The surface-active properties of waste processing of tin ore raw materials

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Abstract. The article presents the results of a study of the surface-active properties of tin ore wastes due to their impact on the environment and public health. The object of the study is the ore dressing waste from the closed mining enterprise “Solnechny GOK” of the Khabarovsk region of the Far Eastern Federal District. Sodium oxalate, Trilon B, methylene blue, sodium humate were used as sorbates. Methods of establishing the fact of interaction of waste with sorbates focused on the discoloration of colored complexing agents in the presence of waste. The use of titrimetric methods allowed us to establish the number of reaction centers of waste. To determine the nature of the active centers of the waste, foam quenching formed by anionic and non-ionic surfactants was applied. The effect of the molar mass and the structure of sorbates on the nature of their interaction with the surface of the waste is shown. Low molecular weight sorbates promote the formation of soluble complexes of heavy metal compounds and contamination of groundwater. High molecular polydentate complexing agents form surface films. The revealed physicochemical properties will make it possible to predict an increase in the probability of contamination of groundwater with low molecular weight organic complexing agents, as well as the probability of a better fixation of soil on waste in the presence of high molecular weight organic substances of the soil absorption complex.

1. Introduction

Many non-reclaimed tailings containing toxic waste were abandoned as a result of intensive development of tin ore raw materials in the Far East and the subsequent bankruptcy of mining and processing plants in the region [1]. They pose a great threat to the environment [2, 3]: as a result of “dusting” and the release of sulfur-containing gases, the pollution of soils, rivers, sources of drinking water, and snow cover by heavy metal compounds regularly occurs. As a result, there is a decrease in the germination of seeds of wild plants and the deterioration of the health status of the population of nearby settlements. Land withdrawal, reduction of green mass reproduction and, accordingly, a decrease in the oxygen content in the air contributes to the formation of a hypoxide regime in the region. Far Eastern scientists are fully aware of the consequences of the negative impact of repositories of waste processing of mineral raw materials on the environment and the need to eliminate this effect [4, 5].

Disposal of a huge amount of waste dispersed throughout the region [6] requires an economically, environmentally, and technologically optimized system approach [7] when developing a program of activities aimed at reducing the negative impact on the ecosphere. When developing such a program, a comprehensive study of the properties of waste is necessary to select the most efficient and effective
ways to neutralize them. It is proposed to use them as a secondary raw material, during reclamation, treatment with the purpose of neutralizing polluting components, isolation from the environment.

The physicochemical state of the objects of technogenic origin, the trends of this state in time and space, the processes occurring in the waste, are characterized by a number of indicators: acid-base and redox pH - Eh, the mineral composition of groundwater, the formation of new mineral forms [8]. One can also give an example of the study of technological properties (binders) of mineral processing waste [9,10]. The surface-active properties of dispersed solid waste provide a significant contribution to the complex of properties inherent in this object. Properties such as adhesion, wettability, physical and chemical adsorption are associated with surface phenomena and processes [11]. For highly dispersed solid phases, surface processes cause the phenomena of coagulation, sedimentation, and foam quenching [12]. As a rule, adsorption processes are accompanied by the release of heat. The amount of heat released depends on many factors: the state of the surface, the mechanism of adsorption, competitive processes, wettability and others. Chemical adsorption can lead to significant changes in the state of the waste [13]. This may be due to the appearance on the surface of insoluble films of chemical reaction products. By chemical nature, these can be metal oxides and hydroxides, salts and complex compounds, both soluble and formed as a soil-absorbing complex [14, 15]. Surface processes can reduce the “dusting” of waste due to changes in the physico-chemical nature of the surface. The surface modified in a certain way may contribute to the fixation of humus compounds on it, which will contribute to soil formation in the recultivation process. The presence of complexing agents can in two-ways affect the waste. The formation of soluble complexes with small ligands and large stability constants facilitates the transition of metals from stationary mineral forms to mobile ones, which contribute to the pollution of the hydrosphere. Organic acids of plants, such as oxalic acid, are complexing agents of this type. On the other hand, a polydentate chelate-type organic complexing agent with a large molar mass can form organo-mineral layers due to chemisorption, which impede the migration of waste components to the environment. From the above, it follows the relevance of the study of the surface-active properties of waste processing of tin ores in connection with their influence on the state and processes in these man-made formations.

2. Objects and Methods
Waste processing of tin ores of the former mining and processing plant “Solnechny” of the Khabarovsky region served as objects of research. Organic substances with different molar masses and polydentate capacities were chosen as ligands [16]: sodium oxalate 0.05 n, trilon B 0.05 n, methylene blue dye 0.01%, sodium humate 0.01%. In order to study the effect of acidity of the environment on the surface activity of waste in the aquatic environment and 0.01 n and 0.1 n $\text{H}_2\text{SO}_4$ and 0.01 n NaOH environments, 30-minute contact of 1 g of waste with ligand solutions was carried out.

Chemical methods used for the study: direct and reverse titrimetry. Stained solutions of ligands (methylene blue and sodium humate) from the burette were gradually added with stirring to a titration flask containing 1 g of waste in an appropriate medium (aqueous, acidic or alkaline) until a permanent, non-disappearing ligand color appeared. Colorless ligands (sodium oxalate and Trilon B, 0.05 n) were added in precisely measured quantities to 1 g of waste in a glass, the appropriate medium was added and kept in contact for 30 minutes while stirring. Then the solid phase was separated on the filter “red tape,” after which the filtrate was titrated with reagents: sodium oxalate - with a solution of $\text{KMnO}_4$, 0.05 n. in an acidic environment; Trilon B - $\text{MgSO}_4$ solution in ammonia medium with eriochrome black indicator. More research was needed to explain the behavior of sodium oxalate. To identify the fact and nature of the interaction of sodium oxalate with waste, we used its recovery and complex formation functions. This fact allows us to conclude that the oxalate ion forms soluble complexes with metal cations of the waste and then extracts them into the aqueous phase.
3. Results and Discussion

Titration with KMnO₄ allowed to establish that after contact with waste almost all sodium oxalate passed into the filtrate and was not fixed on the surface of the waste. By titration with Trilon B, an increase in the concentration of metal cations in the water-oxalate extract (568 mmol / kg) compared with the water (2.5 mmol / kg) was established. According to the results of titration, the amount of ligands absorbed per 1 kg of waste was calculated (Table 1).

Table 1. The results of determining the amount of mmol (mg) of ligands in the reaction on the surface after contact with 1 kg of waste tin ore processing.

| Ligands         | M.m. g / mol | The number of adsorbed ligands, mmol (mg) per 1 kg of waste |
|-----------------|--------------|---------------------------------------------------------|
|                 |              | H₂O  | 0,1 n H₂SO₄ | 0,1 n H₂SO₄ | 0,01 n NaOH |
| Na₂C₂O₄         | 134          | 0,0  | 0,0         | 0,0         | -           |
| Trilon B        | 336          | 40 (13448) | 11,5 (3864) | 67 (22512) | 39 (13104) |
| Methylene Blue  | 320          | 0,734 (235) | 0,640 (205) | 0,734 (235) | 0,672 (215) |
| Sodium Humate   | More 5-6 thous. | -   | (795) | (490) | (320) |

An analysis of the results suggests the following:
- The molar mass of the ligand is only relevant if it reflects the size of the molecule. The more complex the molecule and the more donor centers it has, the fewer moles would be placed on the surface of the waste.;
- Low molecular weight ligands of small size may not be fixed on the surface of the waste, but rather contribute to the extraction of metal cations from them due to the formation of soluble complexes. Thus, the presence of organic acids of plant origin can stimulate the migration of toxic metal cations into the hydrosphere, thereby increasing environmental pollution.

Neutral and weakly acidic environments are most favorable for the formation of surface complex compounds. An increase in acidity contributes to the process of surface sorption, probably due to the dissolution of oxide-hydroxide and carbonate forms and the formation of surface complexes in their place. Alkalization of the medium reduces the amount of sorbed molecules, probably due to the formation of insoluble bases on the surface. To test the assumption that cations serve as active centers of complex formation, which are part of minerals, studies were conducted to establish their anionic or cationic nature by quenching foam formed by anionic and non-ionic surfactants. Stearox (4%) was chosen as an anionic surfactant, and prevotsel (4%) as non-ionic. Preliminary tests showed that tailings waste has the property to extinguish foam formed by surfactants. During the experiment, different amounts of waste were used and the height of the column of foam in the cylinder was measured in time. The results of these measurements are presented in table 2.3.

Table 2. Foam heights h (mm) in the presence of stearox and prevotsel in different environments.
Table 3. Changes in foam height after 400 seconds (Δh) mm as a result of the addition of different masses of waste in the environments.

| Surfactants | Environment | 0.0 g | 0.1 g | 0.5 g | 1.0 g |
|-------------|-------------|-------|-------|-------|-------|
| Stearox     | H₂O         | 780   | 610   | 840   | 430   |
|             | H₂SO₄       | 650   | 1170  | 1050  | 1000  |
|             | NaOH        | 740   | 550   | 630   | 630   |
|             | H₂O         | 330   | 200   | 250   | 290   |
| Prevotsel   | H₂SO₄       | 200   | 180   | 180   | 170   |
|             | NaOH        | 335   | 330   | 370   | 360   |

Also, it can be argued that the tin ore raw waste mass has practically no effect on the damping of the foam of both surfactants, which may indicate that the surfactant properties exhibits mostly finely divided waste phase; therefore, it is necessary to investigate and take into account the dispersion composition of tailings.

With respect to the surfactants studied, the waste exhibits the ability to quench the foam, and for anionic stearox the effect is more significant than for non-ionic prevotsel (Figure 1).

Figure 1. Dependence (Δh) mm for a period of 400 s. by mass of sand for all environments and two surfactants.

The acidic environment enhances the foam quenching effect in the case of stearox, which can be explained by dissolving oxide hydroxide and carbonate forms, as a result of which the number of cationic centers increases on the surface of the waste. The alkaline environment somewhat reduces the effect of quenching of the foam, which may be the result of blocking cationic centers as a result of the formation of insoluble metal hydroxides.
An inverse relationship is observed for non-ionic surfactants – prevotsel: the alkaline medium slightly enhances the effect of quenching of the foam, and the acidic environment, on the contrary, reduces it. Apparently, this is due to the ionization of the phenol groups of prevotsel, which is a surfactant based on ethoxylated alkylphenols of the type OP-10 [17]. Apparently, this is due to the ionization of phenol groups of prevotsel, a surfactant based on ethoxylated alkylphenols of the type OP-10.

The significant effect of waste tin ore processing on the stability of the foam formed by anionic Stearox indicates the prevalence of cationic active centers on the surface of the waste. The adhesive properties of the waste in relation to plant materials were investigated on smooth white writing paper (cellulose), and their manifestation was established qualitatively by comparing the chromaticity of the paper surface after a layer of waste stays on it for 5 minutes. The surface acquired a yellowish color, characteristic of highly dispersed sulfur (sulfur color), which was not washed off with a stream of water. A detailed study of the adhesion process was not conducted, but a preliminary qualitative study suggests consideration of the question of the participation of adhesion in the pollution of plant cover.

Based on the revealed facts, it can be concluded that the study of the surface-active properties of waste processing of tin ores in the Far Eastern region should be continued, given their ability to hold complex organic substances on their surface when developing and implementing of measures for remediation and compensation of environmental damage accumulated during the industrial period. The surface-active properties of the waste can contribute to the health of the population of nearby settlements, in the case of the use of modern biotechnology, for example, with the use of the drug “Polysorb”.

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