accepted formulas for the formation of Portland cement clinker with given modular characteristics.

In Table. 10 shows the chemical composition of the components of the raw mix used in the calculation of Portland cement clinker in the second stage.

| Component  | CaO  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> | MgO  | LOI   | The sum |
|--|------|------------------|--------------------------------|--------------------------------|-----------------|------|-------|---------|
| Limestone (CaCO <sub>3</sub> )                       | 56,3 | 0,04             | 0,06                           | 0,04                           | 0,03            | 0,37 | 42,80 | 99,69   |
| Quartz sand  | 0,03 | 98,8             | 0,45                           | 0,03                           | 0               | 0    | 0,13  | 99,40   |
| Clinker after the decomposition of metastable phases | 69,2 | 18,9             | 7,5                            | 4,4                            | 0               | 0    | 0     | 100,0   |

**Table 90:** The chemical composition of the components of the raw mix used in the calculation of Portland cement clinker in the second stage, mas. %

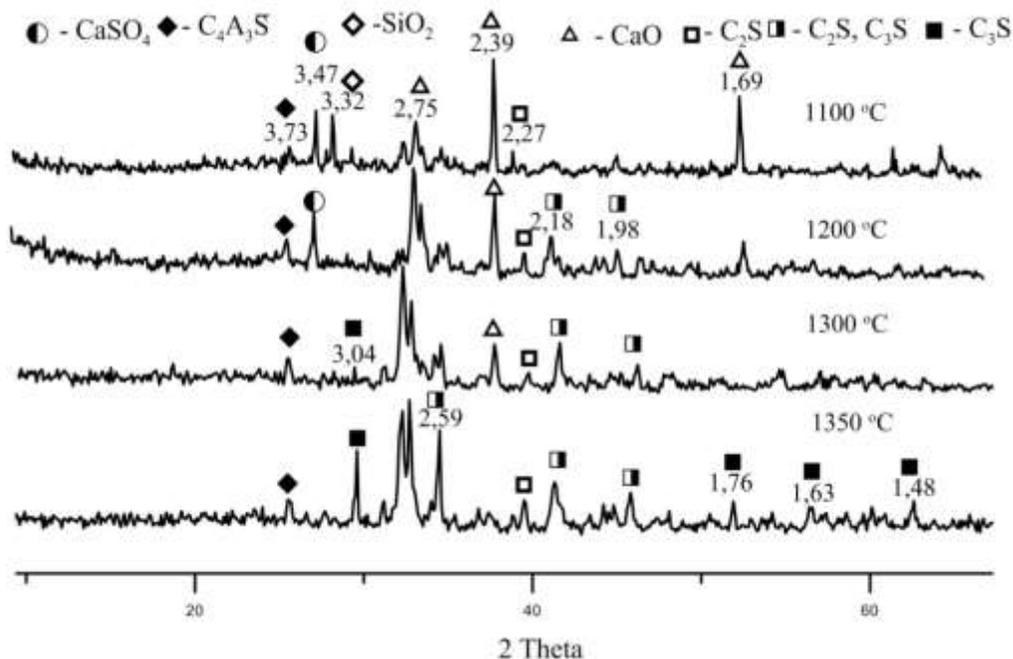
Based on the components of the raw mixture, the chemical composition of which is given in Table. 2 calculation was made for the production of portland cement clinker with modular characteristics  $KSk$  (LSF) = 0.92, SR = 2.3 and AR = 1.69. Estimated composition of raw mix and chemical composition of clinker is shown in Table. 11.

| Clinker name            | Structure of a raw mix, mas. % |             |      | Chemical compound of clinker, mas. % |                  |                                |                                |                 |
|-------------------------|--------------------------------|-------------|------|--------------------------------------|------------------|--------------------------------|--------------------------------|-----------------|
|                         | LS*                            | Quartz sand | DC** | CaO                                  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> |
| Portland cement clinker | 17,1                           | 77,5        | 5,8  | 68,2                                 | 22,1             | 5,9                            | 3,7                            | 0               |

\* - lime stone, \*\* - clinker after the decomposition of metastable phases

**Table 101:** Estimated composition of raw mix and chemical composition of clinker, mas. %

In Figure 6 are presented results of x-ray analysis of clinker, prepared according to the calculation, given above and calcined at temperatures of  $1100, 1200, 1300$  and  $1350\text{ }^\circ\text{C}$ .



**Figure 6:** Results of qualitative x-ray analysis of clinker, prepared according to the calculation, given above and calcined at temperatures of 1100,1200,1300 and 1350 ° C.

Analysis of x-ray data indicates the absence of free lime in a clinker, prepared according to the calculation, at a firing temperature above 1300 ° C. At a temperature of 1100 °C free quartz is fixed, which is fully absorbed at a temperature of 1200 °C. Free gypsum is not fixed at a temperature of 1300 °C.

A stable alite is formed at a burning temperature of 1350 °C, as evidenced by the appearance at this temperature of diffraction maxima characteristic for alite with  $d = 3.04 \text{ \AA}$  and  $d = 1.76 \text{ \AA}$ .

A quantitative x-ray data phase analysis was performed to determine the actual phase composition of the clinker prepared in accordance with the calculation and synthesized at a temperature of 1350 ° C, the results of which are shown in Table. 12.

| The name of phases     | Amount of phases, mas. % in clinker |
|------------------------|-------------------------------------|
| Alite $C_3S$           | 65,9                                |
| Brownmillerite $C_4AF$ | 11,7                                |
| Belite $C_2S$          | 22,5                                |

**Table 112:** Results of quantitative x-ray data phase analysis

The results of the tests show , that in the preparation of clinker on the basis of a high-sulfate raw mix. initially containing 12.6%  $SO_3$ , after adjusting the composition of the raw mix, a significant amount of alite remains. In the clinker is not fixed  $C_3A$ . Absence in clinkers  $C_3A$  in is high-sulfur clinker is possibly also connected with isomorphic replacement Si in silicate phases by the Al, that will be coordinated with data of paper [4].

Based on the clinker, formed at a temperature of 1350 ° C, cement was prepared by grinding clinker. Activity of cement was defined on cubes with a size 2x2x2 the sm, prepared of the cement test of normal density.

Results of definition of physico-mechanical properties of cements are presented inTable 13 and Table 14.

| The name of clinke  | Material structure |         | $SO_3, \%$ | $S, \text{ m}^2/\text{кг}$ | $R_{008}, \%$ | ND, % | Terms of cementation, hour-minute |      |
|---|--------------------|---------|------------|----------------------------|---------------|-------|-----------------------------------|------|
|   | clinker            | gyp-sum |            |                            |               |       | begin                             | end  |
| The clinker, prepared on the basis of the corrected raw mix | 100                | -       | 12,7       | 378                        | 3,1           | 28,3  | 1-50                              | 2-15 |

\*S – a specific surface;  $R_{008}$  – the rest on a sieve № 008; ND – normal density

**Table 13:** Results of tests of Portland cement

| The name of clinke  | Strength at compression, MPa, through, days |      |      |      |
|---|---|------|------|------|
|   | 2   | 7    | 14   | 28   |
| The clinker, prepared on the basis of the corrected raw mix | 10,1  | 14,7 | 20,0 | 44,7 |

**Table 14:** Results of tests of Portland cement

## VI. Conclusions

The reason of suppression of alito-formation in is high-sulfur clinkers is formation at heating clinker a significant amount of free lime.

The thermodynamic analysis of reactions of formation of clinker's phases in the presence of calcium sulphate has shown, that in such conditions synthesis aluminate phases proceeds on mono aluminate to the scenario.

At presence mono aluminate of calcium formation in a firm phase of  $C_3A$  and  $C_4AF$  thermodynamically is impossible; hence formation CA instead of  $C_3A$  leads to formation of a significant amount of free lime, suppressing alito-formation. As instead of alit in clinker it is formed belit, super fluous quantity of lime is formation, equal to a difference of its maintenance in the given minerals, it is allocated in a free kind. The total maintenance free lime at the synthesis closing stages makes about 11 %.

Updating of structure of a raw mix allows to generate in is high-sulfur clinker a significant amount of alit. Calculation should be made on formation in is high-sulfur clinker the intermediate metastable low-lime alluminate, silicate and ferrit minerals.

The physico-mechanical properties of cement synthesized on a high-sulfate clinker are determined.

Method of adjusting the composition of Portland cement clinker on the base of highe sulfur raw mix is patented [13].

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