Using the low-temperature plasma in cement production

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Abstract. The calculation of the raw-material mixtures and mineralogical composition of the cement clinkers which are synthezed on their base taking into account the disbalanced crystallization of the melting and glassing under conditions of the low-temperature plasma was performed. The difference of the actual values from the calculated ones is 0.69–3.73 %. The composition which is characterized as the saturation coefficient 0,88; the silicate module – 3.34, the alumina module – 2.52 in melting of which the alite in amount 78.7 %; $3CaO{\cdot}SiO_2$ – 4 %; $3CaO{\cdot}Al_2O_3$ – 9.8 %; $12CaO{\cdot}7Al_2O_3$ –2.9 %; CaO_{free} – 1 % formed using the lime-stone from the quarry «Pereval» in the town of Slyudyanka and the clay from the deposit «Maximovski» in Irkutsk Region is considered as the optimal one. The structure of the melted clinker is represented as the metastable minerals of alite in the lamellar form with the dimensions up to (3–20)×(80–400) μm and the ratio of length to width 26.6–133. The elongated crystal form may stipulate the high cement activity based on the melted clinkers, which is 82.7–84.2 MPa. Validing the revealed high activity of the viscous substance was confirmed by the results of the scanning electronic microscopy, X-ray phase analysis, with using of which the quantitative and qualitative analyses of the clinker minerals having the deformed crystalic lattice; were performed the morphology of the minerals in the clinker and cement stone, received on its ground, was studied.

1. Introduction

Using the low-temperature plasma (LTP) is known to be one of the progressive methods of physico-chemical process intensification allowing to use liquid-phasic reactions instead of hard-phasic ones in the age of high-speed technologies. Using the high-concentrated heat streams in the production of cement is stipulated by developing the effect of «thermal stroke», which may provide a high reaction ability of raw-material mixture, intensify the decarbonization processes, promote the increase in the amount of the liquid phase up to 90–100 % as well as the decrease in viscosity of (the liquid phase) melting by 27.38–83.93 times relatively to the traditional technologies [1], the complete assimilation of the mineral-forming oxides and, as the consequence, the high clinker quality. Along with this, the plasmic technology allows to solve a number of the actual problems, correlated with the decrease in quality of the raw-material components, use the technogenic wastes; the production of the low-tonnage sets of special cement types, which is considered as the unprofitable task based on the objective technological situation for the traditional technologies. However, it is necessary to take into account that the processes under conditions of the low-temperature plasma are considered as the liquid-phasic ones and characterized by the disbalance which may promote the appearance of the additive amount of the glass, CaO_{fr} and C_3A, $C_{12}A_7$. The disbalanced crystallization is revealed in the absence of the reactions between the crystals and the remaining melting [2]: as well as glassing the remaining liquid phase. This influences on the mineralogical composition of the synthesed cement clinker and, as the consequence, on the calculation of the component composition of the mixture. In this connection the represented work is devoted to the calculation features of the optimal charge composition taking into account the disbalanced crystallization and glassing of the liquid phase in plasma-chemical synthesis of cement clinker and studying the features of the received viscous substance based on this aspect.

2. Technological regimes and study methods

The definite succession of preparing the mixture consisting in pre-dosing the components, the following grinding up to the fraction not more than 160 mcm and homogenization is considered as the distinctive feature of the technological schema in cement production based on the plasma-chemical technology. Moreover, the granulation or briquetting the raw-material mixture which is necessary to remove its blowing in exposure to the high-concentrated heating streams, is considered as the necessary technological stage. Thermal processing the prepared granulated mixture is performed using the experimental installation – the plasma-chemical reactor [3], the temperature in which is 3000 °C. Cooling the samples was performed using the air. The time period of isothermal self-control under conditions of the low-temperature plasma may change from 10 to 12 minutes. Then the melted synthesable cement clinker was grinded in the planetary ball miller PQ-N2 using 3 % gypsum. The instrument PSCH-12 was used to determine the specific surface of the viscous substance.

Studying the raw-materials and the synthesable cement clinker under conditions of LTP was performed based on the chemical analysis method accordingly to the claims of GOST 5382–91 «Cement and materials for cement production. Methods of chemical analyses». Moreover, the roentgen-phasic analysis (RPhA), the scanning electronic microscopy (SEM) were performed. The diffractograms were received using the X-Ray instrument Shimadzu XRD-7000 X-ray Diffractometer. The survey was performed on the copper Cu-K_{α} radiation with the step 0.05°, in the angle range 3–80°. The qualitative identification of the cement clinker phases and the cement stone was performed based on the program Match, the quantitative – Reflex based on the method by Rietveld [4]. The data base ICDD PDF-2 was used for the qualitative phasic analysis. SEM was performed using the equipment JEOL JIB-Z4500 and Phenom Pro.

3. Raw-material components and mixtures

In the studies the marmoreal lime-stone from the quarry «Pereval» in the town of Slyudyanka and the clay from the deposit «Maximovski» in Irkutsk Region were used. The chemical composition of the rocks studied is represented in table 1. The content of the main oxides in the raw-materials is traditional one [5], which allows to use the lime-stone as the carbonate and the clay – as the alumosilicate components for the synthesis of the cement clinker.

Table 1. Chemical compositions of primary raw-materials.

Component	The content of the main oxides (mass. %)						Sum
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	L.O.I.	(mass. %)
Marmoreal lime-stone	6.92	2.56	0.94	48.96	0.66	39.97	100.00
Clay	62.86	15.42	8.07	1.93	2.38	9.35	100.00

The calculation of the mixtures was performed based on the formulas [6]. The saturation coefficient (SC) of the raw-material mixtures may change from 0.8 to 1.0 (relatively, the mixtures #1 and #21) with the step 0.1. The prognosed mineralo-composition of the cement clinker was determined taking into account the features of the disbalanced crystallization of the melting in dependence on placing the figurative points of the compositions on the concentration triangle (figure 1).

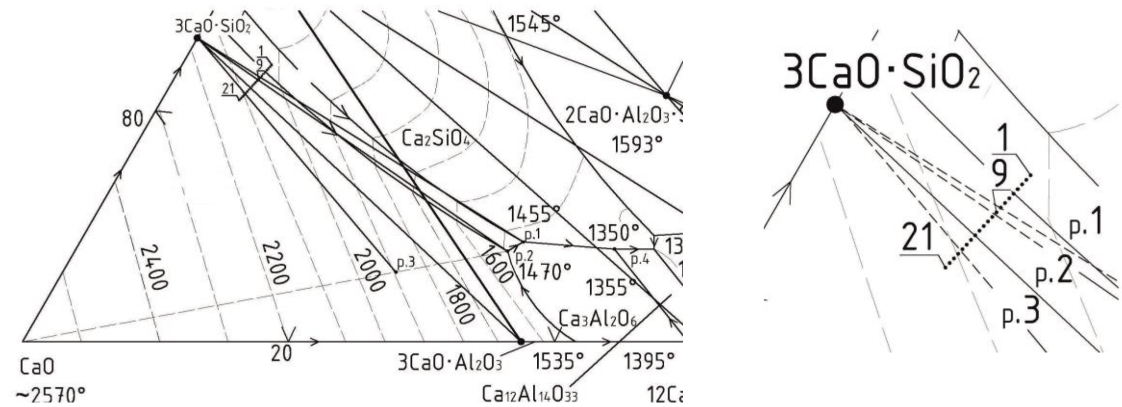

Figure 1. Part of state Diagram CaO-SiO_2-Al_2O_3. Placing the figurative points of the raw-material mixtures #1–21.

Three main aspects are considered: over the line C_3S – p.1; between C_3S – p.1 and C_3S – p.2; under C_3S – p.2. Re-calculation of their composition for the system: CaO, SiO_2 и Al_2O_3 was performed to determine the coordination of the figurative points on the state diagram. With this aim, the translated coefficients, introduction of which was grounded according to the rule the rapid-melted oxides may decrease in the temperature of material melting based on their equivalent weights [7], were used.

4. Results discussion

The calculation results have shown that 79.1–82.9 % of the marmoreal lime-stone and 17.1–20.9 % of the clay are needed for the synthesis of cement clinker under conditions of LTP. Moreover, the module characteristics of the mixture may change in the following ranges: saturation coefficient from 0.8 to 1.0; the silicate module (n) – 3.31–3.38; the alumina module (p) – 2.51–2.55. In the disbalanced crystallization in the cement clinker the alite content may exceed the tradition values 0.9–24.8 %; belite less 23.74–2.74 %; C_3A – 2.47–0.36 % (figure 2).

It was found that the synthesis of the maximal alite amount (more that 60 %) under conditions of LTP is possible with using all the calculated mixtures – #1–21; in the balanced crystallization only based on #10–21. The increase in the phases in different crystallizations may depend on the coordination of the figurative points of the clinkers on the state diagram (figure 1): in their placing over the connected line $3CaO\cdot SiO_2$ – p.1 (the compositions #1–8) – the continuous exceeding of the content of tricalcium silicate (24.8 %) relatively to the balanced conditions was observed. It is connected with that the reactions of C_3S with the melting in the p.1 may practically absent and the resting liquid consisting of C_2S, $C_{12}A_7$, C_3A may be crystallized independently. The saturation coefficient is, moreover, higher than SC in the balanced conditions by 1.527 times. As the consequence, the alite amount in the melted clinker may exceed the mineral content in the clinkers of the analogous composition but crystallized with balance.

The composition #9 placed between the lines C_3S – p.1 and C_3S – p.2 may have the increased by 23.88 % amount of alite in connection with that the crystallization before point 1 may go through the line 2–1 without p.2. Calcium aluminates may by formed not only from the liquid (p.1), the crystallization of C_3A is possible up to this point (along the line 2–1 in changing the composition of the liquid phase). The phasic composition of the products of disbalanced crystallization is represented as C_3S, C_2S, C_3A, $C_{12}A_7$. The clinkers under the line C_3S – p.2 may have both the increased by 1.77–20.99 % (the compositions #10–17) and the decreased by 0.84–8.47 % (mixtures #18–21) alite amounts. This is connected with that the crystallization may go through p.2 – the invariant point, in which the reactions between the calcium oxide and the melting may be realized with the temperature 1470 °C. Under conditions of LTP the reactions in p.2 doesn't realize and the resting melting may be crystallized independently along the line p.2–p.1–p.4 (the point of the field intersection of the primary crystallization C_2S–C_3A–$C_{12}A_7$). As the consequence, such compounds as C_3S, C_2S, C_3A, $C_{12}A_7$, CaO_{fr} may present in the disbalanced crystallization. Moreover, the absence of balance in p.1 may increase in the saturation coefficient and in p.2 – decrease. The line C_3S – p.3 is the border direct one, representing the geometric point place which is satisfactory to the balance condition of the saturation coefficients in disbalanced and balanced crystallization. In this connection, the compounds over this line may have the increased amount of alite, under it – decreased one. From the point of view of the disbalanced crystallization, the composition of clinker in which the free calcium oxide may absent and have the maximal alite amount is considered as the optimal one. This mixture is revealed based on the point coordinates on the line C_3S – p.2 or near it. The composition #9 (SC=0.88; n=3.34; p=2.52) in which the alite content 82.43 % may be considered as the actual one (figure 2, d). The composition after melting under conditions of the high-concentrated heat streams was objected to the physic-chemical studies.

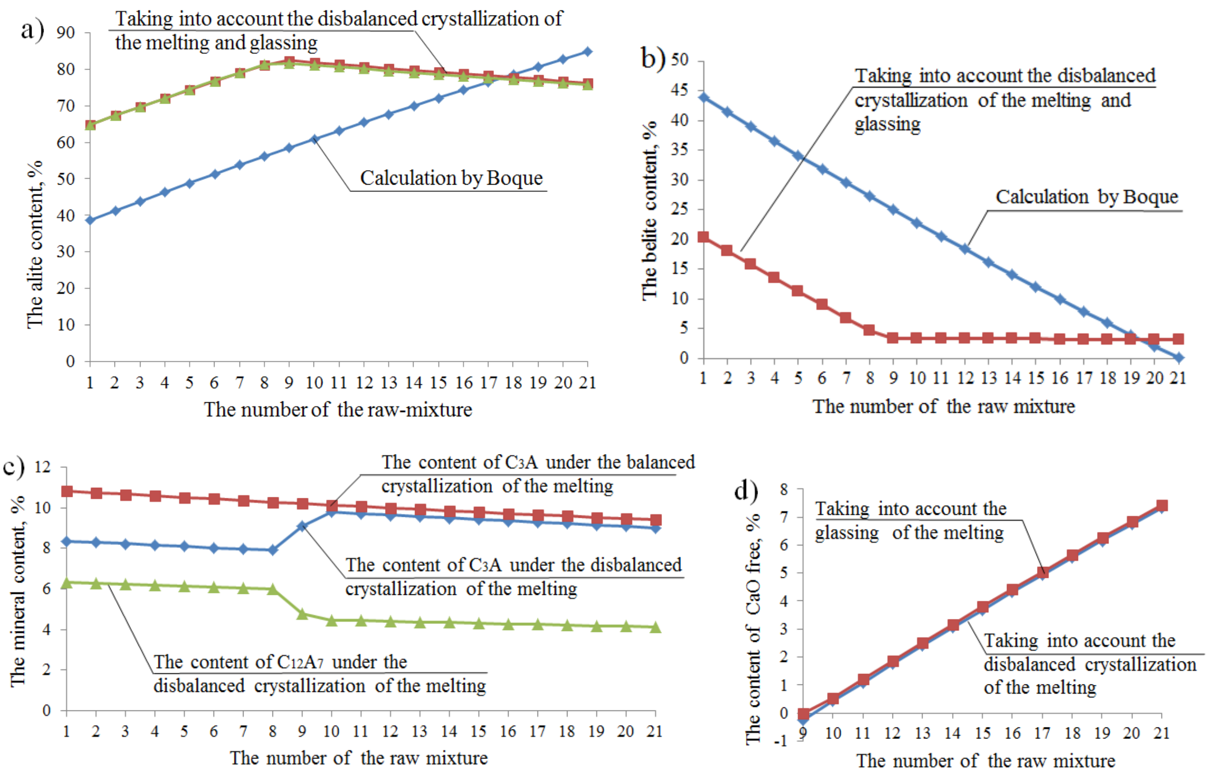

Figure 2. Calculated content in melted cement clinker: a) alite; b) belite; c) $3CaO{\cdot}Al_2O_3$ and $12CaO{\cdot}7Al_2O_3$; d) free calcium oxide (CaO_{fr}).

It was found that the mineralogical composition of the melted clinker #9 is presented by the alite phases in the amount 78.7 %; belite – 4 %; $3CaO{\cdot}Al_2O_3$ – 9.8 %; $12CaO{\cdot}7Al_2O_3$ – 2.9 %; CaO_{fr} – 1 %, which is declined from the calculated value (0.69–3.73 %). While the difference between the actual values of the mineralogical compositions and the received data (calculation by Boque) is 0.42–20.99 %. This may testify the significance of the calculation performed taking into account the disbalanced crystallization of the melting and glassing. The morphology of the clinker minerals formed under conditions of the low-temperature plasma is interesting. The instaneous reactions of clinker formation together with the high temperature gradient in cooling the melting may stipulate the synthesis of the fine-disperse matrix sample model [8] which is monadoblastic one. The structure of the melted clinker (figure 3) is presented by the metastable minerals of alite in the lamellar form with the dimensions up to (3–20)×(80–400) μm and the ratio of their length to width 26.6–133. The elongated crystal form may stipulate the higher cement activity based on the melted clinkers because the more rapid developing sides (in the crystal growth process) are less stable in hydration. The most minerals are fine-dispersive ones: up to 85 % of alite may have the width less than 4 mcm and up to 65 % of belite may have the identical dimensions (figure 4). Along with this, some structure elements of the given compound are more deformed relatively to C_3S (figure 5): alite has the formulae $54CaO{\cdot}16SiO_2{\cdot}Al_2O_3{\cdot}MgO$ and it is formed in substation of two ions Si^{4+} for two ions Al^{3+} and introduction of Mg^{2+} into interknitting of the lattice. This may increase in the hydraulic activity of the viscous substance received based on the melted clinker [9, 10]. The intensive heat release which exceeds the traditional one by 1.3–4.5 times in the process of cement hydration with the synthesis based on plasma-chemical technology is observed.

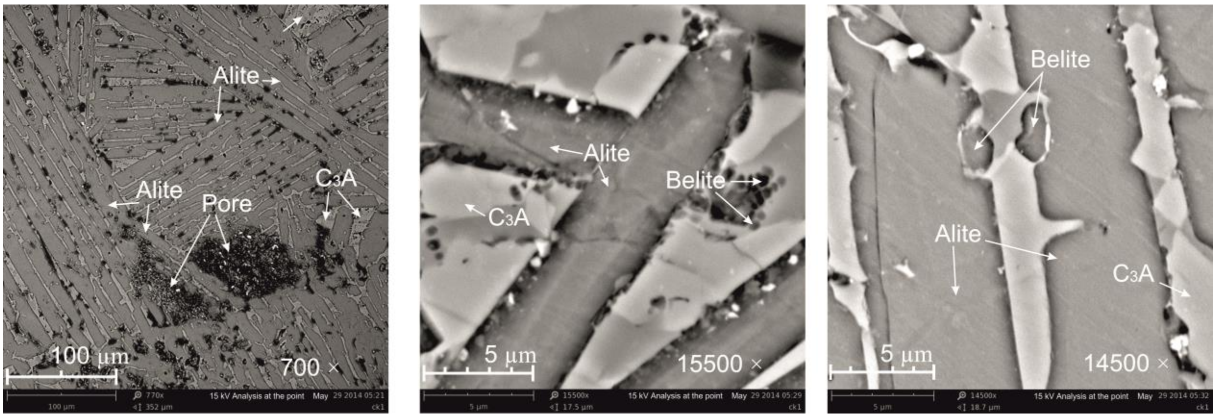

Figure 3.Microstructure of cement clinkers synthezed under conditions of low-temperature plasma based on the mixture #9.

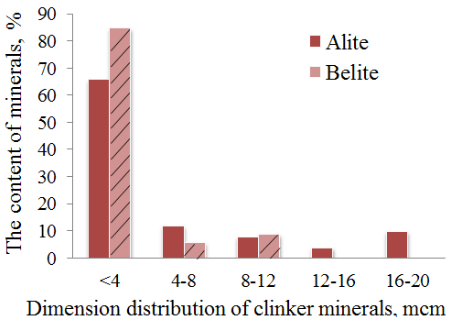

Figure 4. Dimension distribution of clinker minerals.

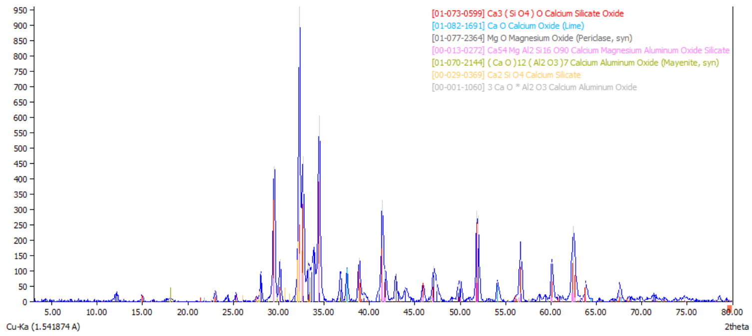

Figure 5. Diffractogram of cement clinker produced under conditions of low-temperature plasma based on the mixture #9.

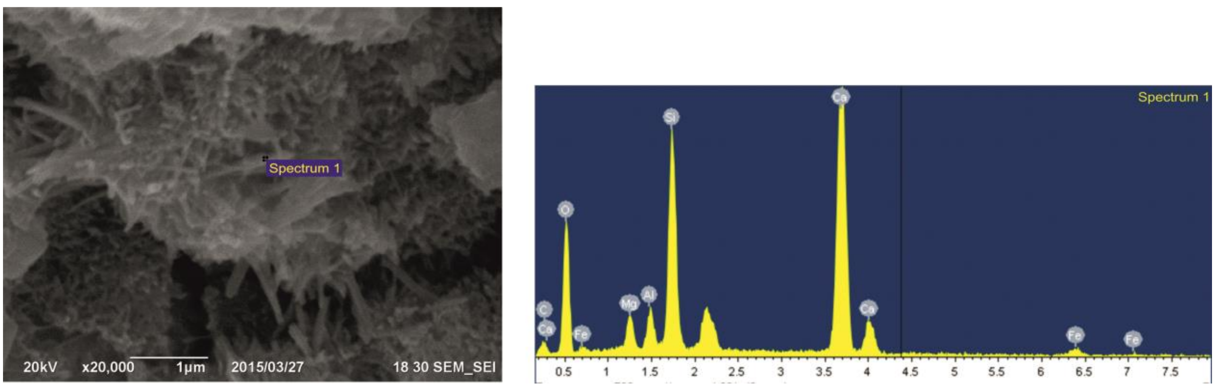

Figure 6. Scanning electronic microscopy and spectral analysis of cement stone in age of 7 days.

The cement gel, portlandite, and the additive nidi of the new-formation growth having the colomn-like habitus are clearly revealed in the structure of the cement stone produced based on the melted clinker. The presented hydrosilicates of calcium (figure 6) are non-traditional ones for the cement systems. The appearance of the analogous compounds is realized in the introduction of nano-crystalic modificators. However, the absence of the additives in the system may testify the type influence of the viscous substance used – the melted cement clinker, in hydration of which the new formations are formed which may cover the available pores and microcracks. This allows to increase in the pressing strength of the samples up to 82.7–84.2 MPa.

5. Conclusions

The study results have shown that in disbalanced crystallization and glassing of the cement clinker synthesed under conditions of the low-temperature plasma (LTP) based on the raw-material mixtures using 79.1–82.9 % of the lime-stone from the quarry «Pereval» in the town of Slyudyanka and 17.1–20.9 % of the clay from the deposit «Maximovski», the sample synthesis which based on the mineral content of C_3S may be considered as the alite (#1–21) and the traditional (#1–9) clinkers based on the rock used, is possible. The composition #9 which is characterized by SC=0.88; n=3.34; p=2.52; and has no CaO_{fr} and represented as alite, the calculated amount of which is 82.43 %, is considered as the optimal composition. The actual mineralogical composition of the melted clinker of #9 is represented as the following compounds: $3CaO{\cdot}SiO_2$ in the amount 78.7 %; $2CaO{\cdot}SiO_2$ – 4 %; $3CaO{\cdot}Al_2O_3$ – 9.8 %; $12CaO{\cdot}7Al_2O_3$ –2.9 %; CaO_{fr} – 1%, these values decline from the calculated ones 0.69–3.73 %. This may confirm the significance of the calculations performed. The structure of the melted clinker is monadoblastic and represented as the metastable minerals of alite with the lamellar form and dimensions up to (3–20)×(80–400) μm and their ratio of length to width 26.6–133. Alite and belite in the amounts 85 and 65 %, relatively, may have the width less than 4 mcm. Hydration of the viscous materials shows the high intensity which is followed by the heat release which exceeds the traditional one by 1.3–4.5 times. The structure of the cement stone is represented by the portlandite, the tobermorito-like gel and the new formations having the colomn-like habitus, they are non-traditional for the cement systems. This allows to increase in the pressing strength of the samples up to 82.7–84.2 MPa.

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