

The usage of iron-containing sludge wastes in ceramic bricks production

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Abstract. The article considers the opportunity of utilizing sludge wastes, generated at the vanadic pentoxide and ferrovanadium alloys production cycle, in walling ceramics production. The considered materials belong to polymineral systems in their chemical and mineral composition, and contain the crystalline phases – calcium carbonate and sulphate, and the iron-containing components – hematite, wustite, the sulphate form of hydrated calcium sulfoferrite and the residual amount of lime. The metal oxides are contained in the amorphized state. The ferriferrous concentrate sludge, added to the raw mix, due to the high content of iron compounds in it, demonstrates mineralizing and fluxing properties. At baking the raw mix, containing limestone-gypseous composition, the processes of intensive release of such gases as CO₂ and water vapor is observed, as the products of carbonate and sulphate components. The adding of sludge materials to the raw mix composition results in the alteration of the color of the obtained samples from red-brown to black-brown. The adding of sludge to the raw charge of ceramic brick in amount of 3–5% of weight doesn't impair its physical and mechanical characteristics. The increase of its content to 30% causes the porous structure formation and reduces the density and strength characteristics of materials. The obtained wall ceramic products can be used as structural and heat-insulating materials for making enclosing structures and interior partitions.

1. Introduction

The considerable amounts of the accumulated waste of various types cause the serious economic and ecological problems. According to the statistics [1], at the beginning of 2016 about 31.5 billion tons of production and consumer waste was registered in Russia. Only about 10% of this amount is recycled and utilized, and the rest is either buried or dumped at the disposal areas [2]. Expenditures for disposal, dumping and arrangement of the storage of industrial waste, generated at this or that industrial process, amount to 8–10% of the manufactured product cost [3]. The degree of the industrial solid wastes' impact on natural systems is determined by their composition and the technology of their processing.

Among all the types of industrial waste the sludge wastes belong to the bulkiest ones. Of 3.5 bln tons of waste, generated in the Russian Federation every year, 800 mln tons is represented by sludges. They include galvanic sludge, groundwater purification sludge, wastewater neutralization sludge etc. They are characterized with the following properties – the high dispersity and water-holding capacity, the wide range and instability of chemical and mineral compositions, the presence of heavy metal ions and pathogenic flora, and a number of other peculiarities, which hinders solving the problem of their



large-scale utilization. So, in most cases the sludge wastes are stored at disposal areas or buried, but it doesn't solve the problem of environment protection. Even in the neutralized form the sludge components remain toxic to this or that extent. As a result of their dumping at sludge reservoirs, the environment can be polluted with the dust particles of sludge, formed at the drying of the upper layer and accumulating in the soils of the nearby territories. This provides the adverse effect on the development of the soil biota, which determines the soil fertility, and on plant and animal life. The soluble components can be washed away under the action of atmospheric precipitations and pollute the water-bearing strata.

According to their chemical composition all sludges can be divided into three groups [4, 5].

I – compounds, which have tendency to structural ordering. They are generated in the form of crystal sediments, consisting of bivalent metals hydroxides;

II – trivalent elements compounds. They are characterized with the initial formation of active metastable forms, which then transform into active forms of crystalline structure;

III – metals hydroxides, which have low tendency to the structural order. As sediment, these compounds are X-ray amorphous, and only after long aging and heating they begin to show the evidence of passing to the crystalline state.

Reclamation of technogenic materials in this or that manufacturing cycle is very promising. It allows not only enhancing the raw materials base for the main product manufacturing, but also providing the ecological safety and protecting the environment, as well as saving the natural resources. In this regard, the most promising is the usage of sludge wastes in building materials production, and especially in the production of ceramic materials. This is due to the fact that the high-temperature processing, used in ceramics production, transforms the heavy metals, contained in these wastes, into their unleachable forms, which neutralizes them and safely binds them in the end product composition. This allows recycling even the most hazardous and toxic types of waste, which include most of the sludge formations, generated as a result of wastewater neutralization.

Some wastes are used as admixtures, which allow enhancing the scale of low-grade stock application, reducing the energy resources consumption and cutting the production costs of the obtained product with the improved technological parameters [6].

Thus, there were designed the compositions of raw charge for ceramic bricks production, modified with galvanic sludge. The suggested technological solutions were implemented at a number of enterprises in the Vladimir Region, Russia, [7].

The adding of some water treatment sludges to the raw mixture produces the pore-formation effect, reduces the density and heat conductivity of the obtained products, which allows using bricks for making interior partition walls or as part of multilayered enclosing structures [8–10]. The other wastes are considered to be used as main raw materials, which allow partially or completely replacing the non-replenishable mineral resources – clay minerals [11, 12].

In the work [13] the possibility of using the iron-containing waste in the form of electroplating industry wastewater sludge from the leading enterprises of Belarus for the course and facing ceramic bricks and stones production has been presented. It has been demonstrated that the content of sludge in the raw mix in amount of 15–25% ensures the obtaining of durable construction products with the required decorative and physical-mechanical properties.

In the work [14] the results of using float wastes from the Kashtaysky mine, generated at tungsten and molybdenum ores processing, as a raw material for ceramic tiles production are presented. The adding of these wastes to ceramic mixtures in amount of 46–55% allows obtaining the façade and facing tiles with good physical and mechanical properties.

The article [15] considers the usage of galvanic sludge for obtaining magnetic sorbents for oil-containing wastewater purification. The sludge was preliminarily exposed to the chemical treatment – ferritization in order to provide it with magnetic properties, then blended with a polymeric binder (paraffine), pelletized and dried. The application of the binder prevents the migration of heavy metal ions to liquid media.

Though a considerable number of research works dealing with the utilization of multicomponent sludge formations from various industrial processes has been carried out, the increase of their generation necessitates the improvement of the existing methods of their recycling and the search of the new methods.

2. Experimental section

The earlier studies have demonstrated the good prospects of using sludge wastes, generated at the vanadic pentoxide and ferrovanadium alloys production, in expanded clay gravel manufacturing process [16]. The purpose of this research is considering the opportunity of using the sludge materials from vanadic pentoxide and ferrovanadium alloys production in the composition of the raw charge for ceramic bricks production.

The sludge materials under study are generated as a result of two-stage process of acid wastewaters neutralization at the OAO «EVRAZ Vanadii Tula», Tula, Russia. As a neutralizing agent the lime is used. As a result of the process, the sludge wastes are generated, which are notionally named ferriferrous concentrate (FFC) and limestone-gypseous composition (LGC). Their chemical composition and some processing characteristics are presented in Table 1 and 2.

Table 1. The chemical composition of sludge materials, wt. %

Sludge	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	MnO	Cr ₂ O ₃	SO ₃	Na ₂ O	TiO ₂
FFC	16.68	11.01	2.20	32.48	0.88	4.38	3.00	19.11	0.23	6.83
LGC	37.14	2.22	0.32	0.71	4.04	17.67	0.06	33.11	0.20	–

Table 2. Some technological characteristics of FFC

ID	Characteristics	FFC	LGC
1	Loose density, kg/m ³	1020–1100	640–700
2	True density, kg/m ³	2150–2200	1480–1530
3	Specific surface, cm ² /g	2200–2500	2800–3300
4	pH water extract	4.5–5.2	11.9–12.4
5	CaSO ₄ ·2H ₂ O content, wt. %	20–29	65.0–90.0

The mineral composition of sludge wastes was evaluated according to the results of X-ray phase analysis (fig. 1).

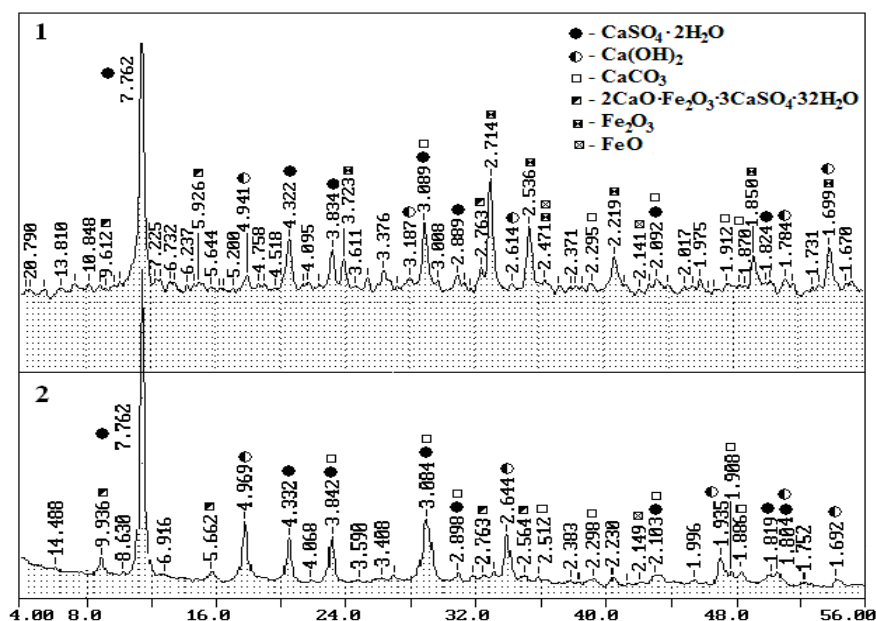


Figure 1. The X-ray pattern of sludges, generated in the setting of «EVRAZ Vanadii Tula»: 1 – FFC; 2 – LGC

The main crystalline phases are calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium carbonate (CaCO_3), the iron-containing components are wustite (FeO), hematite (Fe_2O_3), the sulphate form of hydrated calcium sulfoferrite ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) and the residual amount of lime (Ca(OH)_2) (fig.1) [17]. The other components, mostly metal oxides, are contained in the amorphized state, so they are not easy to identify.

The sludges under study were added to the raw charge in amount from 3 to 30% of weight. The cylindrical samples 3 cm high and 3 cm in diameter were prepared by plastic molding method from the raw mix, consisting of clay component and sludge materials. The molded samples were dried at temperature 20–22°C during 24 hours, and then at temperature 105°C to the constant weight. The baking of the samples was carried out in the electric muffle furnace at temperature 1000°C within 1 hour. The selection of the temperature mode was conditioned by the peculiarities of the raw mix mineral composition and the technological conditions of ceramic bricks production.

3. Results and discussion

The adding of sludge materials to the raw mix composition results in the alteration of the color of the obtained samples from red-brown to black-brown, which is caused by the increase of the total amount of iron compounds in the raw charge.

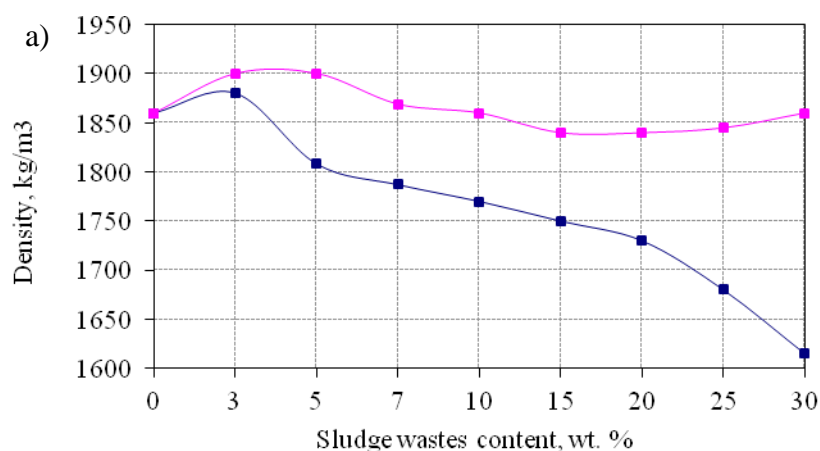
At the baking of samples, containing sludge materials, the following processes are observed: CaCO_3 is decomposed, forming CaO and gaseous CO_2 , gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is dehydrated, forming anhydrous calcium sulfate, and the multistage dehydration and decomposition of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ with the subsequent formation of CaO , Fe_2O_3 and CaSO_4 take place. All this is accompanied with gas release and liquid phase formation.

The FFC sludge, introduced to the raw mix, due to the high content of iron compounds in it, demonstrates mineralizing and fluxing properties. The mineralizing role of iron oxides in ceramic mixtures has been studied in a number of works [18–20]; it has been pointed out that the iron oxide is one of the most efficient additives. In the work [18] it has been demonstrated

that adding the iron oxide (chemically pure or in the form of iron-containing component) to a ceramic mixture allows obtaining at temperatures 1000–1050°C a ceramic body with low water absorption capacity. The iron protoxide compounds, being highly reactive, cause the early melting and the intensive formation of ferriferous silicate melts and glass, which contributes to the high compaction (sintering) of a ceramic body [18, 19].

In case of using the FFC sludge in the raw mix, due to the increased amount of iron compounds, during baking the processes of ferriferous silicate melts formation prevail. At the FFC content up to 5% the liquid phase is formed on the surface of the raw mix particles; it penetrates into the capillars, formed as a result of slight release of CO₂ and water vapor – the decomposition products of sludge components (CaCO₃, 2CaO·Fe₂O₃·3CaSO₄·32H₂O and CaSO₄·2H₂O) and clay minerals, and acts as a cementing binder, forming thin films at the phase contacts. The gases are bound with the melt and the pores are fixed as well. As a result, the more porous structure is formed, than in the control sample, and the water absorption capacity increases from 12.8% (in the control sample) to 13.31% (with 3% of FFC) with the slight increase of the compression strength – from 22.0 to 24.1 MPa (fig. 2), respectively. The formed porosity in terms of water absorption capacity value is close to the upper limit of the allowable values – 14%. Increasing the FFC sludge content to 30% causes the further intensification of liquid phase formation and gas generation, which results in the further pores formation in the samples (which increases the water absorption capacity) and the decrease of their strength properties.

At baking the raw mix, containing LGC, the processes of the intensive release of such gases as CO₂ and water vapor prevail, as the products of carbonate and sulphate components and clay minerals decomposition. This is accompanied with the formation of Fe₂O₃ and CaO, which are strong flux agents in clay-containing mixtures, as they form relatively low-melting compounds with Al₂O₃ and SiO₂. But the formed liquid phase is not enough to bind the gaseous products and to strengthen the pores, which ultimately results in the increase of porosity. At the LGC content of 3% the water absorption amounts to 13.8% and is close to limit values (fig. 2). With the increase of LGC up to 30% the intensive pore formation in the structure is observed, which results in the decrease of ceramic materials density and, consequently, the decrease of their strength characteristics.



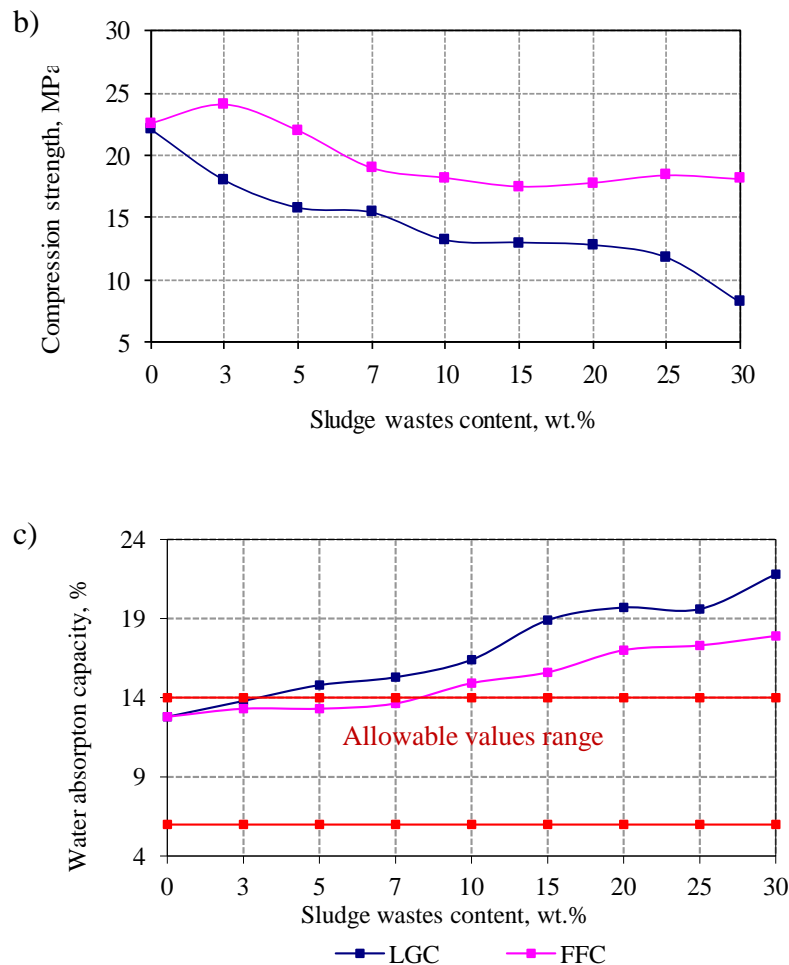


Figure 2. Alteration of physical and mechanical properties of walling ceramics samples with the use of LGC and FFC sludges:
 a – density; b – compression strength; c – water absorption

The porous structure of the ceramic brick, formed at using the FFC and LGC sludge wastes in its composition, causes the reduction of its heat conductivity, which results in the improvement of the finished product's thermophysical properties, but can affect the material's frost-resistance in the course of time.

Conclusion

So, the FFC and LGC sludge can be used in the raw charge for walling ceramics production without reducing its physical and mechanical characteristics only in amount of 5% and 3% of weight, respectively. The ceramic products with the increased content of sludge (up to 30%) are characterized with the increased porosity and the reduced physical and mechanical properties, so they can be used only as a structural and heat-insulating material.

So, the obtained walling ceramics samples with the use of LGC and FFC sludge wastes are characterized with various degrees of structure porosity and can't be used as facing bricks, but can be applied as structural and heat-insulating materials for making enclosing structures and interior partitions.

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