Bottom sediments of wastewater treatment settling ponds system as a promising complex raw material

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Abstract. The paper considers the potential possibility of using sediments formed by settled suspended solids from settling ponds of the wastewater treatment system as a complex raw material. Leaching of pre-agglomerated suspensions with 2% sulfuric acid using 30% sulfuric acid as a binder in 90 days made it possible to extract 36% of copper and 55.7% of nickel. The sorption properties of fired granules made with the use of sulfite-alcohol stillage as a binder in relation to copper and nickel ions have been demonstrated. In the first few days of the experiment, it was possible to adsorb 68-73% nickel and 90-92% copper from the model solution supplied to the percolator. The possibility of obtaining a brucite-containing sorbent by hydrochloric acid opening of the initial material of suspensions and its use for purifying model solutions from fluorine ions with an efficiency of up to 62% is shown.

1. Introduction

Over the past several decades, the world has seen a steady decline in the quality of ores supplied for processing. Revision and improvement of existing enrichment technologies require a lot of time and money. The search for new sources of raw materials is also becoming an urgent task. Waste generated in the course of mining operations, off-balance ores or poor ore material can become thus raw materials.

On the territory of the Russian Federation, over 300 thousand hectares of land are occupied by technogenic waste, about 100 billion tons of waste have been accumulated in dumps and tailings [1, 2]. Large mining enterprises are located in the Murmansk region: JSC Kola MMC, JSC Kolvorsky GOK, JSC Apatit and others. The region annually stores more than 200 million tons of mining waste (MWP) - off-balance ores, waste dumps, tailings and slags, the total volume of which has reached about 8 billion tons by now.

Maintenance of dumps of overburden and slag, tailing and sludge storage requires significant capital and material costs. Large areas of land are removed from economic circulation for a long time [3, 4].

In a number of works [5, 6], technologies are presented that make it possible to extract valuable components from the tailings of concentration of copper-nickel ores at Kola MMC. At the same time,
such raw materials as flotation tailings make it possible to obtain a sorbent based on them, and then use them for purification of industrial effluents.

The purpose of this work is to consider the fundamental possibility of using suspended solids settled in the settling ponds of the Kola MMC, Zapolyarny, both as a technogenic raw material in a geochemical barrier for the purpose of wastewater treatment, and for additional extraction of non-ferrous metals.

2. Materials and methods

The object of the study was bottom sediments formed by suspended solids deposited in the sedimentation ponds of the mine waters of the Severny mine at Kola MMC. Samples were taken in 2016 during the reconstruction of ponds.

![Figure 1. Dried pond at the Severny mine, Kola MMC.](image)

According to the results of X-ray phase analysis, typical minerals are: calcite CaCO3, quartz SiO2, chlorite (Mn, Al) 6 (OH) 8 ((Si, Al) 2, enstatite Mg2Si2O6, antigorite (Mg, Fe) 3Si2O5 (OH) 4, talc Mg3Si4O10 (OH) 2, forsterite Mg2SiO4, montmorillonite (Na, Ca) 0.3 (Al, Mg) 2Si4O10 (OH) 2 × nH2O, magnetite Fe3O4, chalcocite Cu2S, pentlandite (Fe, Ni) 9S8, and pyrrhotite Fe1-xS.

Two possible directions of using the investigated material are considered: for additional recovery of non-ferrous metals and for obtaining a sorbent for wastewater treatment.

According to the results of atomic adsorption spectrometry of the samples opened by the open acid method, it was found that the bottom sediments of the ponds contain 0.32% nickel and 0.16% copper, which makes it possible to consider the studied material as poor ore, since such contents are typical for heap leaching objects [7-9].

From the experience of working with similar types of waste, it is known that after a certain treatment they can also be considered as sorbents for non-ferrous metals [6].

![Figure 2. Dried bottom sediments (a) and sediment pellets (b).](image)
The material was pre-granulated using SSB as a binder, followed by firing in a muffle furnace (700°C, 2 hours) to obtain a sorbent (figure 2). For the subsequent leaching, two batches of granules were made using a 30% sulfuric acid solution as a binder. One of the batches was additionally treated with an oxidizing agent solution (ferric iron). The resulting granules were in the form of compressed tablets 3-4 mm in diameter, and 1-1.5 mm thick.

Then the granules were placed in glass percolators.

To test the possibility of using suspensions as a technogenic raw material for the extraction of non-ferrous metals, two batches of granules (initial and with the addition of ferric iron) were leached with a solution of 2% sulfuric acid. To study the sorption properties of fired granules, a model solution prepared from copper and nickel sulfates containing 1 g / L of Cu2 + and Ni2 + ions was fed into the percolator.

At the outlet, the volume of solutions, pH, Eh were recorded, the filtrate was analysed for the content of copper and nickel.

The experiment lasted 90 days.

3. Results and discussion
The results of an experiment on sulfuric acid leaching of granules from suspended solids from settling ponds of JSC Kola MMC are shown in figure 3. For 90 days of treatment with a sulfuric acid solution of untreated granules, it was possible to extract 55.7% nickel and 36% copper. The pH of the solutions practically did not change and amounted to 1.2-1.3, Eh decreased from 490 to 402 mV.

Pre-treatment of the granules with an oxidizing agent solution did not lead to an intensification of the process: over 90 days, the extraction of copper and nickel was 28.5 and 52.47%, respectively.

X-ray phase analysis of the granules at the end of the experiment did not reveal peaks of sulfides in the diffractogram. Separately, it should be noted that the granules by the end of the experiment practically did not collapse, and the filtration characteristics worsened slightly.

Figure 3. Extraction of copper and nickel depending on the leaching time,%. Raw granules.

Figure 4. Sorption of copper and nickel ions from model solutions,%. 
The results of the experiment to assess the sorption properties of fired granular suspensions in relation to non-ferrous metal ions are shown in figure 4. During the first ten days, the sorption of copper ions was at the level of 90-93%, nickel - 70%, then it gradually decreased. On the 90th day, about 54% Cu and 29% Ni were extracted from the model solution.

The dissection of the granules showed that the material is being enriched in terms of copper and nickel to contents comparable to industrial ones. Thus, the copper content in the granules in the upper part of the columns increased to 0.9%, in the lower - to 1.6%. Nickel content also increased from 0.32 to 0.84% and 1.22% at the top and bottom of the column, respectively.

By the well-known method of hydrochloric acid processing, previously applied to the tailings of concentration of vermiculite and copper-nickel ores [10], it was possible to obtain a brucite-containing reagent from the material under study. Figure 5 shows an X-ray pattern of the sample. Peaks of brucite, calcite and halite are noted.

![X-ray diffraction pattern](image)

**Figure 5.** X-ray diffraction pattern of a sorbent obtained by hydrochloric acid digging from bottom sediments of settling ponds of JSC Kola MMC. Reflexes: 1 - brucite, 2 - calcite, 3 - halite.

Previously, similar sorbents were tested by us for purification of waste water from fluorine ions [11]. Trial experiments with samples obtained from the test material showed relatively good results. At a consumption of 1 g / L of the reagent thermally activated for two hours at a temperature of 500 °C under static conditions, in one hour, it was possible to purify model solutions containing 10 and 100 mg / L of fluorine ions by 36 and 62.2%, respectively.

4. Conclusion

In the course of the experiment on considering the bottom sediments of the settling ponds of the enterprise as a technogenic raw material, by leaching pre-agglomerated suspensions with a solution of sulfuric acid, it was possible to extract 55.78% of nickel and 35.3% of copper in 90 days.

The possibility of using fired granules as a sorbent for non-ferrous metals in wastewater treatment is also shown.

The material may also be promising for obtaining a brucite-like sorbent for purifying wastewater from fluorine ions.

In the future, it is necessary:
- to study the conditions of material preparation for processing by various methods of metal sorption;
- to investigate the sorption properties of fired granules for purification of waste water from non-ferrous metal ions;
- to investigate the sorption properties of brucite-like sorbent in relation to fluorine and non-ferrous metal ions for wastewater treatment.
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