Application of oil-containing gabbro-diabase waste sludge for ceramic products manufacturing

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Abstract. The paper presents research findings of the possibility of recycling and using the oil-containing sludge, generated at water-oil emulsions purification with gabbro-diabase powder, in ceramic constructional products manufacture. It is suggested to add the sludge to clay mass as a mineral and pore-forming admixture. The influence of the added sludge weight on such physical and mechanical parameters of ceramic samples as strength, compressive strength, water absorption, air shrinkage and firing shrinkage values and density was studied. The ceramic samples were prepared using natural clays from the Bessonovka (Belgorod region) and Podgornoye (Voronezh region) deposits. It has been demonstrated that adding the sludge to clay mass in amount of 2% wt. increases the compressive strength of samples by 90%, the air shrinkage by 1%, and water absorption by 1-2%. The firing shrinkage stays the same. At increasing the amount of the added sludge up to 7% all the parameters are slightly changed – water absorption and air shrinkage are increased, compressive strength, firing shrinkage and density are reduced. But further, at 7% sludge content in the clay mix the ceramic samples’ strength meets the grade not lower than 150 by GOST 530-2012.

In the purification process of multicomponent wastewaters, generated as a result of technological processes in chemical and petrochemical industry, multitudinous and large-tonnage settlings are formed, which pose a serious problem and require their isolation, recycling and neutralization.

These settlings often contain extremely toxic substances: heavy metals (copper, chromium, zinc, cadmium, nickel, lead etc.), phenols, herbicides, chemical pesticides, petroleum and the products of its processing etc.

The volume of the untreated settlings can reach tens of millions tons per year. In most cases they are dumped for permanent storage into waste ponds and not only occupy usable lands, but also pollute the environment.

Under the action of atmospheric precipitation, the toxic substances are partially dissolved and alleviated and penetrate into soil, surface and underground waters.

Due to the high ecological hazard of wastewater treatment settlings for the environment, the necessity of neutralizing such wastes is especially relevant.

The ways and methods of neutralizing and recycling wastewater treatment settlings depend on many factors and, first of all, on the content of toxic substances in them.
At the same time, the selected recycling methods should be reliable in terms of environmental safety, affordable and economically efficient.

One of such methods is using various settlings in building materials production [1-9].

Thus, in the work [4] a method of using sludge wastes (settlings) for vanadium pentoxide and ferrovanadium alloys sewage waters treatment is described.

It is also suggested to use sludge wastes (settlings) in expanded clay gravel production technology. Adding sludge in amount of 1% allows obtaining expanded clay gravel of strength grade P-25; and of bulk density 250 kg/m$^3$. Increasing the weight content of sludge up to 3% allows obtaining expanded clay gravel of strength grade P-15 with bulk density 250 kg/m$^3$.

Ceramic products are traditionally high-demand goods (Table 1) [14].

| Sector of Ceramic industry               | EU-15 Output 2000 (x million tonnes) | EU-15 sales 2003 (x million EUR) |
|------------------------------------------|--------------------------------------|----------------------------------|
| Wall and floor tiles                     | 25.0                                 | 10100                            |
| Bricks and roof tiles                    | 55.0                                 | 6800                             |
| Table and ornamental ware                | 0.5                                  | 2000                             |
| Refractory products                      | 4.5                                  | 3100                             |
| Sanitary ware                            | 0.5                                  | 1900                             |
| Technical ceramics                       | 0.15                                 | 2000                             |
| Vitrified clay pipes                     | 0.7                                  | 300                              |
| Expanded clay aggregates (2002)          | 3.0                                  | 300                              |
| Inorganic bonded abrasives (2003)        | 0.04                                 | 260                              |

There are research works concerning settlings recycling for using them in manufacturing ceramics of various categories.

In the work [10] the sewage sludge ash was used for manufacturing glass-ceramics, high in strength and superior in acid resistance. Other researchers have published the findings about using: Sludge from the washing process of natural aggregate was used as the raw material for the production of dry pressed ceramic bodies [11].

In construction sector of Jordan a big problem is Marble Sludge Slime, which is formed in the process of parent rocks cutting and polishing. The research demonstrates [12], that it can be used: in ceramic production, which would decrease the expensive management of the residues with landfill and preserve an equivalent amount of natural mineral resources (pentonite).

A waste sludge rich of Cr, Ni, Fe,… generated from electroplating wastewater treatment plant could be used to replace inorganic pigment in brick production after being primarily treated [13]. Sludge of ceramic tiles industry can be successfully recycled in brick industry to produce green building units with reasonable cost [15].

There are also some other works concerning the usage of settlings in ceramics production [16, 17].

At the semi-dry process of ceramic mixtures preparation it is recommended to add sludge in form of paste, and at the soft-mud process it is reasonable to use the admixture in the powder form, to avoid excessive moistening of the raw mix.

The purpose of this work was studying the possibility of using the oily wastewater treatment sludge, containing waste gabbro-diabase powder sorption material, as a mineral and pore-forming admixture for the raw mix in ceramic bricks production.

The oil-containing sludge was obtained at purifying model wastewaters, represented with Devonian oil emulsions with concentration 1000 mg/dm$^3$.

X-ray diffraction analysis (XRD) of gabbro-diabase was performed with a diffractometer «DRON-4» using CO-anode emission (Ne attenuation filter of B-component of the emission) by powder diffraction technique. The diffraction patterns were identified by catalog [ICDD international Centrefom Difraction Data (USA)].
pH of the water extract was determined by means of pH-meter. The oxides composition of samples under study was determined with «ARL Intellipower Workstation» device, which allows carrying out fluorescence analysis of elements using an X-ray tube with R-H-anode. Concentrations in phase and sequential analysis of elements were calculated with software package: «UniQuant 5.56» and «Siroquant version 3.0». The microstructure of material was studied with a scanning electron microscope «TESCAN MIRA 3 LUM» (Poland).

To obtain ceramic material samples the plastic forming technology was used, at which the molding moisture content of the batch was % by weight, the firing temperature was = 950°C. The cylinder-shaped samples, 30 mm high and 30 mm in diameter, were prepared in sets. Each set consisted of 3 samples.

Differential thermal analysis was carried out with a NETZSCHSTA 449 F1 Jupiter device, with the combined mass spectrometric analysis of exhaust gases by means of QMS 443 A®olos device.

The physical and mechanical performance of samples was assessed on the basis of research findings by determining the following parameters: density (ρ, kg/m³); compressive strength (σ, MPa), water absorption (W, %). Besides, the air shrinkage (Y_v, %) and fire shrinkage (Y_0, %) values were also determined. The measurements were taken according to standard procedures for ceramic materials.

As a reference sample the samples without sludge were prepared.

The generated sludge contained 3.75% of gabbro-diabase powder, 1.25% of petroleum products, and the rest was water. The composition of gabbro-diabase is presented in Table 2.

Table 2. Gabbro-diabase composition.

| Component | SiO₂ | Al₂O₃ | MgO | Fe₂O₃ | CaO | Na₂O |
|-----------|------|-------|-----|-------|-----|------|
| Content, % by weight | 50.23 | 13.78 | 13.76 | 10.03 | 7.28 | 2.99 |
| Component | TiO₂ | K₂O | MnO | P₂O₅ | SO₃ | Cr₂O₃ |
| Content, % by weight | 0.932 | 0.314 | 0.156 | 0.146 | 0.0912 | 0.0868 |
| Component | V₂O₃ | RuO₂ | CuO | PdO | ZnO | CeO₂ |
| Content, % by weight | 0.0581 | 0.0272 | 0.0171 | 0.0125 | 0.0114 | 0.011 |
| Component | ZrO₂ | ThO₂ | Ag₂O | SrO | NiO | Co₂O₄ |
| Content, % by weight | 0.0108 | 0.0091 | 0.0085 | 0.0084 | 0.0071 | 0.0057 |
| Component | I | Nd₂O₃ | Nd₂O₅ | Y₂O₃ | Sc₂O₃ | PbO |
| Content, % by weight | 0.0054 | 0.0049 | 0.0037 | 0.0022 | 0.0018 | 0.0013 |

Wastewater treatment sludge (WTS) appears as pasty mass with color range from dark gray to black, moisture content 95% and density 1.151 g/cm³.

The wastewater treatment sludge was added to clay mixes, prepared with the Bessonovka (Belgorod region) and Podgornoe (Voronezh region) clays.

The clay from the Bessonovka deposit contains such clay minerals, as montmorillonite (d = 14.853; 3.715; 2.574; 1.822), illite (d = 10.106; 1.986), kaolinite (d = 7.138; 4.945), anorthite (d = 3.367; 3.266; 2.912; 2.574), impurities of quartz (d = 4.270; 3.367; 2.287; 2.132) and calcite (d = 3.038) (Figure 1).

The composition of the Podgornoe deposit clay includes: montmorillonite (d = 14.608; 4.484; 3.786; 2.571), illite (d = 10.106; 1.983), kaolinite (d = 7.225; 4.844), anorthite (d = 4.040; 3.786; 3.198; 2.898), ilmenite (d = 3.786; 2.755; 2.574; 2.287), quartz (d = 4.270; 3.351; 2.458; 2.287; 1.983; 1.819) and calcite (d = 3.038) (Figure 2).
Both clays have similar mineral composition, but the cumulative mass content of clay minerals makes up 79.7% for Bessonovka clay and 71.2% for Podgornoye clay.

Differential thermal analysis (DTA) allows assessing the temperature and energy modes of the processes, as well as identifying the changes, which take place at heating the substance (Figures 3, 4).
Figure 4. DTA with NETZSCHSTA 449 F1 Jupiter, clay of the Podgornoye deposit Voronezh region

The first stage of weight reduction (80–120 °C) can be referred to removal of physical water. The further heating of clay samples doesn’t cause any noticeable changes up to 488.3 °C (Bessonovka clay) and 494 °C (Podgornoye clay), which can be explained by constitutional water removal. The peak at 576.6 °C (Bessonovka clay) also corresponds to the removal of constitutional water traces. The next stage of weight reduction is observed for both samples at temperature 724.3 °C. This effect can be apparently associated with the process of removal of water in form of coordinated hydroxide ions and deformation of aluminum atoms coordination (kaolinite); interconversion processes in illite; removal of interlayer water in montmorillonite. The exothermic effect at 890.3 °C for the Podgornoye clay can be explained with crystal lattice rearrangement and the formation of a new crystalline substance.

In the course of research, the physical and mechanical parameters of samples on the basis of clays with various amounts of WTS, added to the mix, were determined (Figures 5a, b).

Figure 5. Alteration of density (a) and compressive strength (b) of ceramic samples, made of Podgornoye and Bessonovka clays, depending on WTS amount

As follows from the obtained findings, adding WTS to the batch in amount up to 2 % results in increase of the samples’ compressive strength. The strength increase is apparently due to iron content over 7 % in gabbro-diabase. As the authors [4] have determined earlier, the ferrous additions to the batch are useful components in ceramic materials production. Acting as a fluxing agent in combination with organic matter they facilitate the earlier accumulation of liquid phase and intensify the sintering and
integration processes. At increasing the weight content of WTS admixture to the raw mix up to 7%, the compressive strength is slightly reduced, but is still rather high and exceeds the reference samples’ strength by 1.4 times for the Bessonovka clay and by 1.9 times for the Podgornoye clay.

Increase of the WTS content in the batch up to 2% results in the slight increase of density of Podgornoye and Bessonovka clays samples. This is probably due to the fact that the specific density of gabbro-diabase (3.07 kg/dm$^3$) is somewhat higher than the clay density (1.05 kg/dm$^3$). Besides, the presence of petroleum products in the sludge increases the plasticity of clay mass, which provides the better workability and compacting of particles at compressing.

Further on, the density slightly decreases, which can be explained by the increase of pores amount in the ceramic sample (Figure 6). This is due to the fact that the petroleum products, contained in the samples, are burnt during firing with the emission of gaseous products, which results in pores and voids formation, preventing the sintering of material.

The differences in amount and size of pores in the sintered material can be evaluated by images and micrographs of broken ceramic products samples’ cleavage faces (Figure 6).

Comparing the micrograph images we can make a conclusion that adding wastewater treatment sludge, containing combustible additive – industrial oil I-20А, to the clay mix, results in the increase of number and size of pores in the finished product in comparison with reference samples; in micrographs of the reference samples a relatively uniform structure of the sintered ceramic mass is observed, while in the micrographs of cleavage faces of samples with sludge rather large pores over 1500 µm can be seen.

As a result, the porosity of material and its water absorption are increased as well, which is confirmed by research findings in Figure 7.
In the course of research, a certain alteration of air shrinkage and firing shrinkage of samples, made of both clays, was noted (Figure 8 a, b).

Thus, for the samples, made of Podgornoye clay, air shrinkage is no more than 5.82 % at 7 % sludge content (reference – 4.96 % of shrinkage); for the samples, made of Bessonovka clay the highest air shrinkage is observed at added wastewater treatment sludge content 5%, which amounts to 3.62 %, while the air shrinkage of the reference sample is 4.08%. So, we can make a conclusion that adding wastewater treatment sludge, containing gabbro-diabase and industrial oil I-20A, to the clay mix has no considerable impact on air and firing shrinkage values of the samples.

The paper presents research findings of the possibility of recycling and using the oil-containing sludge, generated at water-oil emulsions purification with gabbro-diabase powder, in ceramic constructional products manufacture. The ceramic samples were prepared using natural clays from the Bessonovka (Belgorod region) and Podgornoye (Voronezh region) deposits. It has been demonstrated that adding the sludge to clay mass in amount of 2 % wt. increases the compressive strength of samples by 90, the air shrinkage by 1%, and water absorption by 1-2 %. At 7% sludge content in the clay mix the ceramic samples’ strength meets the grade not lower than 150 by GOST 530-2012

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