Possible use of processed ferromanganese concretions for production sewage purification

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Abstract. This article describes a possible scenario for ferromanganese concretions usage as a sorbent for purification of wastewater obtained from mining enterprises. To study the chemical and physicochemical properties of iron-manganese nodules, the methods of tomography and X-ray phase analysis were applied. The data obtained during the experiments can be used for a more detailed study of ferromanganese nodules of various deposits, for their use as a sorbent.

1. Introduction
Sewage is produced by all mining enterprises. Most of the enterprises dump sewage in nearby reservoirs that will eventually lead to environmental disaster. In this regard, penalties are increased and measures for sewage dumping become tougher [1]. However, according to researches [2], pollution of water reservoirs of the Russian Federation increases.

Huge variety of the existing chemical compositions of water systems, conditions of their formation and the necessity of individual researches for each case makes waste water purification from phenols, cyanides, oil products and surfactant almost impracticable task [3-8]. The majority of efficient ways of deep cleaning are associated with economic and resource expenses, usage of scarce reagents with its subsequent regeneration, utilization or waste disposal. Therefore, search for new efficient ways of sewage purification is still relevant [9-14]. Its implementation will allow one to reduce negative impact on environment and to decrease investment and operational expenditure for environmental actions.

A great number of enterprises have water treating facilities [15-17] which, however, are not capable to cope with the amount of pollutants in drains. To choose the optimal sewage disposal method one should take into account sewage characteristics and the possibility of pollutants extraction.

2. Materials and methods
There are a lot of ways for sewage disposal. Destructive methods of sewage disposal comprise oxidizing methods, thermooxidizing, electrochemical oxidation and hydrolysis [18-22,28]. Copper, manganese and their compounds, as well as metals of variable valency mainly of the VIII group, their oxides and salts are used as catalysts. This leads to repeated pollution of drains. One of the most widespread and inexpensive purification methods is sorption. Any sorbent has to correspond to the following characteristics: high sorption capacities, high reagent resistance to acids and alkalis. The sorbent has to be low-toxic or non-toxic, it has to possess low abradability, high mechanical strength, and low prime cost [23, 24].
Table 1. FMC sample parameters: specific surface area, porosity, etc.

| Characteristic                        | Quantity       |
|---------------------------------------|----------------|
| Specific area capacity                | 3116 mm$^2$/g  |
| Number of closed pores                | 46564          |
| Specific volume of closed pores       | 3.2 mm$^3$/g   |
| Specific surface area of closed pores | 345.9 mm$^2$/g |
| Occluded porosity                     | 0.64 %         |
| Total specific volume of occluded porosity | 2620.5 mm$^3$/g |
| Open porosity                         | 84.11 %        |
| Total specific volume of pore space   | 2623.7 mm$^3$/g|
| Common porosity                       | 84.21 %        |

Ferromanganese concretions (FMC) are one of the most perspective sorbents, due to its low prime cost in comparison with other sorbents [25]. FMC distribution territory is quite large: from the Arctic tundra to tropics [3]. FMC chemical and phase composition is quite diversified, and is able to change depending on the deposit and depth of its burial, as well as on the time of their formation.

Table 2. Chemical composition of ferromanganese concretions of various deposits [25, 26].

| Element | Mass fraction % | Element | Mass fraction 10$^{-4}$ % |
|---------|-----------------|---------|---------------------------|
| Fe      | 19.97           | Ni      | 228                       |
| Mn      | 12.4            | Co      | 120                       |
| P       | 0.94            | Cu      | 52                        |
| Si      | 11.0            | Zn      | 166                       |
| Al      | 2.0             | Mo      | 254                       |
| Ca      | 1.35            | Pb      | 36                        |
| Mg      | 0.83            | Ba      | 2500                      |
| K       | 1.36            | V       | 114                       |
| Na      | 1.0             | W       | 36                        |
| CO2     | 1.65            | Ge      | 1.5                       |
| Corpr   | 1.25            | Ga      | 11                        |
| S       | 0.08            | Cr      | 50                        |
| Ti      | 0.22            | Zr      | 93                        |
| Mn/Fe   | 0.62            | Hf      | 2.2                       |
| Ta      | 0.5*10$^{-4}$   | Sr      | 410                       |
| As      | 327*10$^{-4}$   | Rb      | 62                        |
| Th      | 5.2*10$^{-4}$   | Cs      | 2.5                       |
| Ra      | 15.4*10$^{-4}$  | Sc      | 6                         |

The surface morphology of FMC ore is heterogeneous (Figure 1), some part of the surface has dense texture formed from globules, having pores of micron size between globules. Sample morphology is more bulky at the FMC granule cleavage than at its surface. Also Figure 1 presents tomographic images of FMC sample, which show specific surface and porosity of structure.
Figure 1. Tomography of FMC sample.

The concretions phase composition was defined by x-ray diffraction method using Shimadzu XRD-7000. The graphs presented in Figure 2 show that the main crystal phase of concretions is manganese oxide. By comparing this result with data from Table 1, one can conclude that iron-containing component of concretions is in X-ray amorphous state. Usually X-ray amorphous hydroxides have a developed surface and, as a result, high sorption capacity.

Figure 2. X-ray diffractometry of the FMC sample.

3. Results and discussion
According to the results of X-ray diffractometry, the ferromanganese concretion samples are completely amorphous.

Ferromanganese concretions are extracted in order to obtain manganese concentrates and iron oxides. The samples less than 0.01 mm are dumped. This fraction can be used as a sorbent. Thus usage of ferromanganese concretions as a sorbent for sewage disposal is perspective and low-cost [26,29].

Table 3. Results of FMC usage as a sorbent for the reference pollutants of sewage from metallurgical enterprises [27].
The method is based on oxidizing adsorption using ferromanganese concretions of the Finnish Gulf, which possess an oxidizing function and catalytic properties [24]. The sewage purified using FMC might contain suspended matters, heavy metals and oil products. These pollutants do not influence the FMC oxidizing ability. During sorption of cations of heavy and non-ferrous metals on FMC, there is no decrease in sorbent capacity, as the process is driven by ion-exchange mechanism. Thus, the presence of heavy metals cations in sewage does not have an impact on oxidizing ability of FMC.

4. Conclusion

Ferromanganese concretions have high specific surface area, due to the structure amortization due to a large number of pores and roughnesses of structure, which are able to act as active sites. The FMC chemical composition is composed of amorphous forms of manganese and iron oxides, which are a catalyst and an oxidizer. This increases sorption capacity of FMC and, as a result, increases sorption capacity of a sorbent based on it. Therefore FMC is reasonable to be used as a sorbent for sewage treatment.

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