The usage of water conditioning sludge from heat power industry enterprises in wall ceramics production

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Abstract. The paper considers the ecological problems of water conditioning systems at heat power industry facilities. It is noted that the stable operation of water-heating equipment is provided with the quality of feed water. Various water-soluble salts, which can incrust the inner walls of boilers or pipelines, are removed from the natural water. For desalination of natural water the physical-chemical methods are mostly used. The by-product of desalination or chemical water-conditioning systems is the sludge waste. This work presents the results of using chemical water conditioning sludge from JSC Verofarm in the raw charge for wall ceramics production. The sludge is a finely-divided powder, the mineral composition of which is presented with calcium and magnesium carbonates, brucite and iron compounds, which make the sludge pink. It has been determined that the baking of sludge-containing ceramic samples at temperature 1000°C results in dissociation of calcium and magnesium carbonates with the formation of gaseous products H₂O and CO₂, which make the structure of ceramic materials porous. The presence of iron compounds in the raw charge promotes the formation of low-temperature silicate melt, which intensifies the baking process of ceramic samples. The optimal sludge content in the charge that doesn’t reduce the strength characteristics of wall ceramics is 10%. Such sludge content forms the liquid phase on the surface of the raw mix’s particles, which solidifies the forming pores. The increase of sludge content up to 20% intensifies gas generation; the amount of the formed liquid phase is not sufficient, which increases porosity and reduces the density and strength of ceramic materials. At that, the engobe layer is formed on the surface of the obtained wall ceramics samples. The wall ceramics products, obtained with the use of chemical water conditioning sludge, can be used as structural heat-insulation materials in making building envelopes or interior partitions.

1. Introduction
The power industry enterprises belong to water-using branches of industry. Near 50% of the water, taken by the industrial enterprises of the Russian Federation from natural water sources, is used for the needs of heat power industry. The stable operation of water-heating equipment depends on the quality of the feed water. For example, for gas-turbine steam boilers the total water hardness shouldn’t exceed 35 µmol /dm³, the feed water for water-tube boilers with working steam pressure up to 4 MPa should
have hardness no more than 30 µmol /dm³. So, the natural feed water is subject to the compulsory conditioning and purification. This process consists in removing from natural water various water-soluble salts, which can incrust the inner walls of boilers and pipelines. Desalination of natural water is performed mostly by physical and chemical methods – like filtering it through special ionite filters, which selectively extract certain microelements. The by-product of desalination or chemical water conditioning systems is the sludge waste, which contains trace elements, extracted from the natural water, metals and reagents of flushing fluids – silicon, aluminum, iron, calcium and magnesium compounds, some organic impurities etc.

In amounts of its generation, the chemical water conditioning sludge can be classified among large-scale waste products. The heat power industry facilities, depending on the amount of the produced heat or electric energy, generate up to 7 thousand tons of sludge annually [1]. Sludge has a high moisture content, with the water existing as free water, pore water, surface adhesion water and internal combined water [2]. Sludge in the form of pulp with moisture content up to 90% is transported to interim storage sites for dehydrating or to sludge depositories for permanent storage.

The arrangement of sludge reservoirs or sludge depositories requires considerable capital investments and inevitably results in environmental pollution. The sludge suspensions can leak during pumping them through pipelines, filter into soil or ground waters, get into the air with evaporation of gaseous products from the surface or the secondary blowing of dusty components, can cause condemnation or pollution of lands, or irreparable changes of landscapes.

Besides, the flooding or erosion of certain elements of sludge depositories can disrupt the operation of drainage facilities, and cause the filtrates’ penetration into ground waters and their pollution. The accidents at sludge depositories are accompanied with spillage of millions of cubic meters of loose sludge sediments to the neighboring territories and water bodies.

So, developing methods of the sustainable utilization of such waste, which would allow reducing the amounts of their accumulation and storage, is a vital task.

At present, chemical water conditioning sludge doesn’t find any large-scale application. Though there are some research works in using sludge waste in building materials production or in road construction [3, 4].

The work [5] considers the usage of sludge wastes, formed in the technological cycle of vanadium pentoxide and ferrovanadium alloys production, in producing ceramic wall materials. It is shown that the optimal amount of sludge in the raw charge of ceramic bricks, not reducing their physical and mechanical properties, amounts from 3 to 5% by weight.

In the works [1, 6, 7] the possibility of using chemical water conditioning sludge, generated at the stage of raw water preliminary lime, coagulation and electrochemical treatment, for obtaining a sorption material, is demonstrated. The obtained adsorbents showed the high efficiency in purifying sewage waters from heavy metal ions and petroleum products, and exhaust gases from hydrogen sulfide [8, 9].

According to data in the work [10] the carbonate sludge from heat power stations’ chemical water conditioning systems can be used as an additive to high-sulfur furnace oils. The findings have shown that the sludge compounds are adsorbed on the surface of furnace oil’s paraffin components, preventing their crystallization and the thickening of oil. This reduces the viscosity and chilling temperature of furnace oil, which in its turn reduces the energy consumption for heating furnace oil and pumping it through pipelines.

The sludge, generated at CHPP in the process of water conditioning, was utilized as filler for gypsum binders [11]. The adding of sludge doesn’t influence the water demand and water resistance of binders, but improves the setting time of a composite binder. The optimal content of sludge is 15%.

On the basis of sludge waste, thermally modified in conditions of lack of oxygen, the hydrophobic oleophilic carbon-bearing sorption materials were obtained for removing heavy metal ions from sewage waters, and petroleum or petroleum products spillages from water surface [12, 13].

The work [14] suggests the technology of recultivation materials production on the basis of sludge. It includes the three-stage dehydration of sludge with the use of geotextile containers system and mix-
ing it with hardening additives – ashes from CHPP, milled boiler refractory waste and sooty waste. The obtained composite material corresponds in its properties to natural soils and can be used for construction and maintenance activities at recultivated lands – for filling pits and ditches, for technical shielding of grounds and vertical land leveling.

The purpose of this research is to study the properties of chemical water conditioning sludge wastes from boiler plants of a pharmaceutical enterprise JSC Verofarm, Belgorod, Russia, and to consider the possibility of its utilization in ceramic bricks production.

2. Materials and Methods
In a sludge depository the sludge appears as waterlogged pink mass with moisture content 83%. After drying at temperature 105-110ºС it acquires the properties of a powder, i.e. has no binding properties. The dry sludge is a polydisperse system, with high dispersion; particle size is from 0.1 µm to 50 µm (figure 1). The chemical composition of sludge is presented in table 1.

![Figure 1. Results of granulometric composition analysis of chemical water conditioning sludge from JSC Verofarm.](image)

Table 1. The oxide composition of chemical water conditioning sludge from JSC Verofarm (wt.%).

|       | CaO   | MgO  | SiO₂ | R₂O  | Fe₂O₃ | Al₂O₃ | SO₃  | chlorides |
|-------|-------|------|------|------|-------|-------|------|-----------|
|       | 46.6 – 61.8 | 16.4 – 20.7 | 3.1 – 14.7 | 2.4 – 7.0 | 1.7 – 2.7 | 0.1 – 0.4 | 0.4 – 0.7 | 0.3 – 19.7 |

According to the X-ray phase analysis results (figure 2-a), the sludge contains the following minerals: calcium and magnesium carbonates, brucite (Mg(OH)₂), iron compounds FeOOH and Fe₂O₃, which makes the sludge pink. By the intensity and area of characteristic peaks we can conclude that the prevailing mineral is calcium carbonate, and the sludge can be characterized as carbonaceous.

In the paper the utilization of chemical water conditioning sludge in the raw charge for ceramic bricks has been considered. For this purpose the thorough selection and optimization of the raw mix composition and its burning conditions are required, which provides the controlled phase formation in the process of ceramic charge material sintering. As an argillous raw material, the clay from Bykovskoye deposit, Belgorod region, Russia, was used.
Figure 2. X-ray diffractograms: a – dry initial chemical water conditioning sludge; b – chemical water conditioning sludge, heat-treated at temperature 1000°C; c - clay from Bykovskoye deposit.
The mineral composition of the clay was evaluated according to the X-ray phase analysis results (figure 2-c). In the X-ray diffraction pattern the strong lines are registered, characteristic for the following minerals:

- clay minerals: montmorillonite \(d(\text{Å})= 15.504; 4.484; 2.238\), albite (anorthite) \(d(\text{Å})= 3.345; 3.261; 2.560; 2.171; 1.918\), kaolinite \(d(\text{Å})= 7.284; 4.484; 2.560\);
- accessory minerals: quartz \(\text{SiO}_2\) \(d(\text{Å})=4.281; 3.357; 2.287; 2.238; 2.129\), calcite \(d(\text{Å})= 3.043; 2.287\), hematite (rutile) \(\text{Fe}_2\text{O}_3\) \(d(\text{Å})= 2.465\). The clay from Bykovskoye deposit is characterized as polymineral with the prevailing montmorillonite-hydromicaceous components, and contains impurities of quartz, calcite and hematite.

Dry chemical water conditioning sludge was added to 100% of raw charge in amount from 0.2 to 20% of solid components mass. The prepared charge was mixed to a homogeneous condition and moistened up to 20%. Then the cylindrical ceramic samples 3 cm high and 3 cm in diameter were made by means of plastic molding. The samples were dried at temperature 105-110°C to the constant weight, and then baked at temperature 1000 °C.

3. Results and discussion
The adding of chemical water conditioning sludge to the raw charge promotes the formation of porous structure of the obtained ceramic materials (figure 3). Such tendency is explained by the ability of the sludge’s components – calcium and magnesium carbonates – to decompose under the action of high temperatures by the following reaction:

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \\
\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2
\]

![Figure 3. The influence of sludge content in the raw charge on physical and chemical properties of ceramic materials: a – compressive strength; b – water absorption capacity.](image-url)
The heat treatment of sludge, apart from intensive gas release, is accompanied with the generation of Fe\textsubscript{2}O\textsubscript{3} and CaO (figure 2-b), which in clay-containing masses act as strong fluxing agents due to forming relatively low-melt compounds with Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}. The mineralizing role of iron oxides in ceramic masses has been studied in a number of works [15]. It is noted that protoxidic iron compounds, having high reactivity, intensively form ferrous silicate melts or glasses [15].

Thus, the sludge content in the raw charge up to 10% doesn’t reduce strength properties of the obtained materials. This allows the use of water treatment sludge from heat power enterprises in the production of building materials [16-18]. As a result of samples’ baking, the forming liquid phase on the surface of raw mix’s particles penetrates into their capillaries, formed as a result of slight gas development, and acts as a cementing binder, forming thin films at phase contacts. The gases are also entrapped by the melt and the pores are fixed, which provides stability of the obtained samples’ compressive strength – 21.0 MPa (in the control sample) and 24.0 MPa (5% of sludge) (figure 3). As a result, the more porous structure, than in the control sample, is formed – the water absorption value is increased from 9.5% (in the control sample) to 12.4% (5% of sludge) and up to 13.5 % (10% of sludge). The formed porosity in its water absorption capacity is close to the upper acceptance limit - 14% (figure 3).

With increase of the sludge content in the raw charge up to 20%, the process of CaO, generated at decomposition of sludge’s carbonate components, absorption with the formed liquid phase is intensified. But at the same time, the volume of the formed liquid phase is not enough for entrapping gaseous products or solidifying pores, which eventually results in the increase of porosity up to 15.6%, and decrease of ceramic materials’ density, which adversely affects the strength properties of samples.

It should be noted that the increased sludge content (10-20%) in the raw charge results in the formation of engobe layer on the surface of ceramic materials. This is due to the excess amount of CaO, formed in the process of thermal dissociation of calcium carbonate, incompletely bonded with clay minerals. The excess of CaO interacts with gaseous components with the formation of light (engobe) superficial layer on ceramic materials samples.

4. Conclusion
So, the usage of chemical water conditioning sludge in the raw charge for wall ceramics without reducing their physical-mechanical characteristics is possible in amount up to 10% by weight over 100%. Ceramic products with the increased sludge content – from 10 to 20% – are characterized with the increased porosity and lowered physical-mechanical properties, so they can be used only as structural heat-insulation materials.

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