INTRODUCTION

Ceramic wall material is one of the most popular building materials in the Russian Federation. However, from 2015 to 2018 the production of wall ceramic decreased by 29%. According to official data from the Federal State Statistics Service of the Russian Federation, in 2014, 557 operating brick factories produced 8.7 billion conventional bricks, and in 2019 their number decreased to 310 with total capacity 5.9 million conventional bricks. One of the negative factors that held back the implementation of the national project “Housing and Urban Environment” was the COVID-19 pandemic. This affected the reduction of the ceramic brick share from 41 to 38% in the total demand for wall materials [1].

But, the implementation of a preferential mortgage program during the pandemic contributed to an increase in the production of ceramic bricks by 3% in 2019 and by 2% in the third quarter of 2020. A moderate increase in housing construction is predicted in 2022. Low real incomes of the population and purchasing power will remain a deterrent.

In recent years special attention has been devoted to aspects of the manufacture of black wall and black road clinker bricks. The characteristics of chromophores for volumetric staining of black bricks are given in [2], taking into account the availability for ceramic enterprises in Russia.

Black color is gradually coming into architectural style, but the main deterrent to the widespread use of wall ceramics and clinker bricks is their quite high cost, which includes expensive coloring pigments.

Wall ceramic in dark shades attracts attention, significantly increases the architectural and artistic merits of buildings and structures, and stands out against the overall architectural background.

The following types of black can be distinguished in the international RAL color matching system: graphite-black with different shades; black-gray, black-blue, black-olive, black-brown, and others.

In [2] it is noted that, taking into account tech-economic factors, the most preferred coloring compounds are: manganese spinel MnO \( \cdot \) Al\(_2\)O\(_3\) (galaxite); ferruginous spinel FeO \( \cdot \) Fe\(_2\)O\(_3\); ferromanganese spinel MnO \( \cdot \) Fe\(_3\)O\(_3\).

For staining in dark colors, waste from the extraction of manganese ores, containing manganese oxides in amounts 24.5 – 29.2 wt.% [3], was added into the ceramic bodies for obtaining wall ceramic.
In [4], (above 100%) 0.7 – 3.8 wt.% manganese-containing dye — manganese tetroxide — a product of the Manganese oxide Mn$_3$O$_4$ Color K/S line from Kimpe (France) was added into the composition of ceramic brick. At content 3.8 wt.% brick had a saturated black color. However, used as a coloring additive this stain significantly increases the cost of the final product. In this regard, the use of technogenic industrial waste for volumetric staining of wall ceramics is an important direction for their processing and disposal.

In a number of works for the production of a variety of building materials (ceramic and facing bricks, foam glass, concrete, porous artificial aggregates, composite glass- ceramic materials, and others), ash and slag waste from thermal power plants was used on the basis of numerous scientific studies [5, 6].

The work [7] examines the possibility of using solid fuel combustion wastes from thermal power plants in the Arctic zone of the Russian Federation. In its composition CHP waste contains iron oxides (5.93 – 7.37 wt.%) and titanium oxides (0.82 – 1.05 wt.%), which can be used for volumetric staining of wall ceramics.

Tailings of KMA ferruginous quartzites containing up to 11.34 wt.% iron oxides could be promising coloring components [8]. So, on glazing wall building materials with technogenic wastes of KMA by plasma melting, high-quality protective and decorative coatings of various colors, including black saturated color, are formed [9].

Expansion of the raw material base for volumetric staining of wall ceramics is an important area for recycling and processing of technogenic industrial waste.

**MATERIALS AND PROCEDURES**

The waste from the vanadium production at EVRAZ Vanady Tula JSC, which is the largest producer of vanadium pentoxide in Europe, served as the object of investigation. According to average estimates, In the process of obtaining vanadium up to 60 thousand tons of manganese-containing wastes, requiring disposal and processing, are generated per year. A promising direction for the recycling of this waste is to use the manganese (III) oxide, present in it, for volumetric staining of wall ceramics. It is assumed that on using red-burning clays, which contain a significant amount of iron compounds, jacobsite MnFe$_2$O$_4$ and bixbyite (Mn, Fe)$_2$O$_3$ will be formed. These compounds intensely color the wall ceramics black. It should be noted that manganese tetroxide can independently be used for volumetric staining of wall ceramics.

The chemical composition of the manganese-containing waste was determined by x-ray fluorescence using an APL 9900 Thermo scientific spectrometer (Switzerland). The radiation parameters of the spectrometer are: cobalt anode and K$_\alpha$ radiation at 60 kV. Differential thermal analysis of the waste was performed on a SETARAM TGA 92-22 thermal analyzer. The phase composition of the waste was investigated on an ARTXTRA Thenno Fisher Scientific diffractometer in the range 2$\theta$ = 4 – 64°. The powder diffraction patterns were deciphered using an ASTM file cabinet with a demo version of the Match program (Phase Identification from Powder Diffraction). The powder diffraction parameters were as follows: copper anode and K$_\alpha$ radiation at 40 kV.

**EXPERIMENTAL RESULTS AND DISCUSSION**

X-ray fluorescence analysis was used to investigate the chemical composition of the vanadium production waste (Table 1).

As can be seen from Table 1, the composition of the waste includes manganese (III) oxide, which can be used for volumetric staining of wall ceramic.

X-ray phase analysis showed that gypsum dihydrate is present as the main component of the waste; and manganese (III) oxide and a small amount of calcite are also present (Fig. 1).

Since the waste from vanadium production is supposed to be used for volumetric staining of wall ceramics, it was heat treated at 200, 500, 600, and 700°C. The scheme of phase transformations of gypsum dihydrate on heating is displayed in Fig. 2 [10].

These heat treatment temperatures were chosen for the waste because the endothermic effects of dehydration of a number of clay minerals lie in the range 105 – 600°C.

In the technology of wall ceramics, dehydration of clay minerals is observed during heat treatment of bodies based on red-burning kaolinite-hydromicaceous clays with an admixture of montmorillonite. The experimental data of differential thermal analysis of some clay materials are summa-
rized in the monograph [11]. According to the results of numerous investigations, on dehydration of kaolinite two endothermic effects are observed with low intensity in the temperature range 105 – 115°C and high intensity at 550 – 600°C. The dehydration of Illite is characterized by three low-intensity endothermic effects in the temperature range 110 – 125 and 540 – 580°C and moderate intensity at 890 – 910°C. On dehydration of nontronite, a mineral of the montmorillonite subgroup, two endothermic effects are observed: one at 140 – 150 and one at 480 – 580°C [11].

After heat treatment, x-ray phase analysis of heat-treated samples was performed (Fig. 3).

At 200°C dehydration of gypsum dihydrate occurs in the waste with partial formation of gypsum hemihydrate and anhydrite. With an increase in temperature to 500°C gypsum dihydrate completely transforms into the hemihydrate and the hemihydrate partially transforms into anhydrite. At 600 and 700°C the main phase in the waste from vanadium production is anhydrite (see Fig. 3).

The influence of the heating rate on the endothermic effects of dehydration of gypsum dihydrate and hemihydrate was investigated at heating rates 5 and 10 K/min (Figs. 4 and 5).

As can be seen from Figs. 4 and 5, two endothermic effects are observed during heating of the vanadium production waste. The first endothermic effect is associated with the dehydration of gypsum dihydrate with the formation of gypsum hemihydrate. The second endothermic effect indicates the dehydration of gypsum hemihydrate with the formation of anhydrite CaSO₄. The total weight loss is equal to 13.78% with heating rate 5 K/min and 13.32% with 10 K/min. With an increase in the heating rate, the endothermic effects shift to high temperatures.

Fig. 2. Scheme of phase transformations of gypsum dihydrate.

Fig. 3. Powder x-ray diffraction pattern of gypsum waste: ○) CaSO₄ · 2H₂O; □) CaSO₄ · 0.5H₂O; ▽) Mn₂O₃; ●) CaSO₄; a) on heating 200°C; b) on heating 500°C; c) on heating 600°C; d) on heating 700°C.
The first endothermic effect is equal to 119.1°C with heating rate 5 K/min and 138.7°C with heating rate 10 K/min.

The second endothermic effect leaves 644.7°C with heating rate 5 K/min and 683.6°C with heating rate 10 K/min.

Since the anhydrite melts and decomposes at quite high temperatures (more than 1350°C), its very low amount in the composition of wall ceramics (3 – 5%) will not greatly affect the strength characteristics of wall ceramic.

The investigations of vanadium production waste showed that, in terms of temperature intervals, during heat treatment the endothermic effects of dehydration are close to the temperature intervals of the endothermic effects of dehydration of kaolinite, illite, and nontrotite. This suggests that the sintering of clays is consistent with vanadium production waste. In vanadium waste, finely dispersed anhydrite can, to a certain extent, act together with free quartz and other minerals, act as a thinner of the ceramic body and help reduce shrinkage during drying and firing of wall ceramics.

CONCLUSIONS

A comprehensive investigation of manganese-containing waste from vanadium production was performed. Using the x-ray fluorescence method of analysis, a high content of manganese (III) oxide, equal to more than 17%, was established. It was found that vanadium waste is represented by gypsum dihydrate and manganese (III) oxide. It was shown that with the heating rate increasing from 5 to 10 K/min the endothermic effects of dehydration of gypsum dihydrate and hemihydrate are shifted to high temperatures and are in the temperature ranges of dehydration of clay minerals such as kaolinite, illite, and nontronite.

The phase composition of vanadium production waste at 200, 500, 600, and 700°C was investigated. It was proved that vanadium production waste can be used for volumetric staining of wall ceramics.

Manganese-containing vanadium-production waste can be recommended for use as an additive for volumetric staining in wall ceramics production plants.

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