

## Low Roasting Cementitious Matter of Lime-Belite Components Using Flotation Waste of Residual Dumps of Wet Magnetic Separation at the Mining and Processing Complex

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**Abstract:** Ferriferous mineralising and modifying components in the mixtures accelerate decarbonisation processes, promote the formation of double-calcium silicate  $\alpha'$ [alpha]- and  $\beta$ [beta] modifications. In this article, using the methods of physical and chemical analysis, the sequence of phase changes has been defined during roasting and structure formation  $2\text{CaO}\cdot\text{SiO}_2$ , which have been presented in the research results of the possibility of the use of waste of wet magnetic separation (WMS) for obtaining low roasting cementitious matter of lime-belite components. During roasting carbonate silicate mixtures with residual dump agents of wet magnetic separation (the hydraulic module  $m=2.22-1.43$ ) at the temperatures of  $1100-1200^\circ\text{C}$  the product is received as part of the CaO except the main minerals and double-calcium silicate which contain calcium ferrite. Thus the admixtures of the raw materials promote the formation of hydraulic active forms of orthosilicate calcium -  $\alpha'$ [alpha]- and  $\beta$ [beta]- $2\text{CaO}\cdot\text{SiO}_2$ . The activeness of the obtained cementitious matter mixture of quartz sand in the autoclave conditions has been investigated. The physicomechanical tests have shown, after 4 hours of solidification in the hydrothermal conditions, the durability of viscosity exceeded 40 MPa and the structural component was presented generally by the hydrosilicates of various layers in which there was hydroferrite calcium. The results of researches afforded the opportunity to estimate qualitatively the product of roasting white lime pigmentation components as the main component taking part in the processes of solidification of the cementitious matter mixtures.

**Key words:** Double-calcium silicate • Polymorphism • Hematite layer silicates • Mineral formation • Cementitious matter of lime-belite components • Modifications • The ferrous waste of mining processing • Tailings of wet magnetic separation • Roasting • hydrothermal conditions • Structure • Activeness • Phase structure • Hydro-silicates calcium • Core layer structure • Solidification • Hydration • Durability • Weather resistance

### INTRODUCTION

In some specific chemical and mineralogical structures, the grinded waste rocks, the obtained construction ballets and as well as the enriched waste wet magnetic separation of ferrous quartzites can be used in the production of various cementitious materials and products on their basis [1]. The production wastes of the public limited liability company (Plc) Mikhaylovsky and Lebedinsky of mining and processing integrated works (GOK) are represented by the residual dump agents

of wet magnetic separation (~39 %) practically not used, various rocky silicates (~38 %) and porous (~23 %) strips [2]. During the enrichment of the iron ore by the method of wet magnetic separation a large volume of waste materials formed are really now in dumpiness. As a result of the wet magnetic separation (WMS) of neon-oxidised ferrous quartzites, the magnetic concentrate and tailings of WMS are formed. For the purpose of obtaining low silicate magnetic concentration, the technology of enriched flotation of magnetitic fraction is used in the Mikhaylovsky mining and processing integrated works.

For the enrichment the residual dump agents of the WMS containing a significant amount of quartz and up to 37 % of hematite and the most effective way is the method of the reverse ion flotation, which in essence consists of adsorption of cationic surfactant species (CSS) and the introduction of depressors i.e. the organic colloids for the purpose of suppression the interaction of ore minerals (magnetite and hematite) with CSS in the course of flotation [3].

The purpose of the genuine work was to investigate possibility of using the wastes of iron ore of GOK for the production of lime-belite components (LBC) (for this reason the example of the waste of flotation of residual dump wet magnetic separation of Kursk magnetic anomaly (KMA) with contents  $\text{SiO}_2$  52.54;  $\text{Al}_2\text{O}_3$  0.27;  $\text{Fe}_2\text{O}_3$  42.12;  $\Sigma(\text{CaO}+\text{MgO})$  3.33;  $\text{FeO}$  3.55 has been taken and other oxides 3.68 %). The mineral structure of residual dumps of WMS are the following: quartz, carbonates, silicates (stratified, feldspar minerals), hematite, magnetite. The stocks of tailings wastes of WMS in the KMA account for hundreds of millions of tons that allow them to be considered as a powerful source of raw materials for the construction materials industry, including cementitious materials.

The structures of the lime-belite components based on the metallurgical slags are known[4], the elimination of g grinded metamorphic shale [5], being part of the main crystal phases i.e. double-calcium silicate and lime. The silicate calcium ( $\text{Ca}_2\text{SiO}_4$ ) is a complex polymorphism and in connection with this, the voluminous changes lead to self-destruction of the material. The Ortho-silicate of the calcium, numbering four to six polymorphic modifications [6, 7], according to various data include isolated silicate tetrahedrons [ $\text{SiO}_4$ ] connected by ions of  $\text{Ca}^{2+}$ . It is known that the hydraulic activeness under natural solidification conditions possess  $\beta$ [beta]- and  $\alpha'$ [alpha]- $2\text{CaO}\cdot\text{SiO}_2$ ;  $\gamma$ [gamma]-modifications of binding effect but solidification effect coming into contact with water at autoclave processing.

Technique. It is proposed that for obtaining the white lime pigmentation components on the basis of chalk and metallurgical slags with the modification of the component of the initial mixture with the purpose of increasing the iron oxide contents, the roasting temperature should be decreased and the intensification of process of synthesis to enter a waste of flotation of tails of wet magnetic separation mining and processing integrated works in the quantity providing primary formation of double-calcium silicate.

The mixtures, consisting grinded chalk of the Belgorod field, slag and flotation waste of residual dumps of WMS of GOK corresponded to different ratios (the hydraulic module of mixtures were to equal 2.22; 2.15; 1.63; 1.43), burning in the silicate furnace at the temperatures of 1000, 1100, 1200 °C. After passing through the indicated temperatures, the roasting product was exposed to drastic cooling and then later grinded until the remainder of 008 left on the sieve was not more than 15 %.

The phase structure of the roasting product was determined through the means of calculation by chemical and radiographic analyses. The roasting product according to calculation data should contain between 59.54 to 36.72 % of  $2\text{CaO}\cdot\text{SiO}_2$ , between 31.12 to 6.53 % of CaO in a free condition ( $\text{CaO}_{\text{remnants}}$ ), from 30.75 to 20.67 % of aluminates and calcium ferrite. Meanwhile the contents of  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  equal more than 10 %.

**Main Part:** According to the chemical analysis the free floating CaO in the roasting product of at temperature 1000°C contains: - 40.6...53.2 %, 1100°C - 34.4...45.3 %, 1200 °C - 25.0...37.2 % and while increase in the hydraulic module the free floating  $\text{CaO}_{\text{remnants}}$  increases, while with temperature increase it falls.

Verifying the results of the X-ray analysis (X-RA), it can be said unequivocally that they confirm the data of chemical method of researches. The distinct diffraction maximum of 0.2784; 0.241; 0.170 millimicron confirm the existence of free CaO and 0.2784; 0.2743; 0.217 millimicron -  $\alpha'$  [alpha]- and  $\beta$  [beta]- $2\text{CaO}\cdot\text{SiO}_2$ . A small hike to the level of 0.298; 0.296; 0.250; 0.2702; 0.244; 0.1945 millimicron indicates the presence of small amount of  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ,  $\text{CaO}\cdot\text{Fe}_2\text{O}_3$  and  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ . The content increase in the components of the initial mixture of waste of GOK (the hydraulic module decreases from 2.22 to 1.43) leads to the increase in the content of ferrite calcium and a large amount of crystals  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  and  $\text{CaO}\cdot\text{Fe}_2\text{O}_3$  have been observed in the phase structure.

Thus, ions of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in the raw mixtures promote not only to formation of ferrite calcium, but also stabilises hydraulic active forms of double-calcium silicate  $\alpha'$  [alpha]- and  $\beta$  [beta]- $2\text{CaO}\cdot\text{SiO}_2$ .

The fall in hydraulic module and temperature increase of roasting, the content of double-calcium silicate in the form of  $\alpha'$  [alpha]- and  $\beta$  [beta] modifications. The existence in the roasting products of

ferrite of calcium predetermines increase activity leading to solidification and durability growth in the hydrothermal conditions.

It has been established that the ferrous mineralisation and modification of components in mixtures accelerate decarbonisation processes, promote formation of double-calcium silicate of  $\alpha'$ [alpha]- and  $\beta$ [beta]-modifications [8]. Using the methods of physical and chemical analysis, the sequence of phase changes has been determined when roasting and forming the structure of  $2\text{CaO}\cdot\text{SiO}_2$ .

The CaO interaction with  $\text{Fe}_2\text{O}_3$ , formed as a result of decomposition of stratified silicates and the enrichment of tailings of wet magnetic separation containing in waste, begin at very low temperatures (250-425°C). With obvious speed and the creation of well identifiable new formation of materials, i.e. calcium ferrite, which form at 600-800°C. The preliminary formation being  $\text{CaO}\cdot\text{Fe}_2\text{O}_3$  and which begin to be formed at ~650°C, crystallising well at 850-1000°C and above the temperature 1000°C there is an increase of lime to  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ .

The exothermal effect (+) 450°C (Fig. 1, a) is caused by the  $\text{Fe}^{2+}$  oxidation into  $\text{Fe}^{3+}$ . In comparison with the decarbonisation of pure chalk proceeding at 950°C, in the chalk-biotite mixtures, the chalk-biotite-hematite decomposition of  $\text{CaCO}_3$  takes place between 700-900°C, on the curve of differential thermal analysis (DTA) (Fig. 1, b and c) endothermic effect (-) 925°C and (-) 915°C respectively. This proves the intensification impact on the process of decomposition of  $\text{CaCO}_3$  of both minerals.

Therefore, biotite, hematite minerals,  $\alpha'$ [alpha]- $\text{Fe}_2\text{O}_3$  accelerate the decarbonisation and mineral formation processes, strengthen the diffusive processes in the  $\text{CaO}\text{-SiO}_2$  system.

In this case, the synthesis of minerals limited by the diffusion of crystals of calcium oxide to  $\text{SiO}_2$  through the layers of new formations occurs under the conditions of solidified silicate. And it is possible that the formation of micro-melting where the processes proceed more intensively and which is proven by the calcium oxide reduction content in free condition at temperature increase and the duration of roasting mixtures (roasting duration in 60 minutes of free  $\text{CaO}_{\text{remnants}}$  in sinters decreases between 2.5-3%).

The data of the x-ray analysis received from the cementitious materials (Fig. 2) indicate the existence of significant amount of silicates and calcium oxide (diffraction maximum, 0.278; 0.275; 0.273; 0.262; 0.240 millimicron).

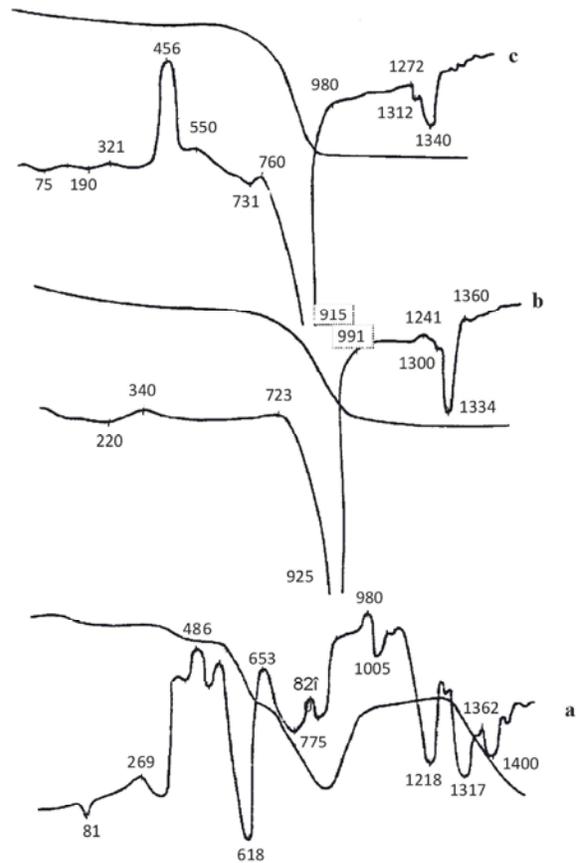


Fig. 1: Thermogramm of mixtures: a - chalk-hematite; b - chalk-biotite; c - chalk-biotite-hematite

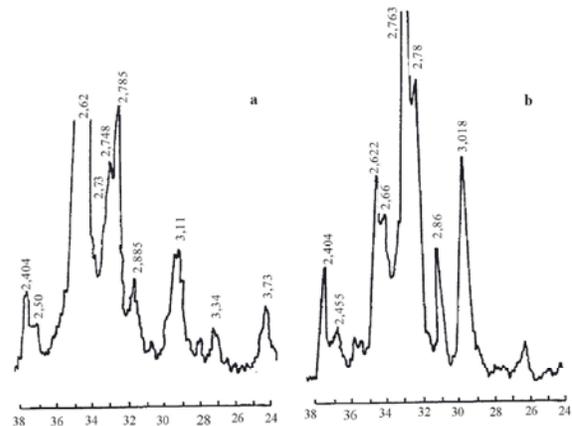


Fig. 2: X-rayograms of roasting product of  $m=2.22$ : a - 1100 °C; b- 1200 °C

These are prominent phases of roasting product. The definition of  $\alpha'$ [alpha]- and  $\beta$ [beta]- $\text{C}_2\text{S}$  on the x-rayograms is possible on the ratio of diffraction maximum of  $I_{2.40}/I_{2.86}$ . At the ratio of intensity of  $I_{2.40}/I_{2.86}$

Table 1: Properties white lime pigmentation components of hydrothermal solidification (according to mode 2-4-2)

Hydraulic module (m) cementitious matter of lime-belite components	Roasting temperature, °C	Humidity formation, %	Solidification during compression, Mpa	Contents Ca(OH) <sub>2remnants</sub> , %
2.22	1000	6.70	23.57	2.5
	1100	6.67	26.12	1.3
	1200	6.68	27.07	0.8
1.43	1000	6.69	28.45	0.5
	1100	6.69	36.62	0.5
	1200	6.70	41.72	0.2
2.11*	1000	6.50	22.40	5.9
	1100	6.71	23.75	3.8
	1200	6.68	24.04	1.6

\* cementitious matter without the use of waste of GOK

<0.95 in roasting product, the quantity of α'[alpha]-C<sub>2</sub>S has been identified. In this specific case of I<sub>2.40</sub>/I<sub>2.86</sub>=0.68-0.75 this is characteristic of α'[alpha]-C<sub>2</sub>S.

In the roasting product, a shift of strips of deformation fluctuations of the group [SiO<sub>4</sub>]<sup>4-</sup> to β[beta]-C<sub>2</sub>S from 470 to 510 cm<sup>-1</sup>, from 890 to 910 cm<sup>-1</sup> shows the structural defect and formation of some quantity of α'[alpha]-C<sub>2</sub>S. In the latter, there is a diffusive character and the widening field range of 800 to 1100 cm<sup>-1</sup> of α'[alpha]-C<sub>2</sub>S.

The tricalcium aluminate in the viscosity is absent; the aluminum phase has presented the C<sub>12</sub>A<sub>7</sub> (d: 0.489; 0.268 millimicron) and CA (d: 0.466; 0.298; 0.253; 0.250 millimicron).

With the hydraulic module decrease at the maximum temperature level, the disappearance of calcium oxide and the roasting product hydration of mineral portion equals to 40°C which corresponds to the content reduction of free calcium oxide of in cementitious matter. The temperature time increase to a maximum does not exceed 25 minutes.

Therefore for the acquisition of lime-belite components on the basis of metallurgical slag and waste of GOK, it is necessary to take raw mixtures of slag+chalk+waste flotation of tailings of the WMS whose ratio provides the m=2.22-1.43 value and at burning temperatures of 1000-1200 °C, which allow the acquisition of a product, whose main crystal phases are CaO<sub>remnants</sub>, α'[alpha]-, β[beta]-2CaO·SiO<sub>2</sub>, CaO·Fe<sub>2</sub>O<sub>3</sub> and 2CaO·Fe<sub>2</sub>O<sub>3</sub> [9]. Thus the acquisition of cementitious matter will lead to considerable fuel consumption decrease as the main energy expenses are used for the decarbonisation process. The raw mixtures contain only 50-70 % of carbonate components, mineral formation when roasting various modifications of 2CaO·SiO<sub>2</sub>, aluminates and calcium ferrite results from the solidification reactions which go with the heat emission.

The acquisition activeness of the roasting product under hydrothermal conditions, was estimated on the compression autoclave durability at the temperature of 175 °C and the pressure concentration with steam of 0.8 Mpa on the mode of 2-4-3 samples formed from the roasting product mixture and quartz sand. The cementitious matter of lime-belite components and quartz sand in the ratio of 1:1 subjected to combined grinding until the remainder of 008 on the sieve was no more than 15 %. Since the temperature of obtaining of white lime pigmentation components does not exceed 1200 °C, it is necessary to expect that in the roasting calcium oxide product of is in the micro crystallised condition capable of completely interaction with water in the formation of Ca(OH)<sub>2remnants</sub> within 25 minutes. The quantity of water for the dissolution was considered taking into account the content of Ca(OH)<sub>2remnants</sub> in the roasting product, water evaporation during the lime hydration and the necessary amount of moisture for the samples formation. After autoclave processing samples have been tested for durability during compression and the Ca(OH)<sub>2remnants</sub> was defined (Table 1).

Analysing the data provided in the tab. 1, it is observed that the more the viscosity, there is in the α'[alpha]- and β[beta]-modifications of CaO·SiO<sub>2</sub>, CaO·Fe<sub>2</sub>O<sub>3</sub> and 2CaO·Fe<sub>2</sub>O<sub>3</sub>, the higher the durability after 4 hours of hydrothermal solidification and so the activeness of the cementitious material.

According to the component of Ca(OH)<sub>2</sub> in free state, it is possible to conclude that: using the tailings of wet magnetic separation for the acquisition of lime-belite components, the calcium hydroxide in the conditions of hydrothermal solidification completely dissolves in the calcium hydro-silicates. A little increased amount of calcium hydroxide of the LBC m=2.22 and roasting temperature of 1100 °C which explains the insufficient time for sustenance of autoclave processing. It should

be noted that all samples passed the test of differential changes of volume at the hydrothermal solidification which proves the absence of huge coarse-crystalline calcium oxide (over burnt) in the roasting product.

According to the X-ray analysis (X-RA) during solidification of hydro-silicates of various originalities, for example low contents CSH(É) - 0.307; 0.280; 0.183NM which are predominant and the high contents  $\alpha'$ [alpha]-hydrate of  $C_2S$  with diffraction deviations of 0.422; 0.390; 0.287 millimicron provide durability and stability structures during atmospheric influences [10]. When using white lime pigmentation components, containing calcium ferrite and after autoclave solidification structure of the new formations of  $3CaO \cdot Fe_2O_3 \cdot 6H_2O$  whose presence also promotes the structural solidification have been found.

### CONCLUSION

Introduction of the flotation waste of tailings of wet magnetic separation of GOK containing to up ~ 40% of oxidised iron contained in the raw mixture for the acquisition cementitious matter of lime-belite components leads to the decrease in the roasting temperature, increase in the component of double-calcium silicate, aluminates and calcium ferrite, as well as the stabilisation of hydraulic active forms of  $\alpha'$ [alpha]- and  $\beta$ [beta]- $2CaO \cdot SiO_2$ . The obtained viscosity in the mixture with quartz sand in autoclave conditions acquires durability at compression to 42 MPa.

It is highly possible to use the flotation waste of tailings of wet magnetic separation as a component of the cementitious matter of lime-belite components hydrothermal solidifications.

### REFERENCE

1. Rakhimbaev, Sh. M., L.I. Yashurkaeva and V.I. Mospan, 2012. A waste of enrichment of the KMA iron ores - raw materials for production of cement: monograph. Belgorod: BGTU publishing house, pp: 161.
2. Gridchin, A.M., G.A. Lesovik, E.N. Avilova and E.S. Glagolev, 2009. Solution to the problem of utilisation of technogenic raw materials of KMA. Vestnik of Belgorod state technological university of V.G. Shukhov, 4: 7-11.
3. Dowling, E.C., I. Hebbard, T.S. Eisele and S.K. Kawatra, 2000. Processing of ore by reverse column flotation. Processing of the XXI International mineral processing congress, Rome, July 23-27, vol. B. Oral Session.
4. Kudayarova, N.P. and N.V. Tsypchenko, 2004. Viscosity on the basis of steel-smelting slags. News of Higher Education Institutions. Construction series, 5: 48-50.
5. C.C. SSSR No. 1655946. Bushueva N.P., Vorob'ev Kh.S., Sokolovskiy V.A., Kudayarova N.P., 1991. Viscosity of manufacturing products of autoclave solidification. Bulletin, 22: 7.
6. Gareev, R.R., A.S. Korolev, M. Kh. Shaimov and B. Ya. Trofimov, 2006. A composite refractory binder based on stabilised belite. Refractories and Industrial Ceramics, 47(6): 381-385.
7. Shmanina, E.A., 2011. Comparative characteristics of electronic structure of structural fragments of double-calcium silicate in various polymorphic modifications. Scientific search. Technical science: materials of the third scientific conference of graduate students and doctoral candidates. Chelyabinsk: Publishing centre JurGU, T.2, pp: 191-195.
8. Shapovalov, N.A., N.P. Bushueva and O.A. Panova, 2013. Influence of ferrous minerals in the process of formation of double-calcium silicate. Technical science - from the theory to practice: materials of XXI international correspondence scientific and practical conference. (on May 15, 2013). Novosibirsk: Prod. SibAK, pp: 146-152.
9. Shapovalov, N.A., N.P. Bushueva and O.A. Panova, 2013. White lime pigmentation components on the basis of waste of GOK. Basic researches, 8(6): 1372-1380.
10. Double, D.D., P.C. Hewlett, K.S.W. Sing and J.F. Raffle, 1983. New developments in the understanding of the chemistry of cement hydration. Phil. Trans. R. Soc. Lond. A., 24 September, 310(1511): 53-66.