Chemical and mineralogical properties research of clay from the Republic of Karakalpakstan - as raw materials for Portland cement production

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Abstract. In the Republic of Karakalpakstan, there are large reserves of unprocessed mineral building materials, which necessitate the development and targeted support of building materials manufacturing industries, which may become one of the engines of economic growth, further modernization, and diversification of the region's industry. This article examined the chemical and mineralogical composition of technological samples of the clay component of the North Jamansay deposit. The results of determining the mineralogical composition of the averaged technological sample of clay from the Dzhamansay deposit are in good agreement with the data of chemical analysis. The heating curve of the averaged clay sample of the Dzhamansaysky deposit is marked by fourteen endothermic effects. The total weight reduction in the temperature range (60–900) °C according to the thermogravimetric curve is 9.53%. On the DTA curves of the clay of the Dzhamansayskoye deposit, endo effects associated with absorbed and ciolet water were identified, as well as endo effects corresponding to the gradual removal of constitutional water from the clay component, accompanied by destruction of the crystal lattice. Electron microscopic analysis of clay showed that the presence of particles of various sizes having a surface with rhombohedral protrusions. This can be seen both on the chips and on the surface of the particles, where rhombohedral protrusions characteristic of quartz are reflected. The chemical composition of the technological sample of the clay component of the North Jamansay field in terms of the content of regulated oxides (SiO2 = 62.64; Al2O3 = 17.54; MgO = 2.00; SO3 = 1.21; TiO2 = 0.46; P2O5 = 0.25; R2O = 3.68)% meets the requirements of O'z DSt 2950: 2015 for the chemical composition of aluminosilicate (clay) raw materials used in the production of Portland cement clinker.

1. Introduction
The West Zhamansay site is located in the Karauzyak district of the Republic of Karakalpakstan, 7.3 km west of the North Jamansai clay deposit, and 3.1 km northeast of the cement plant under construction. The A-380 motorway runs 2.4 km southwest of the Western Zhamansay section [1].

The North Dzhamansaysky clay deposit is located on the territory of the Beruni district of the Republic of Karakalpakstan, 27 km east of the village of Karatau. The nearest villages are located along paved roads and a railway line laid practically on the border of the slopes and irrigated terraces of the Amudarya River. A large industrial village – Karatau – 27
km to the west, at the western foot of the ridge. Sultanuvays, Aktau village - 13km southwest. The substation village “81 km” is located 19 km to the south-west, the Beruni district center is 40 km to the south-east, and the city of Nukus is 110 km to the north-west.

The Karauzyak railway station of the Nukus-Turtkul-Uchkuduk railway line with a large tank farm on its territory is located 22 km west of the field. The distance from the Karauzyak station to Nukus is 90 km, to Uchkuduk – 340 km.

The productive stratum of the deposit is represented by clays of the Albian layer of the Lower Cretaceous, which are part of the cover of Cretaceous deposits, framing from the south a ledge of the Paleozoic rocks of the Sultanuways ridge.

The thickness is folded in two packs. The upper one consists mainly of clays of yellowish-brown and brownish-gray color with a greenish tint. In separate layers and lenses with a thickness of 1.4 to 10.0 m, clay is silty. The thickness of the upper member varies from 9.0 to 28.8 m, an average of 20.9 m. The lower member consists of argillite-like clays of dark gray and bluish-gray color, dense, massive. The thickness of the layer is from 16.0 to 30.0 m [2].

The mineral composition of clays is aggregates of montmorillonite – hydromica composition with an admixture of kaolinite and grains of quartz, feldspars, and pyrite.

According to the complexity of the geological structure, the Severo-Dzhamansayskoye clay deposit, according to the GKZ instruction, belongs to type I of group 2.

Clay reserves were calculated using the method of geological blocks on an area of 360 thousand m2 with a maximum depth of 53.5 m, in accordance with the following condition parameters (GKZ, protocol No. 2443-k of 11/21/1990):

The clay deposit is located in the Beruniy district of the Republic of Karakalpakstan, 27 km east of the village of Karatau, and 10.7 km. northeast of the cement plant.

Considering that at the cement plant, for the production of products, the company plans to receive 200.0 thousand tons of clinker per year, the annual supply of clay component (23% clay), it is planned to supply 46.0 thousand tons or 23 to the factory’s ex-warehouse, 0 thousand m3 in a dense body (bulk density - 2.0 t/m3).

With such productivity, the requested clay reserves will provide the cement plant with raw materials for 25 years [2].

2. Methods
Determination of the phase composition of the raw material by modern analysis methods, such as chemical, x-ray phase, differential thermal, petrographic, IR spectral.

Chemical analysis of raw materials was performed following the requirements of State Standard 5382-91 “Cements and materials of cement production. Chemical analysis methods” [3].

Assessment of the quality of raw materials for the production of clinkers was carried out following the requirements of State Standard (O’z DST 2950: 2015 “Raw materials for the production of Portland cement clinker. Technical conditions ”)[4].

The X-ray phase analysis method was used to study the structure, composition, properties of raw materials, and firing products. With its help, the mineralogical and phase compositions were studied [5]. The study was performed on a DRON-3 diffractograph with cobalt filtered radiation. Shooting mode: voltage 25kv, current 20 mA, cylindrical tubes – 1.0 mm (vertical), 2.0 mm (horizontal), receiving slots in front of the detector – 1.0 mm; anti-scatter 12 mm.

The speed of the detector is 2° / min, the speed of the chart tape is -600 mm/ h. The measurement range is 4x102imp.sec, slots: 1x2x1mm. The shooting was carried out in the range of angles (3-23)°.

Differential-thermal analysis of the samples was carried out using a F. Paulik and L. Erdey, I. Paulik system derivatograph with a speed of 10 deg/min and a sample (0.077-0.180) g at a sensitivity of $T - 900$, $TG - 200$ galvanometers. $DTA - 1/10$, $DTG - 1/10$ [6]. The study was conducted under atmospheric conditions. The holder was a platinum crucible with a diameter of 10 mm without a lid. $Al2O3$ was used as a reference.
The morphological surfaces of the samples, as well as the study of the microstructure, were performed using a SEM scanning electron microscope - EVO MA 10, and the elemental analysis of the samples was performed using an energy-dispersive elemental analyzer of the EDX (OxfordInstrument) brand - AztecEnergy Advanced X-act SDD.

Images of the samples were obtained at various scales, magnified 500, and 1000 times for each sample. Elemental analysis was performed at a magnification of 500 times (10 microns).

Infrared absorption spectra of the samples were taken on a SPECORD 75 JR spectrophotometer.

3. Results and discussion

Chemical (table 1.), X-ray phase (Fig. 1), thermogravimetric (Fig. 2), petrographic (Fig. 3), clay raw materials analyzes of the Northern Dzhamansay deposit were carried out [8, 9, 10, 11, 12, 13, 14, 15].

Table 1. The chemical composition of technological samples of clay Dzhamansaysky deposits, (in terms of 100%)

| №  | Name of samples                        | piercing products | SiO₂  | Al₂O₃  | Fe₂O₃  | CaO | MgO | SO₃  | R₂O  | P₂O₅ | TiO₂ |
|----|----------------------------------------|-------------------|-------|-------|--------|-----|-----|------|------|------|------|
| 1  | Tech sample No. 1                       |                   | 7.58  | 62.64 | 17.54  | 4.37| 0.27| 2.00 | 1.21 | 3.68 | 0.25 | 0.46 |
|    | (Clays of the Northern Jamansay deposit)|                   |       |       |        |     |     |      |      |      |      |      |
| 2  | Tech sample No. 2                       |                   | 7.90  | 61.91 | 20.50  | 4.05| 1.99| 2.03 | 1.62 | -    | -    | -    |
|    | (Clays of the Northern Jamansay deposit)|                   |       |       |        |     |     |      |      |      |      |      |

Figure 1. X-ray diffraction pattern of the averaged technological sample of the clay component of the Jamansay deposit, nm.
X-ray phase analysis (Figure 1.) established that the material composition of the averaged technological sample of the clay component of the North Jamansay deposit is represented by a natural aluminosilicate mixture characteristic of clay rocks: quartz with d/n = (0.422, 0.334, 0.244, 0.227, 0.222, 0.210) nm. Minerals of the hydromica group with d/n = (0.442, 0.331, 0.297, 0.255, 0.236, 0.222) nm. Minerals of the feldspar series with d/n = (0.384, 0.375, 0.363, 0.348, 0.317, 0.290, 0.251, 0.190) nm [5].

The results of determining the mineralogical composition of the averaged technological sample of clay from the Dzhamansay deposit are in good agreement with the data of chemical analysis.

![Figure 2. Heating curves of an averaged clay sample of the Dzhamansaysky deposit.](image)

The heating curve of the averaged clay sample of the Dzhamansaysky deposit is marked by fourteen endothermic effects at 92; 154; 175; 191; 220; 255; 300; 311; 432; 546; 736; 766; 852; 883°C. The total weight reduction in the temperature range (60–900) °C according to the thermogravimetric curve is 9.53%. On the DTA curves (Fig. 2.) of the clay of the Dzhamansaysky deposit, endo effects were detected at a temperature of 92; 154; 175; 191; 220; 255; 300°C with removal associated with absorbed and violet water, endo-effects at a temperature of 432; 546; 736; 766; 852 and 883°C correspond to the gradual removal of constitutional water from the clay component, accompanied by the destruction of the crystal lattice [6-7].
Element | Weight % | Sigma Weight %
--- | --- | ---
O | 53.63 | 0.24
Na | 0.87 | 0.06
Mg | 1.62 | 0.05
Al | 10.73 | 0.10
Si | 23.69 | 0.15
S | 0.37 | 0.04
K | 2.07 | 0.08
Ca | 1.49 | 0.07
Fe | 4.00 | 0.16
In | 1.52 | 0.18
Sum: | 100.00 |  

Electron microscopic images of the averaged clay sample of the Jamansay deposit, 50 nm.

Electron microscopic analysis (Fig. 3.) of an average clay sample was made from the surface of the samples. The microstructure of the samples was also studied using a SEM scanning electron microscope - EVO MA 10, and elemental analysis of the samples was performed using an Aztec Energy Advanced X-act SDD energy-dispersive elemental analyzer (EDX) (Oxford Instrument). Images of the samples were obtained at various scales, magnified 500, and 1000 times for each sample. Elemental analysis was performed at a magnification of 500 times (10 microns). [16 – 26].

Analysis of clay showed the presence of particles of various sizes with a surface with rhombohedral protrusions. This can be seen both on chips and on the surface of particles where rhombohedral protrusions characteristic of quartz are reflected [5].

4. Conclusions
The chemical composition of the technological sample of the clay component of the North Jamansay deposit in terms of the content of regulated oxides (SiO2 = 62.64, Al2O3 = 17.54, MgO = 2.00, SO3 = 1.21, TiO2 = 0.46, P2O5 = 0.25, R2O = 3.68)% meets the requirements of O’z DST 2950: 2015 for the chemical composition of aluminosilicate (clay) raw materials used in the production of Portland cement clinker [6].

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