Application of oil-products-containing water treatment sludge in wall ceramics production

I V Starostina¹, R G Shevtsova², Yu L Starostina³

¹Institute of Chemical Technology, Department of Industrial Ecology, Belgorod State Technological University n.a. V.G. Shukhov, 46, Kostyukova Street, Belgorod 308012, Russia
²Institute of Chemical Technology, Department of Theoretical and Applied Chemistry, Belgorod State Technological University n.a. V.G. Shukhov, 46, Kostyukova Street, Belgorod 308012, Russia

E-mail: starostinairinav@yandex.ru

Abstract. The article presents the research findings concerning the usage of carbon-containing water treatment sludge of test solutions, containing emulsified oil products, in raw charge for wall ceramics production. For removing oil products kieselghur sludge was used, generated at the refined vegetable oil production at winterization stage (removing waxes and waxlike substances), thermally modified at temperature 450°C. Water treatment sludge is characterized with organo-mineral composition. It was determined that baking ceramic samples with water treatment sludge at temperature 950°C causes the oxidation of oil products with the formation of gaseous products CO, H2O and CO2, which makes ceramic materials' structure porous, which in its turn reduces their density and improves their heating-performance characteristics. The presence of organic substances in the charge for ceramic materials creates favorable thermodynamic conditions for iron oxides reducing reactions, which contribute to the formation of low-temperature silicate melt and intensify the samples' baking process. The wall ceramics products, obtained with the use of water treatment sludge, can be used as construction material and heat-insulating material in enclosing structures and at internal partitions installation.

1. Introduction

Sorption methods of wastewater purification and removing of various pollutants, both mineral and organic, have found wide application. They have a stable place in technological processes, as they are characterized with high efficiency and the possibility of using natural materials [1, 2], as well as industrial and agricultural production waste [3-6], as adsorbents. But the spent adsorbents, which form sediments or water treatment sludge, are reused or recycled in very small amounts, and in most cases they are dumped at long-storage industrial waste disposal sites, filtration fields or waste dumps [7].

The facilities for water treatment sludge storage are sensitive and demanding hydrotechnical constructions. When storing sludge in holding ponds the filtration flow is formed [8], which can have adverse effect on its basement, flood certain elements of sludge dump and disrupt the operation of drainage system. Besides, it is necessary to take into account the ecological hazard of wastewater sludge effect on the environment – pollution of surface and ground waters due to penetration of the filtration flow or washing-out of the adsorbed substances with atmospheric precipitations, storm and
melt waters; dust pollution of the neighboring area as a result of drying of sludge surface layer; accumulation of heavy metals in soil etc. So, the currently used long-term storage technologies of sludge imply constant acquisition of large areas of land and their complete subsequent pollution with no opportunity of further use.

The most promising area of the usage of large-capacity sludge wastes from water-treating facilities is building materials production and, particularly, ceramic production [9-15]. This is conditioned by large capacities and large material consumption of building sector production, as well as by the wide range of manufactured products.

In the work [12] the application of water treatment sediment, containing both mineral impurities – calcium carbonate and sulphate, and organic impurities – fats, oils, oil products and synthetic surface-active substances, as a pore-forming additive for ceramic bricks production is shown. It is demonstrated that the baking of finished products, containing the sludge, results in decomposition of its components with the release of CO$_2$ and H$_2$O, which makes ceramic materials porous. Increasing the amount of the added wastewater treatment sludge reduces the physical-mechanical characteristics of the obtained products – density and strength, and increases their heat-insulation and sound-proof properties. The optimal content of sludge (15-20 wt.%) provides obtaining the ceramic materials, which can be used for enclosing structures [16].

In the works [8,17] the application of CHP plants water conditioning sludge as an aggregate for gypsum binders is shown. The adding of optimal amounts of sludge (15%) contributes to the increase of composite binders' setting time, not affecting their water demand or water resistance.

The usage of oil-contaminated sludge wastes from oil-water emulsion purification in ceramic bricks production is shown in work [18]. The optimal content of oil-contaminated sludge in the raw mix amounts to 25%; the further increase results in the sharp decrease of physical and mechanical properties of the obtained finished products.

The authors of the work [19] developed a raw charge composition for the production of ceramic porous aggregate on the basis of industrial waste – slate clay and oil sludge. The developed recommendations have allowed excluding the usage of conventional natural materials.

Production of low-density wall ceramics products for bearing and enclosing structures is nowadays one of the relevant tasks. Such materials in their thermo-technical characteristics belong to high-efficiency products with heat conductivity below 20 W/(m°C).

Though there are quite a lot of research studies devoted to the usage of various water-treating facilities' sludge wastes, the problem of generation and accumulation of sludge indicates the necessity to expand the existing areas of their recycling and to develop new ways of their recuperation.

2. Research objective

The purpose of this work is to consider a possibility of using the sludge, generated after the adsorption treatment of wastewater from emulsified oil products, in the raw charge for wall ceramics production. To achieve this purpose the following objectives have been solved:

- determining the main properties of wastewater treatment sludge;
- evaluating the influence of sludge content in the raw charge on main physical-chemical characteristics of ceramic brick samples.

3. Results and discussion

As the earlier studies have shown [20], the most efficient adsorption material for extracting emulsified oil products from wastewaters is kieselghur sludge, thermally modified at temperature 450°C. Kieselghur sludge is the waste product of refined vegetable oil production, generated at winterization stage – i.e. removal of waxes and waxlike substances by filtering in conditions of low temperatures, and is an organo-mineral product with fat-and-oil mix content 60-70%. The mineral part is presented with diatomite - sedimentary rock, formed of siliceous shells of microscopic diatomic algae – diatoms and radiolarians.
As a result of treatment at temperature 450°C, the organic substances, contained in kieselghur sludge, are carbonized (charred) with the formation of carbon layer particles on the surface and the material becomes black.

The obtained thermally modified kieselghur sludge (TKS_{450}) was used as carbon-containing adsorption material for extracting from wastewaters the emulsified oil products with the initial concentration 300 mg/dm³. As an oil product the mineral oil I-20A was used. The generated wastewater treatment sludge, dried at temperature 105°C, has the following composition, wt.%: SiO₂ – 87; carbon – 10; oil products – 3. In Figure 1 there is the infra-red spectrum of water treatment sludge particles. As we can see, the appearance of high-intensity peaks at 2855, 2926, 2951 cm⁻¹ is associated with the presence of C-H symmetrical and asymmetrical parts of methylene groups' radicals on the surface of sludge particles. The appearing of absorption bands in these values of wave numbers indicates the adsorption of oil I-20A on TMS_{450} and confirms the presence of oil in the wastewater treatment sludge.

Figure 1. Infra-red spectrum of wastewater treatment sludge.

Taking into account the organo-mineral composition of wastewater treatment sludge, it is expedient to use it as a leaner and combustible additive in ceramic materials production. According to the literature data, the combustible additive group includes both solid and liquid fuels of various types, particularly anthracite, coke fines, oil sludge, spent oils and others [21].

As the main raw clay material for obtaining ceramic brick samples the clay from Ternovskoye deposit (Belgorod region, Russia) was used. By plasticity index it belongs to moderately plastic clay raw materials with true density 2.15 g/cm³. The chemical composition of Ternovskoye clay is presented in table 1.

Table 1. Chemical composition of clay from Ternovskoye deposit.

|   | SiO₂  | Al₂O₃ | Fe₉ gen | FeO   | Fe₂O₃ | TiO₂ | CaO  | MgO  | SO₃  | R₂O |
|---|-------|-------|---------|-------|-------|------|------|------|------|-----|
|   | 67.47 | 12.91 | 5.48    | 0.44  | 0.75  | 0.75 | 2.76 | 1.44 | 0.48 | 2.38 |
The X-ray phase analysis of Ternovskoye clay was performed with a diffractometer DRON-6 using \( \text{K}\alpha \)-radiation at the rotation rate of stage with sample 1 grad/min. In Figure 2 the X-ray pattern of Ternovskoye clay is presented.

In the X-ray diffraction pattern of Ternovskoye clay powder the characteristic strong lines of the following minerals are registered: in the minerals of the montmorillonite group \( d (\text{Å}) = 18.8; 15.78; 12.45; 4.495; 1.899; 1.776 \), quartz \( d (\text{Å}) = 4.27; 3.351; 2.132; 1.821 \), micaceous minerals \( d (\text{Å}) = 10.1; 5.011; 3.25; \text{CaCO}_3 \) \( d (\text{Å}) = 3.043 \). So, the clay fraction is presented mostly with minerals of montmorillonite group and with hydromicaceous minerals.

![Figure 2. X-ray phase analysis of Ternovskoye clay.](image)

To determine rational technological conditions of recycling wastewater treatment sludge and obtaining wall ceramics samples the sludge, dried to constant weight, was added to raw charge in amount from 1 to 20% by weight. Cylindrical samples 20 mm high and 20 mm in diameter were formed by plastic compaction method at the charge moisture 20%. The formed samples were dried at temperature 105-110\( ^\circ \text{C} \) until the constant weight and baked in a muffle furnace at temperature 950\( ^\circ \text{C} \). The isothermal time of samples at final temperature amounted to 1 hour. The selected temperature conditions of baking were determined by the peculiarities of clay raw materials and by the fact that most of wall ceramics factories use this temperature range.

Taking into account the composition of raw charge, at baking temperature 950\( ^\circ \text{C} \) the following reactions can take place:

1. Dehydration reactions of clay minerals - montmorillonite:
   \[
   \text{Al}_2\text{O}_3\cdot4\text{SiO}_2\cdot\text{H}_2\text{O} = \text{Al}_2\text{O}_3\cdot4\text{SiO}_2 + \text{H}_2\text{O}
   \]
   and of micaceous minerals:
   \[
   \text{K}_2\text{O}\cdot3\text{Al}_2\text{O}_3\cdot6\text{SiO}_2 = \text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot4\text{SiO}_2 + 2\text{Al}_2\text{O}_3 + 2\text{SiO}_2
   \]
   \[
   \text{K}_2\text{O}\cdot3\text{Al}_2\text{O}_3\cdot6\text{SiO}_2 = \text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot6\text{SiO}_2 + 2\text{Al}_2\text{O}_3
   \]
2. Decomposition reactions of calcium carbonates – the impurities of clay raw material:
3. Oxidation reactions of carbon – a component of TMS_{450} adsorption material, and oil products, extracted from wastewater:

\[ \text{CaCO}_3 = \text{CaO} + \text{CO}_2 \]

\[ \text{C} + \text{CO}_2 = 2\text{CO} \]
\[ 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \]
\[ \text{C} + \text{O}_2 = \text{CO}_2 \]
\[ 2\text{C} + \text{O}_2 = 2\text{CO} \]
\[ \text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \]
\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]

As a result of organic substances burning-off the reducing atmosphere is formed.

4. Reduction reactions of iron oxides – the impurities of clay raw material in the reducing atmosphere:

\[ 3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \]
\[ 3\text{Fe}_2\text{O}_3 + \text{C} = 2\text{Fe}_3\text{O}_4 + \text{CO} \]
\[ 4\text{FeO} = \text{Fe} + \text{Fe}_3\text{O}_4 \text{ (at temperatures below 570°C)} \]

The color of baked samples depending on the amount of added wastewater treatment sludge alters from dark brown to straw. The peculiarities of mineral formation in clay raw materials in reducing environment are associated with the pass of iron compounds at relatively low temperatures (950°C) to the liquid phase, as the formed ferrous iron oxide (FeO) is an active fluxing agent. The early formation of liquid phase, according to [22], creates favorable conditions for reactions of spinel, hercynite and mullite formation.

According to findings of the research, presented in the work [23], the baking of clay materials containing organic substances creates favorable thermodynamic conditions for reduction reaction of iron oxide and the formation of low-temperature silicate melt. According to the equilibrium diagram, iron with oxygen forms three stable oxides: Fe_{1-x}, Fe_3O_4 and Fe_2O_3 [22]. The process of iron reduction from oxides according to the Baykov principle concerning the pass from higher oxides to lower oxides proceeds by the following scheme:

\[ \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \]

At the reduction of Fe_2O_3 to FeO the molecular concentration of iron oxide is doubled, which results in the considerable decrease of melting temperature of the system with the simultaneous generation of gaseous reaction products – H_2, CO and CO_2. These factors have a significant influence on the formation process of strong and porous structure of wall ceramics samples.

With the appearance of liquid phase the process of ceramic materials’ sintering begins, which can be presented in the following way: at the very beginning of liquid phase formation on the raw mix grains' surface interparticle necks are formed, the liquid penetrates capillaries and cements and fixes the pores due to the formation of thin films at phase contacts. At the further increase of the flux amount and the increase of its viscosity the gases are entrained within pores, which contributes to the formation of porous structure. So, the liquid phase compacts and strengthens a ceramic body and participates in phase formation processes of ceramics.

The increase of wastewater treatment sludge content in the range from 7 to 20% in the raw charge results in the further intensifying of gas generation and the increase of liquid phase, which contributes to the formation of porous structure and influences the alteration of main physical-mechanical characteristics of the obtained samples (Figure 3, Table 2). At the increase of sludge content the
density decreases from 1865 kg/m³ in the test sample to 1440 kg/m³ at 20% of sludge, while the strength alters from 32.3 MPa to 6.41 MPa, respectively.

Though the increase of porosity impacts on strength characteristics of the material and can in prospect be a cause for low frost resistance, it improves the thermal-physical properties of the finished products. The heat-conductivity coefficient is reduced from 0.609 W/m°C in the test sample to 0.209 W/m°C at sludge content 20%, which allows recommending the obtained ceramic products to be used as construction materials and heat-insulating materials in enclosing structures and at internal partitions installation.

Figure 3. The influence of wastewater treatment sludge content in the raw charge on main physical-mechanical characteristics of wall ceramics samples: a – density, b – compressive strength; c – water adsorption.

Table 2. Some characteristics of ceramic samples at various sludge content.

| №  | Sludge content, (wt %) | Water adsorption, (wt %) | Heat conductivity coefficient, (W/m°C) |
|----|------------------------|--------------------------|---------------------------------------|
| 1  | 0, test                | 12.56                    | 0.609                                 |
| 2  | 1                      | 15.54                    | 0.541                                 |
| 3  | 3                      | 15.48                    | 0.530                                 |
| 4  | 5                      | 16.90                    | 0.500                                 |
| 5  | 7                      | 17.49                    | 0.485                                 |
| 6  | 10                     | 19.85                    | 0.432                                 |
| 7  | 15                     | 24.27                    | 0.357                                 |
| 8  | 20                     | 28.89                    | 0.290                                 |
4. Conclusions
The samples of ceramic wall materials were obtained with the use of wastewater treatment sludge, containing emulsified oil products.

The wastewater treatment sludge under study is characterized with organo-mineral composition and can be used in a raw charge for ceramic materials as a leaner and combustible additive.

The burning-off of organic substances in sludge at the baking of samples forms the reducing atmosphere. This influences mineral formation processes in clay raw materials, associated with the reduction of Fe$_2$O$_3$ to FeO, which results in the considerable decrease of melting temperature of the system, formation of low-temperature silicate melt with the simultaneous generation of gaseous reaction products and the formation of porous structure.

The wall ceramics samples obtained with the use of wastewater treatment sludge are characterized with various porosities and can be used as construction materials and heat-insulating materials in enclosing structures and at internal partitions installation.

References
[1] Vezentsev A I, Peristaya L F, Nguyen Fuk Kao, Peristiy V A and Kopilova E V 2018 Research of sorption properties of natural montmorillonitovy clays of different fields for water purification from ions of lead (II) Sorption and chromatographic processes 18 (1) 43–51
[2] Moskvicheva E V, Doskina E P, Sakharova A A, Moskvicheva A V, Katerinina K V, Batmanov V P and Belousova Yu B 2017 The use of natural mineral for wash water purification Bulletin of the Volgograd University of Architecture and Civil Engineering. Series: Building and Architecture 47(66) 249–60
[3] Shaikhiev I G, Galblaub O A and Grechina A S 2017 The use of waste from the processing of barley as a sorption material for the removal of pollutants from aquatic environments (literature review) Bulletin of the University of Technology 20(23) 110–7
[4] Sverguzova S V, Tarasova G I and Malahatka Yu N 2012 About the possibility of using dust from the production of building materials for the treatment of waste water from heavy metal ions Bulletin of BSTU named after V.G. Shukhov 4 169–72
[5] Starostina I V, Stolyarov D V and Kosukhin M M 2017 Proc. Int. Conf. on Industrial Engineering (Chelyabinsk) vol 265 (Swizerland: Trans Tech Publications) pp 319–24
[6] Govindarao Venneti M H 1980 Utilization of rice husk. Apreliminary analysis J. Sci. And Ind. Res. 39 495–515
[7] Schegolnikova N M 2015 Sludges water treatment plants and water treatment: a problem or a business? Water Magazine 9 28–32
[8] Valeyev R Sh and Shaykhiev I G 2010 Recycling of Sludge Waste Products from Heat-Power Main Lines in Building Materials Production Ecology and industry of Russia 2 28–9
[9] Komleva G P 2007 Volumetric dyeing and application of an engobic layer on the front ceramic brick using industrial waste Construction Materials 2 36–8
[10] Vasilenko T A 2013 Use of mineral sludge in the production of building materials Modern problems of science and education 5 10032
[11] Levitskiy I A, Pavlyukevich Yu G, Bogdan E O and Kichkaylo O V 2013 The use of sludge from electroplating industries in ceramic bricks production Glass and Ceramics 3 7–13
[12] Sverguzova S V, Saponova Zh A, Shaykhiev I G, Fetisov R O and Shamshurov AV 2012 Water treatment precipitate as a pore-forming additive to ceramic mixtures Bulletin of Kazan State Technological University 15(7) 137–9
[13] Vasilenko T A and Salekh-Zhafer A Zh 2015 Ehe use of calcium-containing technogenic raw materials in the production of expanded clay gravel Modern problems of science and education 1-2 19899
[14] Sverguzova S V, Saponova Zh A and Starostina I V 2016 Disposal of synthetic surfactants-containing wastewater treatment sludge in the ceramic brick production Procedia Engineering 150 1610–16
[15] Starostina I V, Simonov M M and Denisova L V 2017 Proc. Int. Conf. on Industrial Engineering (Chelyabinsk) vol 265 (Swizerland: Trans Tech Publications) pp 501–506

[16] GOST 530-2007 2007 Ceramic Brick and Stone. General Technical Conditions (Moscow: Standartinform) p 39

[17] Valeev R Sh and Shaykhiev I G 2011 Recuperative technology of utilization of sludge waste water treatment in building materials using plasticizer C-3 Bulletin of Kazan State Technological University 13 41–5

[18] Gracheva E O, Shevaga O N and Tarasova G I 2017 The destruction of oil emulsion wastewater with hard demulsifiers and the use of waste sludge in production of ceramic materials Bulletin of BSTU named after V.G. Shukhov 11 128–132

[19] Kolpakov A V, Abdakhimova E S, Kairakbaev A K, Abdakhimov V Z and Roshchupkina I Yu 2015 Use of oil sludge in production of heat-insulation materials based on intershale clay Environmental protection in the oil and gas complex 6 21–5

[20] Nikitina A E, Starostina I V, Porozhnyuk E V, Anishenko I V and Bodnar O B 2018 Using the carbonized carbonaceous waste of oil-extraction production for sorption treatment wastewater from emulsified petroleum products Automation, telemechanization and communication in oil industry 12 23–9

[21] Kashkaev I S and Sheyman Ye Sh 1970 Production of Clay Bricks (Moscow: High School) p 284

[22] Kubashevsky O 1985 State Diagrams of Iron-Based Binary System (Moscow: Metallurgy) p 184

[23] Abdakhimova E S, Dolgiy V P and Abdakhimov V Z 2005 Structural transformations of iron compounds in low-melting clay at different firing temperatures Materialovedenie 2 39–43

Acknowledgments
The work is realized in the framework of the Program of flagship university development on the base of the Belgorod State Technological University named after V.G. Shoukhov, using equipment of High Technology Center at BSTU named after V.G. Shoukhov.