THE TECHNOLOGY OF OBTAINING MODIFIED SORBENTS BASED ON SILICATE PRODUCTION WASTE

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Abstract. The article deals with the problem of rational use of waste of enterprises for the production of silicate cement. Currently the production gliezh waste (burnt clay) does not find its application and is disposed of. A method of obtaining a sorbent based on the gliezh waste is suggested, the aluminium oxide content in which ranges from 15 to 40 % and silicon oxide – from 55-75 %. Pre-burnt clay is treated with sulphuric acid, and then calcined in a muffle furnace at \( t = 300 \) °C. The resultant sorbent has high rates of wastewater treatment from heavy metals.

Key words: sorbent, sorption material, secondary material resource, modified sorbent, wastewater treatment.

1. Introduction.

Waste water of metallurgical and thermal power plants often exceeds the maximum permissible concentrations of harmful substances. The search for effective methods to control harmful emissions into the environment is an urgent task of the modern world. One of these methods is the use of sorbents. They are often used in heat power plants for purification of petroleum products [1–6]. The heavy metal ions, ammonium salts, phosphates, chlorides and other compounds contained in them also cause environmental damage to the environment. Therefore, the use of sorbents helps to significantly reduce the level of hazardous substances to the maximum permissible concentrations. At the same time, methods and technologies of modification of the sorption material are constantly being searched for in order to improve the efficiency of wastewater treatment and obtain economic benefits [7–13]. Thermal and chemical types of sorption material treatments, as well as their combination, are widely used.

The search for ways to modify sorbents is often associated with the use of production waste [1, 6, 7, 11–15]. Environmental friendliness of the solution is achieved not only by cleaning water environments, but also by reducing the impact of waste materials on nature [13]. In this paper the technology of the gliezh modification, a residue from the production of silica brick is considered.

2. Materials of research

A sample of raw material based on the gliezh for the production of sorbents with the selective ability to extract heavy metals has been studied. The general characteristics are given in Table 1, where the main parameters are the sorption capacity and the degree of extraction of the pollutant.
Table 1. General characteristics of the studied sample

| Indicators                                           | The studied sample |
|------------------------------------------------------|--------------------|
| Base                                                 | Gliezh             |
| Type                                                 | 1.15-1.3 mm free-form granules, white - cream color |
| Sorption capacity (absorption capacity) for copper, mg / g | 15.79–26.7        |
| Application temperature, °C                          | +4...+25           |
| Degree of heavy metal extraction                     | 80.5 %             |
| Cu                                                   | 62 %               |
| Fe                                                   | 86.6 %             |
| Pb                                                   | 92.9 %             |
| Maximum dose of sorbent, g/ l                        | 5.0–12.8           |
| Dose of discharged sorbent, mg/l                     | 0.83               |

The gliezh-based clays used for the aluminum sulfate production are to contain a significant amount of kaolinite and are to be easily decomposed by acids. Kaolinite clays containing 15–40 % Al₂O₃, 55-75% SiO₂, 1-2% Fe(III) 0.5–1 % Fe(II) meet these requirements. As a sample, grey clay was used, the main fraction of which is SiO₂ quartz (d = 3.33, 2.45, 1.81 Å), and diffraction peaks relating to kaolinite Al₂O₃·2SiO₂·2H₂O (d = 7.10, 3.56 Å) and to feldspar with d = 3.23, 3.18 Å are observed. In addition, impurities of muscovite are available in clays (d = 9.9, 4.95 Å). A diffraction pattern, made with the help of the D8 ADVANCE diffractometer (Bruker, Germany) is shown in Fig. 1. The results of the thermal analysis carried out with the help of the synchronous thermal analysis STA 449 F1 Jupiter (NETZSCH, Germany) device are presented in Fig. 2.

![Fig. 1. The diffraction pattern of the initial grey clay sample: v – Quartz (SiO₂), + – Kaolinit, • – Feldspar, o – Muscovit](image-url)
Fig. 2. Thermogram of the initial sample of grey clay

In this case deep endoeffect at 500–600 °C is observed in the DSC curve related to the $\text{Al}_2\text{O}_3$ $2\text{SiO}_2\cdot2\text{H}_2\text{O}$ kaolinite – there is an allocation of water from the hydroxyl groups, the process of the kaolinite amorphization is taking place and the mass of the sample (TG curves) is reduced by 5.57 %. The content of the kaolinite calculated according to the graphs, is about 39.9 %. The clay chemical composition is given in Table 2.

Table 2. Chemical composition of the initial sample, mass %

| Sample     | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO  | SO$_3$ | Na$_2$O | K$_2$O | TiO$_2$ |
|------------|---------|-------------|-------------|------|------|--------|---------|-------|--------|
| Grey clay  | 7.65    | 68.02       | 19.90       | 0.90 | 0.19 | 1.09   | 0.12    | 0.13  | 0.98   | 0.1    |

3. The experiment methodology

A portion of the clay is ground and calcined in a muffle furnace at a temperature of 750–800 °C for one hour. The resultant cake is cooled, crushed and then treated in sulphuric acid for leaching of Al2O3. Concentrated sulfuric acid is added in excess (105% of the stoichiometric ratio), then diluted with water and stirred at a temperature of $\approx$ 100 °C. The resulting solution is decanted; the sludge is washed with hot water to extract aluminum sulfate. Wash water is added to the solution, filtered, evaporated in a water bath until a thick mass is formed. Then the thickened mass is calcined in a muffle furnace at a temperature of 300 °C, obtaining a white crumbly mass consisting almost of pure aluminum sulfate.

The calculation of the characteristics of sorption materials was carried out by the following method:

1. The maximum dose of sorbent is determined by the formula:

$$ D_{sb}^{\max} = \frac{c_{en} - c_{ex}}{a_{sb}^{\min}} $$
where \( C_{en}, C_{ex} \) – concentration of petroleum products in the source and filtered water, \( a_{sb}^{\text{min}} \) – the minimum sorption capacity of the sorbent, defined as \( a_{sb}^{\text{min}} = 253\sqrt{C_{ex}} \); 

2. Maximum sorption capacity

\[
a_{sb}^{\text{max}} = 253\sqrt{C_{en}}.
\]

3. Dose of sorbent discharged from the adsorber

\[
D_{sb} = \frac{C_{en} - C_{ex}}{K_{sb} \cdot a_{sb}^{\text{max}}}
\]

where \( K_{sb} \) – the degree of exhaustion of the capacity of the sorbent. According to the experimental data \( K_{sb} = 0.5 \).

4. The approximate height of the load, which ensures the cleaning of the drains, is determined by the formula:

\[
H = \frac{D_{sb}^{\text{max}} \cdot t_{ds}^{\text{op}}}{k_{ds} \cdot a_{sb}^{\text{max}}}
\]

where \( t_{ds}^{\text{op}} \) – the approximate duration of operation of the plant to the skip; \( k_{ds} \) – the specified degree of exhaustion of the sorbent capacity.

5. The degree of extraction of metals is defined as

\[
R = \frac{(C_1 - C_2)}{C_1} \cdot 100\% ,
\]

where \( C_1 \) is the initial concentration of metal in the solution; \( C_2 \) is the concentration of metals in the filtrate.

4. Results of research and discussion

The diffractogram and the thermogram \( \text{Al}_2(\text{SO}_4)_3 \) are shown in Fig. 3 and 4, respectively. The sludge remaining after decanting and washing with water is quartz containing minor impurities of calcium, aluminum and iron compounds (0.1 %). The diffractogram of the sludge is shown in Fig. 5.

Thus, the presented clays are suitable for the production of coagulant – aluminum sulfate and sludge used to produce microspheres. The results of the use of the modified sorbent are presented in Table 3. The degree of extraction of metals is given in Table 4. The number of experimental lines-6. The error of experimental studies is 5 %, which characterizes a sufficiently high degree of reliability of the results.

Table 3. The results of experimental research

| Pollutants     | Before treatment | Substance concentration, mg/l | After treatment with small particle gliezh in suspended layer | After treatment with large particle gliezh filtering |
|----------------|------------------|-------------------------------|-------------------------------------------------------------|-----------------------------------------------------|
| Pb             | 7–7.5            | 8–10                          | 9–10                                                        |                                                     |
| Copper (Cu)    | 5                | 1.8                           | 1.9                                                         |                                                     |
| Iron (Fe)      | 13.5             | 0.15                          | 1.8                                                         |                                                     |
| Plumbum (Pb)  | 0.7              | 0.002                         | 0.05                                                        |                                                     |
Fig. 3. The diffraction pattern of aluminium sulphate: A – Al$_2$(SO$_4$)$_3$

Figure 4. Thermogram of Al$_2$(SO$_4$)$_3$ aluminum sulfate
Fig. 5. The sludge after the decomposition of the clay with sulfuric acid: $\gamma$ – Quartz (SiO$_2$)

Table 4. The degree of extraction of metals

| Pollutants   | The degree of extraction of metals, % | After treatment with small particle gliezh in suspended layer | After treatment with large particle gliezh filtering |
|--------------|--------------------------------------|-------------------------------------------------------------|---------------------------------------------------|
| Copper (Cu)  |                                      | 64                                                          | 62                                                |
| Iron (Fe)    |                                      | 98.9                                                       | 86.7                                              |
| Plumbum (Pb) |                                      | 99.7                                                       | 92.9                                              |

5. Conclusion

It is obvious that sorbents on the basis of gliezh are possible to use in the treatment of wastewater from heavy metals (waste water of metallurgical complex), in the treatment of waste water of the energy complex, as well as for the oil refining industry at the stage of reservoir water preparation.

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