COMPLEX ESTIMATE OF COMPOSITION AND PROPERTIES OF CALLOVIAN CLAY MINERALS

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The prospects are considered for applying the clay rocks of Callovian overburden stratum of the Mikhailovsk iron ore deposit for pelletizing. It is established that mechanochemical activation of clays favors additional dispersion and increases the specific surface, as well as exchange capacity. This leads to improvement in technological properties of clays.

Clay minerals, Callovian, mechanical activation, pellets

When mining the mineral reserves, their complex processing and raising the degree of valuable component extraction with obtaining of additional kinds of production becomes one of the actual problems. The rocks of thick overburden stratum (sands, clays) are mined in the Mikhailovsk deposit. Sodium bentonites are the best binders, but they are considerably distant from the main regions of the iron-ore base of Russia and very expensive. The cheaper component ensuring the rational use of the whole mineral and raw material potential of the deposits is required to reduce the specific expenditures per unit of the finished product.

There are two ways for choosing the binder: the search for high-quality bentonites or their substitutes (clays, complex organic additives, peat, mineral astringents) with preliminary activation. For example, in the Poltavsk Mining and Metallurgical Integrated Works, an organomineral binder was approved [1], and in the Severny MMIW — a complex organic additive (activated peat) improving the granulometric composition of pellets with conservation or increase in their strength properties and reducing the gas consumption due to carbon combustion in peat. As a result of experiments, some enterprises determined the composition of binding additives for the conditioned pellets [2, 3].

The Callovian clays as the substitute for bentonite are the components of overburden stratum of the Mikhailovsk deposit. They are characterized by low turgescence, admixture of sand and limestone inclusions; however, these disadvantages are compensated by their low cost. To produce pellets, the clay is taken from the north-west section of the quarry. The raw material quality can be estimated by studying its chemical and mineral composition. The investigations were conducted on the basis of chemical, X-ray phase, spectral, thermal, and X-ray spectroscopic analyses, as well as the methods of electron microscopy.

Bulgarian and Greek bentonites representing plastic colloid clays with the basic component — montmorillonite — were chosen as the samples for comparison. They are formed as a result of aluminosilicate weathering in the acid medium. The alkaline bentonite clays are characterized by high content of montmorillonite (70%), turgescence (10–15 units), cation-exchange capacity (no less than 90), the Enslin number (200–600), and viscosity (30–50 sP), which makes it possible to obtain the pellets with high indices [4].


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The peculiarity of clay mineral structure and predominance of any component govern the distinctions in technological properties of this raw material. Many aluminosilicates differing in crystallochemical structure and physical properties relate to the montmorillonite-kaolin class. The distinction of montmorillonite from kaolin is that the Al(OH)$_3$ crystals are located between two layers of silicon oxygen tetrahedrons, one of the vertices of which is occupied by the oxygen ions, and the others — by the hydroxyl ions directed outside and retaining the water molecules.

The features of montmorillonite are the swelling in water and the capacity for cation exchange. The parameter $c$ of the crystal lattice varies from 9.6 to 28.4 Å depending on the quantity of water molecules in the mineral structure. There are 60–100 mg-equivalents of exchange cations (Ca$^{2+}$, Mg$^{2+}$, K$^+$, and Na$^+$) in 100 g of clay. After fine grinding, the exchange capacity of clays increases by a factor of 3, which supposes the cation arrangement on the surface and within the particles [5, 6].

The crystal structure of clay minerals changes, and their active surface grows in grinding [7]. This causes amorphization of quartz, which leads to retention of adsorbed water. After the complex activation, the swelling capacity of clays depends on the structural changes in these minerals.

The presence of montmorillonite and other turbogeneric minerals in the Callovian clays made it possible to realize activation successfully. Intensive dispersion of clays caused by additional grinding (especially with soda) increases their cation-exchange capacity and replaces a part of calcium ions by sodium ions. Therefore, it is possible to use bentonite-like clays including the minerals of the illite-smectite type. The X-ray diffractometer simulation showed that illite is close to muscovite and biotite with respect to the structure and composition. Illite has a lamellar shape. The thermal analysis indicates the presence of water in its structure, which is governed by surface hydration.

Clays also include chlorites — triocahedral minerals which also can be finely dispersed. The changes in the structure and composition of chlorites in glycerine, their partial dehydration during heating, and the increase in the interplanar spacing $d$ made it possible to distinguish the swelling chlorites [8]. High capacity of clays to be activated by soda is connected with the presence of exchange centers in their structure. Therefore, low-valence ionic bonds can be replaced by high-valence ones. The predominant negative charge of active centers favors the cation adsorption. Hence, apart from the exchange cation complex (Ca$^{2+}$ $\leftrightarrow$ 2Na$^+$), the surface adsorption of sodium ions from the water composition is also possible in finely ground high-activated clays. The hydrate shells, whose sizes determine the swelling capacity of clays, form around cations during moistening.

On the basis of investigations, it was revealed that the clays of the Mikhailovsk deposit include different types of silicates. The Callovian clays differ from bentonites by the higher content of iron, calcium, phosphorus, sulfur, and carbon dioxide (Table 1). The mineral composition is also variable: the clay fraction makes up 60.8% on the average with respect to the seam thickness; in the sections of qualitative finely dispersed clays, it is 70–80% (Table 2). From the comparison between the samples of the Callovian clays of the north-west section and bentonites and clays of other deposits, it follows that their basic component are the minerals of the illite-smectite type (Table 3).

Using the X-ray phase analysis, it is established that Callovian clays contain montmorillonite, quartz, hydromica, chlorite, calcite, and pyrite. The intensity of montmorillonite reflections (peaks 1–3) with the maximums 17.6; 8.8; and 5.86 Å increases when the sample is saturated with glycerine (Fig. 1a), and the intensity of hydromica (9.93), as well as chlorite reflections (13.81 Å) increases after preliminary calcination (Fig. 1b). From Fig. 1, it is evident that the amount of silicates of hydromica and chlorite types in clays is approximately 10–30%. Figure 2 shows the X-ray patterns of the investigated samples of clays and bentonites from different deposits.