Thermal transformations in polymineral technogenic cement raw

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Abstract. The results of physicochemical studies of composition and thermal transformations of large-tonnage wastes of skarn-magnetite ore dressing in Kazakhstan are presented. To determine materials’ composition of the following methods were used: X-ray, differential and thermal, Mössbauer and infrared spectroscopy. The stepwise nature of transformation of anthropogenic material during firing, due to polymineral composition of ore dressing wastes is revealed. Provides information on the chemical and mineral composition, thermal transformations of ore dressing wastes. It has been established that the chemical-mineral characteristics of natural silicates determine formation processes and properties of clinker phases. The features of the formation of clinker phases with the participation of the technogenic component of the raw mix, which consist in the activity of low-temperature interactions, the variety of intermediate phases are revealed. It has been established that the staging of belite formation with the participation of actinolite, albite, andradite, grossular, diopside, chlorite, epidote is due to gradual transformations of minerals into intermediate phases $C_2AS$, $C_3MS_2$, of which $C_2S$ is formed at temperatures of 1000 – 1300°C. Alite formation is intensified due to high-temperature belite formation and doping impurities. Skarn-magnetite ores wastes are an effective cement raw material, providing high-quality portland cement clinker using low-energy and resource-saving technology.

1. Introduction

Intensive development of metallurgy is accompanied by an increase in production and processing of natural raw materials. During extraction and processing of most minerals, 50 – 90% of mineral raw materials are sent to dumps. On the other hand, mineral and raw material base of the construction industry is depleted, which often leads to excessive consumption of fuel and energy, and a decrease in quality of finished products. Reducing reserves of natural raw materials for building materials requires search for its substitutes. Features of building materials technology provide the opportunity for wide involvement in production of waste from various industries.

A large consumer of industrial raw materials is the cement industry. Resource conservation is ends and means of cement technology improving. The further development of the industry is facilitated by saving of material, fuel and energy resources. Depletion of natural reserves determines a fundamental change in the raw material base due to the development of technogenic sources. Logical continuation of the development of recent decades to replace scarce raw materials with waste is optimization of technological solutions with the rational use of technogenic materials [1 – 20]. Experience of a number of industry enterprises indicates that the use of waste is associated not only with expansion of raw material base, but with an increase in technological processes efficiency.
Waste management efficiency is often low due to the lack of an integrated approach to assessment of technogenic sources. Selection of new raw materials is often limited to replacing the scarce traditional component with waste that is similar in composition and condition. For example, the valuable properties of large-capacity man-made materials of complex chemical and mineral composition remain unclaimed. Strict regulation of dispersion of new raw materials virtually eliminates the use of coarse reactive materials. Wastes of enrichment plants vary significantly depending on the type of a deposit, methods of raw materials processing and require individual research [7, 9, 16, 17].

The world's largest deposits of skarn-magnetite ores are located in Kazakhstan. At the first stage of skarn-magnetite ores dressing, more than 4 million tons of tailings of dry magnetic separation (DMS) are formed annually. Information on the use of crushed-stone tailings of DMS ores of various deposits in cement production is scarce.

To justify the possibility of using skarn-magnetite ore dressing waste in cement clinker production, it is necessary to understand thermal transformations of minerals, the nature of technogenic component mixture influence on clinker phases formation.

A comprehensive study of technogenic material was the objective of this work.

2. Object and research methods

Dry magnetic separation waste is a disintegrated mass (particle size up to 25 mm) with low humidity (1 – 2%), exceeding cement clinker and quartz sand in grinding ability. Therefore, the introduction of a technogenic component will not complicate the grinding of the raw material charge.

Low values of the specific effective activity of radio nuclides (53 – 55 Bq kg\(^{-1}\)) indicate radiation and environmental safety of ore dressing wastes.

Mineral base of DMS tails is composed of silicates that differ 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; grenades (andradite, grossular) 7 – 12; amphiboles (actinolite) 7 – 14 (figure 1). In the waste is present, wt. %: calcite 4 – 7; pyrite 4 – 8; quartz 2 – 4; magnetite 3 – 4.

![XRD pattern of dry magnetic separation waste](image)

**Figure 1.** XRD pattern of dry magnetic separation waste.
Chemical composition of dry magnetic separation tailings is presented, wt. %: SiO$_2$ 40 – 45; Al$_2$O$_3$ 10 – 12; Fe$_2$O$_3$ 16 – 18; FeO 6 – 8; CaO 12 – 13; MgO 5 – 6; in the order 3 – 6. A number of catalytic and modifying elements, wt. %: S 2 – 5; R$_2$O 2 – 4; TiO$_2$ 0.50 – 0.53; P$_2$O$_5$ 0.25 – 0.30; MnO 0.35 – 0.40; V$_2$O$_5$ 0.04 – 0.06; Cl 0.09 – 0.12; Cu 0.04 – 0.05; Ni 0.007 – 0.008.

Presence of clinker-forming oxides, an increased concentration of alloying and modifying impurities of sulfur, alkalis, magnesium, titanium, phosphorus, manganese, chlorine, copper, vanadium, and nickel are capable of ensuring the efficient use of waste in the composition of cement raw material mixture. The silicate base of a technogenic material, presence of non-carbonate calcium oxide determines material and energy advantages of raw mixtures with a technogenic component.

Materials were calcined in a laboratory furnace with silicon heaters. Exposure at maximum temperature is 15 min. Mineral composition of a technogenic material and firing products were identified by X-ray diffraction, differential thermal microscopic methods, as well as by infrared spectroscopy.

The Mössbauer method was used to determine the composition of iron-containing compounds. X-ray phase analysis was carried out on a DRON-3 general-purpose X-ray diffractometer with a copper cathode and a nickel filter according to the powder method in the double-angle range 2$\theta$ = 4 – 65$^\circ$. Thermo chemical processes were studied by the differential-thermal analysis method, which was performed on a “MOM” derivatograph by F. Pauilik, I. Pauilik and L. Erdey. Infrared absorption spectra were recorded on “Specord – 75JR" automated spectrometer. To determine a degree of oxidation, a coordination number of iron atoms and phase composition of iron-containing minerals, the nuclear gamma resonance spectroscopy method (Mössbauer) was used. The studies were carried out on “YaGRS – 4M” spectrometer in the speed range up to 10 mm s$^{-1}$ with Co$^{57}$ source in a Cr matrix.

3. Results and discussion

3.1 Thermal transformations of ore dressing wastes

Investigations of transformations during the firing of wastes from skarn-magnetite ore dressing in the temperature range of cement clinker formation were made. Variegated chemical and mineral composition of skarn-magnetite ore dressing waste led to the multi-step nature of thermal transformations (figure 2).

Firing of DMS tailings is accompanied by complex transformations and interactions of separate minerals (figure 3). Low-temperature transformations (exothermal effects at 300 – 600$^\circ$C) are associated with magnetite and pyrite oxidation. Decomposition of pyrite seems to be multi-stage [14]. A noticeable removal of sulfur from pyrite occurs at a temperature of about 500$^\circ$C, then the reactions begin:

\[ S_2 + 2O_2 \rightarrow 2SO_2 \]  
\[ FeS + 1,5O_2 \rightarrow FeO + SO_2 \]

The general scheme of pyrite oxidation has the form:

\[ 4FeS_2 + 11O_2 \rightarrow 2F_2O_3 + 8SO_2 \]  

Under the catalytic effect of iron oxides at temperatures up to 600$^\circ$C, SO$_2$ is oxidized into SO$_3$. Intensity of thermal effects at 300 – 600$^\circ$C indicates a significant heat release during oxidative processes. Calculations showed that the amount of released heat is 831 kJ mol$^{-1}$ of FeS$_2$ according to the reaction (3); 147 kJ mol$^{-1}$ FeO due to its transition into Fe$_2$O$_3$ and 98 kJ mol$^{-1}$ of SO$_2$ during the
formation of SO\textsubscript{3}. Ambiguous nature of the change in the test sample mass upon heating (figure 2) confirms oxidation of magnetite (increase in mass at 300 – 400°C) and decomposition of pyrite, accompanied by partial removal of gaseous products (decrease in weight at 400 – 500°C).

When DMS tailings are heated up to 580°C, mass growth is observed due to oxidation of residual Fe\textsubscript{3}O\textsubscript{4} and FeO released in the reaction (2). Presence of pyrite accelerates thermal processes: under the catalytic influence of FeO, calcite decarbonization is intensified. Released CaO interacts with SO\textsubscript{2} and SO\textsubscript{3} to form CaSO\textsubscript{4}. Firing of DMS tailings at temperatures above 800°C is accompanied by decomposition of CaSO\textsubscript{4} anhydrite and a decrease in concentration of sulfur-containing compounds. In the temperature range of 600 – 800°C, amphiboles, epidote dehydration, removal of bound water from talc-like layers of chlorites occurs [7]. This is confirmed by intense loss of material mass (figure 2). Significant changes are observed when the temperature rises up to 1000°C: minerals of a late geological period (scapolite, epidote, chlorites) are absent; amphibole content decreases (figure 3). Disappearance of aluminosilicate reflections on the DMS tailings X-ray under a simultaneous increase in the intensity of pyroxenes maxima, garnets and feldspars indicates a close interconnection of processes. Epidote decomposes with the formation of anorthite, garnets; amphiboles when heated pass into pyroxenes. A decrease in the content of calcium sulfate and quartz indicates participation of the latter in these transformations. An additional amount of pyroxenes (diopside) is formed by interaction of the decomposition products of chlorite with calcium oxide. Melting of DMS tailings takes place stepwise (figure 2): at first, the crystal structure of garnets and feldspars is destroyed (end effect at 1140°C). When heated to a temperature of 1200°C, the content of pyroxenes decreases. It is known [15], that the initial temperature of melting of clays – traditional cement raw materials varies in the range of 1135 – 1300°C, and the end of melting occurs at temperatures of 1400 – 1500°C. DMS tailings are completely melted at a temperature of 200 – 300°C lower than clay.

The heat treatment of DMS tailings is accompanied by structural changes in silicates (figure 4). After firing at a temperature of 800°C, layered minerals (950 cm\textsuperscript{-1}) are not diagnosed. An absorption band of 1050 cm\textsuperscript{-1} indicates the presence of garnets, and its decrease confirms the destruction of minerals at temperatures above 1000°C. The spectra of wastes calcined at temperatures of 800 – 1000°C are characterized by simultaneous amplification and expansion of the absorption region.
of 850 – 1000 cm\(^{-1}\). This indicates an increase in the proportion of chain and frame structures. Heating of DMS tailings to a temperature of 1200°C is accompanied by strong amorphization and disordering of silicon-oxygen tetrahedra: absorption intensity of the band of 850 – 1050 cm\(^{-1}\) decreases. Consequently, pyrogenic changes in the constituent tailings of DMS mirror the formation of minerals. First of all, late formations are destroyed, their transformation into primary minerals is observed. Composition of new formations during firing of DMS tailings is not limited to the listed compounds. However, a very complex nature of pyrogenic transformations complicates their detailing.

Iron is concentrated in ore minerals (33 – 35%), sulfides (18 – 22%), silicates (45 – 47%). Among iron-containing silicates the following dominate; they are andradite, actinolite, epidote, and chlorite. Isomorphic substitutions in minerals determine the presence of iron ions in diopside, grossular. The nuclear-gamma-resonance spectrum of the initial DMS tailings (figure 5) can be interpreted as overlapping lines characterizing iron ions in various oxidized and coordination states [18].

![Figure 4. Infrared spectra of dry magnetic separation waste.](image1)

![Figure 5. Mössbauer spectra of dry magnetic separation waste.](image2)

Multivalent iron ions are predominantly represented by octahedral coordination. Oxidation of pyrite and magnetite upon heating the DMS tailings to a temperature of 800°C is marked by appearance of on the spectrum of hematite sextet. A subsequent increase in hematite content is associated with its release during the decomposition of silicates (andradite, actinolite). The nitrous form of iron oxide persists at elevated temperatures: at 1150°C, transformations in the tailings of DMS are accompanied by the formation of magnetite and an increase in the content of pyroxenes. As a result, the area of the central doublet grows, while the size of hematite sextet decreases, and magnetite lines appear. The advantage of octahedral coordination of iron ions when heating the DMS tailings is retained. This provides high mobility of the melt. In DMS tailings calcined at temperatures of 800, 1000 and 1150°C, the oxidation coefficient of \(\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})\) is 0.78; 0.85; 0.76; in initial – 0.48; this corresponds to the nature of transformations of iron-containing minerals during waste firing.

### 3.2 The formation of clinker phases with the participation of the wastes

The study of phase transformations during firing of mixtures of calcium carbonate with minerals predominant in the composition of skarn-magnetite wastes allows determining the influence of technogenic minerals on the main phases formation of the cement clinker (belle C\(_2\)S and alite C\(_3\)S). Activity of reactions depends on the composition and structure of natural minerals (table 1).
It has been established that the staging of belite formation with the participation of natural silicates is due to gradual minerals transformation into intermediate phases $C_2AS$, $C_3MS_2$, from which $C_S$ is formed.

Table 1. Influence of the structure of natural silicates on phase formation in mixtures of “calcium carbonate – mineral”.

| Minerals-silicates | Structural formulae of intermediate silicates | Temperature of cement clinker phase formation, °C |
|--------------------|---------------------------------------------|-----------------------------------------------|
| Grossular (insular) | $[\text{SiO}_4]^{4-}$                       | $\text{Ca} [\text{Al:Si:O}_8] – \text{frame}$ $\text{Ca}_2\text{Al}[\text{AlSiO}_7] – \text{ring}$ $950 – 1300$ $1300 – 1350$ |
| Andradite (insular) | $[\text{SiO}_4]^{4-}$                       | $\text{Ca}(\text{Al,Fe})[\text{AlSiO}_7] – \text{ring}$ $950 – 1300$ $1250 – 1350$ |
| Epidot (insular)    | $[\text{SiO}_4]^{4-} \times [\text{Si:O}_3]^{5-}$ | $\text{Ca}(\text{Al,Fe})[\text{AlSiO}_7] – \text{ring}$ $950 – 1300$ $1250 – 1350$ |
| Diopside (chained)  | $[\text{SiO}_4]^{4-}$                       | $\text{Ca}:\text{Mg}[\text{Si:O}_3] – \text{ring}$ $1000 – 1300$ $1350 – 1400$ |
| Actinolite (belt)   | $[\text{SiO}_4]^{5-}$                       | $\text{Ca}:\text{Mg}[\text{SiO}_4] – \text{insular}$ $1000 – 1300$ $1350 – 1400$ |
| Chlorite (layered)  | $[\text{AlSi}_3\text{O}_8]^{5-}$            | $\text{Ca}:\text{Al}[\text{AlSiO}_7] – \text{ring}$ $1000 – 1300$ $1250 – 1400$ |
| Albite (frame)      | $[\text{AlSi}_3\text{O}_8]^{5-}$            | $\text{Na}[\text{Al:Si:O}_8] – \text{frame}$ $1100 – 1300$ Not revealed |
| Scapolite (frame)   | $[\text{Al}_{1+X}\text{Si}_{2-X}\text{O}_8]^{5-}$ | $\text{Na}[\text{Al:Si:O}_8] – \text{frame}$ $950 – 1300$ $1300 – 1350$ |

The temperature of the onset of belite formation is determined by transformation complexity of silica oxygen motifs of skarn minerals into an orthosilicate structure and rises in the series: isular $\rightarrow$ chain $\rightarrow$ layered $\rightarrow$ frame. The rate of belite formation depends on the stability of intermediate silicate phases. Formation of the highly basic $C_S$ phase occurs in a very narrow range, often bordering the melting point (fracture) of minerals structure or intermediate phases formed from them.

The regularities of individual minerals influence are revealed in synthesis of the clinker based on skarn-magnetite ore dressing waste during the firing of the raw mixture “limestone – DMS tailings” containing 35% of a technogenic component. Exothermic oxidative processes intensify decarbonization reactions and decomposition of unstable minerals (figure 6).

Figure 6. Thermograms of the raw material mixtures.
Interactions of components begin at low temperatures due to the Hadwall effect during the period of structural transformations of minerals. Low-temperature melting of the technogenic component until a clinker molten appearing ensures formation of a liquid low-viscosity phase and promotes the activation of phase transformations. Difference in crystalline structures of natural silicates and intermediate silica-containing phases predetermined the staging of belite formation with the predominant formation of C$_2$S in the high-temperature region (1050 – 1250°C). Formation of alite is accelerated during the melt enrichment with magnesium oxide and is intensified due to high-temperature whitening and alloying impurities.

The increased temperature of belite formation, deformation of the crystal lattice, and doping of clinker phases provide increased hydration activity of clinkers with a limited content of the high-temperature phase C$_2$S. This allow to synthesize low-energy clinker.

4. Conclusions
Stepwise nature of thermal transformations of poly-mineral wastes from skarn-magnetite ore dressing waste, accompanied by interactions of minerals with the formation of numerous intermediate compounds is established.

Regularities of technogenic minerals influence on the formation of clinker phases were revealed. Relationship of clinker formation with the crystalline structure of minerals is noted. It is shown that due to the clinker phases inheriting the crystalline structures of natural minerals, close contact of the main and isomorphic elements, dicalcium silicate (belite) of increased reactivity is formed.

Possibility of obtaining cement clinker based on skarn-magnetite ore dressing waste is proved. Preference for the synthesis of active cement clinkers with a high content of belite, characterized by low energy intensity is substantiated.

The need for a comprehensive study of technogenic raw materials is shown. An integrated approach to the study of technogenic raw materials made it possible not only to substantiate the possibility and expediency of using skarn-magnetite ore dressing wastes in cement production, but also to determine preference for the phase composition of cement clinker. The research results are the basis for development of low-energy cement clinkers with a high content of belite phase.

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