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To cite this article: O A Miryuk 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **510** 012012

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The effect of waste on the formation of cement clinker

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Abstract. The article is devoted to the development of resource-saving technology of Portland cement clinker using man-made raw materials. Wastes of skarn-magnetite ores enrichment were used in the experiments. Influence of the man-made component on the processes of clinker formation and composition of clinker phases were studied. Differential thermal and X – ray phase analysis methods were used to study the processes of formation and composition of clinker. It was revealed that the polymineral composition of the waste determines the intensity of low-temperature reactions, the variety of intermediate compounds. The formation of belite proceeds in three stages based on the structures of natural silicates (andradite, grossular, pyroxenes, amphiboles, chlorites, scapolite, epidote and feldspars). The bulk of the belite is formed at a temperature of 1050 – 1150 °C, this contributes to the intensification of the final stage of the formation of alite. Low-base clinker synthesized using ore dressing waste contains active modifications of alite and belite. Low-base cements (KN = 0.77 – 0.87) are characterized by increased strength. Man-made component provision into the raw mix reduces fuel consumption by 7.4 – 21.6 kg / ton of clinker. The research results prove the effectiveness of the use of technogenic materials for the production of cement clinker.

1. Introduction

The state of cement production determines the level of modern construction. Efficient development of the industry is promoted by saving raw and energy resources. Depletion of natural resources predetermines a fundamental change in the resource base due to the development of technogenic sources [1 – 15]. New raw materials differ from traditional materials in mineral composition [2, 7 – 11, 16]. Influence of mineral composition of technogenic raw materials on the cement clinker synthesis is not fully realized. Scientific ideas about consistent patterns of minerals influence of new raw materials on physicochemical transformations during formation of clinker phases are important in order to improve the efficiency of technogenic materials use.

The purpose of the work is to study the effect of technogenic raw materials on formation of cement clinkers and their properties.

2. Materials and methods of research

When enriching skarn-magnetite ores, waste of dry magnetic separation (DMS) is released, which is being crushed stone with a grain size of up to 25 mm. DMS waste has a stable chemical composition, wt.%: SiO₂ 40 – 45; Al₂O₃ 10 – 12; Fe₂O₃ 15 – 17; CaO 12 – 13; MgO 5 – 6; S 2 – 3; R₂O 2 – 4; TiO₂ 0.50 – 0.53; P₂O₅ 0.25 – 0.30; MnO 0.35 – 0.40; V₂O₅ 0.04 – 0.06; Cl 0.09 – 0.12; Cu 0.04 – 0.05; Ni 0.007 – 0.008. The mineral base is formed by silicates, differing in genesis, composition, structure, physical properties, chemical activity and thermal stability, wt.%: pyroxenes (diopside) 20 – 25; epidote 10 – 13; feldspars 8 – 12; chlorites 7 – 10; scapolite 8 – 11; garnets (andradite, grossular) 7 – 12; amphiboles (actinolite) 7 – 14.



Waste also contains minerals, wt.%: calcite 4 – 7; pyrite 4 – 8; quartz 2 – 4; magnetite 3 – 4.

Pyrogenic transformations in a raw mixture were studied with the differential thermal analysis method, which was carried out on a derivatograph of the Q –1500 D of system F. Paulik, J. Paulik, L. Erdey. The phase composition of the raw mixture, burnt at temperatures of 500 – 1400°C, was determined using general purpose X – ray diffractometer, type DRON – 3M. The diffractometer is equipped with an BSV – 24 type X – ray tube with CuK α – radiation. The diffractograms were processed using difWin program. Strength properties were determined on samples with the size of 20x20x20 mm, made with dough of normal density.

3. Results and discussion

Influence of technogenic material on clinker formation processes was studied using the example of a raw material mixture of 70% limestone and 30% ore dressing waste.

3.1 The influence of technogenic material on clinker formation processes

Burning of the studied raw material mixture is accompanied by numerous transformations (figure 1). Low-temperature heat release (exothermic effect at 500°C) is associated with the oxidation of pyrite and magnetite. Exothermic oxidative processes intensify decarbonization reactions and the decay of unstable minerals. Interaction of components begins at low temperatures due to the Hedvall effect during the period of structural transformations of minerals. Low-temperature melting of the technogenic component until appearance of a clinker melt ensures formation of a low-viscosity liquid phase and contributes to the activation of phase transformations.

The difference in crystalline structures of natural silicates and intermediate silica-containing phases predetermined the multi-stage bleaching with the predominant formation of C₂S in the high-temperature region. The number of stages corresponds to the number of exothermic effects on the thermogram (figure 1).



Figure 1. Thermogram of the raw material mixture «limestone – ore dressing waste».

In the solid-phase region (temperature 850 – 1050°C), dicalcium silicate is formed with the participation of the source minerals as a result of the introduction of excess amounts of calcium oxide into structure of garnets, scapolite [17].

At the next stage (temperature 1050 – 1150°C), it is formed by decomposition of intermediate phases and minerals of the technogenic component. The activity of belite formation in this temperature range is due to appearance of a sufficient amount of melt with a low viscosity.

The third stage (temperature 1150 – 1250°C) is characterized by formation of a belite based on aluminum silicates of calcium and sodium; magnesium silicates of calcium and aluminum, which were

formed on the basis of natural silicates.

The main mass of the belite in the mixture under study is formed in the last two stages. The shift of the whitening reactions to the high-temperature region provides an increase in the heat stress during sintering the mixture. This creates prerequisites for the active formation of clinker phases and improvement of the crystal structure of clinker.

The presence on the thermogram of a double maximum at temperatures of 1250 and 1310°C is caused by a change in the rate of formation of alite. Alite formation, initially suppressed by influence of alkalis and sulphates, is accelerated when the melt is enriched with magnesium oxide and intensified due to high-temperature belite formation and dopants [16].

Increased temperature of belite formation, presence of dopants in mixtures with waste ensure the activity of low-base clinkers ($KN = 0.73 - 0.83$) [17 – 20]. Formation of belite at elevated temperatures prevents passivation of C_2S , increases doping of the phases of clinker. In clinker, from a technogenic raw material the phases inherit the features of the crystalline structures of natural minerals, which are characterized by close contact of various elements.

X – ray phase analysis of low-base clinkers determined modification of silicate clinker phases (figure 2).

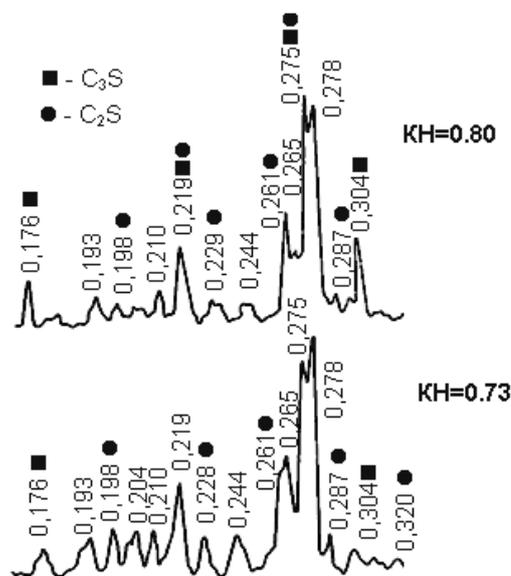


Figure 2. X – rays of clinkers on the basis of ore dressing waste.

Dicalcium silicate is represented by β -modification ($d = 0.287; 0.278; 0.219$ nm), which is stabilized by an increased concentration of SO_3 in the clinker. Presence on the radiograph $d = 0.320; 0.278; 0.275$ nm indicates the presence in the clinker of α' – C_2S , stabilized with magnesium oxide, manganese impurities. According to configuration of the maximum $d = 0.176$ nm, modification of the alite was determined: rhombohedral C_3S ($KN = 0.80$) and monoclinic C_3S ($KN = 0.73$).

3.2 Influence of technogenic material on fuel consumption during clinker burning

To determine the effect of technogenic material on properties of cements, clinkers were synthesized on the basis of raw mixtures with different content of DMS waste. In mixtures of the G series, waste functions as an iron-containing and aluminosilicate component. Mixes of the F series were obtained by replacing DMS in the control S series of the glandular component only (table 1). The resulting cements are characterized by high strength properties. Low-base cements ($KN = 0.77 - 0.87$) are characterized by increased hydraulic activity.

Efficiency of introduction of the technogenic component is determined from theoretical heat consumption for physicochemical transformations in the raw mix. The thermal effect of clinker formation was calculated as an algebraic sum of the heat of endothermic processes (decarbonization of

limestone, dissociation of minerals, formation of a liquid phase) and exothermic reactions (pyrite oxidation, formation of clinker phases).

Table 1. Cement strength characteristics.

Cement series	KN	Modules		Strength at compression, MPa, at age, days		
		<i>n</i>	<i>p</i>	2	7	28
G – 1	0.95		0.9	95	103	125
G – 2	0.87		0.9	83	90	110
G – 3	0.77		0.9	50	70	105
F – 1	0.95		1.2	101	108	118
F – 2	0.87	2.5	1.2	81	95	110
F – 3	0.77		1.2	54	73	100
S – 1	0.95		1.2	78	85	110
S – 2	0.87		1.2	77	82	110
S – 3	0.77		1.2	48	60	95
Control cement M550				90	108	120

Presence of calcium and magnesium silicates in waste contributes to a reduction by 4 – 11% of the thermal costs of decarbonization in mixtures with the same KN value. Saving heat on dissociation of carbonates is also achieved by KN changing from 0.95 to 0.77; for mixtures of the G, F, and S series, the savings are 165, 151 and 116 kJ/kg clinker, respectively. The theoretical heat consumption for the highly basic mixtures G – 1 and F – 1 is less than for the mixture of low basicity S – 3 from traditional raw materials (figure 3).

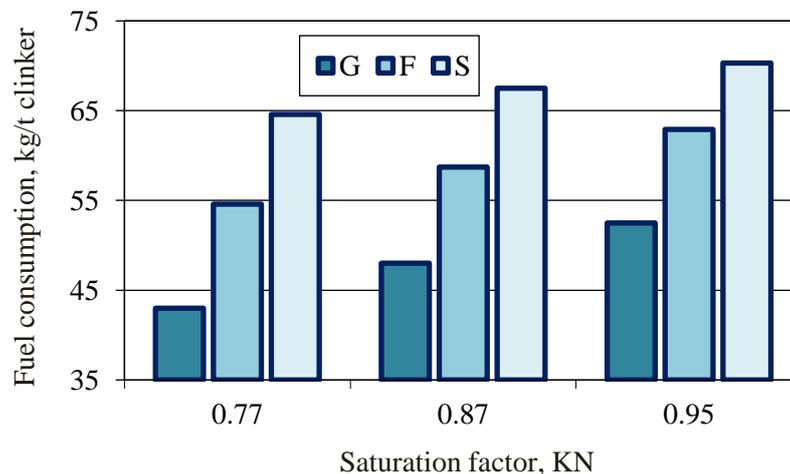


Figure 3. Specific fuel consumption for clinker formation when burning raw mixes with different content of waste DMS.

As clay is removed from the raw material mixture, thermal costs of dehydrating minerals are reduced, and the savings reach 47 – 150 kJ/kg clinker. A large part of heat consumption in the raw material mixtures with waste compensates heat released during the oxidation of pyrite. Energy benefit from presence of pyrite in the mixtures with DMS waste is comparable to or exceeds that from a decrease in KN for mixtures of compositions S – 1 and S – 3. The efficiency of mixtures with waste illustrates change in specific fuel consumption for clinker formation (figure 3). With introduction of the raw

material mixture of technogenic component fuel economy is 7.4 – 21.6 kg/t clinker.

4. Conclusions

The use of ore dressing wastes to produce cement clinker minimizes natural materials content in the raw mix. With participation of the technogenic component, clinker formation is of a stepped nature, characterized by activity of low-temperature interactions, complex transformations of minerals, and a variety of intermediate phases.

Polymineral composition of ore dressing waste contributes to the formation of low-power clinker with high hydraulic activity. Reducing carbonate and fuel consumption will decrease harmful effects of production emissions.

Therefore, production of cement clinker using technogenic raw materials is technically feasible, cost-effective and environmentally preferable.

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