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## Research of Surface-Active Properties of Waste of Processing of Tin Ores

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# Research of Surface-Active Properties of Waste of Processing of Tin Ores

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**Abstract.** The object of research is the waste of enrichment of ores of the closed mining enterprise "Solnechny GOK" of the Khabarovsk territory of the Far Eastern Federal district. The article discusses the results of research of surface-active properties of waste of enrichment of tin ores due to their impact on the environment and public health. Sodium oxalate, trilon B, methylene blue, sodium humate were used as sorbates. Methods for the determination of interaction of waste with the sorbates – thermal effect and discoloration of colored complexing agents in the presence of the waste. Titrimetric methods were used to determine the number of reaction centers of waste. For to determine the nature of the active centers of wastes was use the extinguish of the foam generated by the anionic and nonionic surfactants. The influence of molar mass and structure of sorbates on the nature of their interaction with the waste surface is shown. High molecular polydentate complexing agent form a surface film. Low molecular weight sorbates contribute to the formation of soluble complexes of heavy metals and pollution of water systems. The revealed physico-chemical properties will allow to predict the increase in the probability of groundwater contamination by low molecular weight organic complexing agents and also probability of the best fixing of soils on waste in the presence of high-molecular organic substances of soil absorption complex.

## 1. Introduction

As a result of the active development of reserves of tin ores in the Far East and the subsequent bankruptcy of mining and processing plants in the region were left great number non recultivated waste repositories[1-3]. Abandoned non remediated waste of tin ores sites pose a threat to the environment. Researchers of these man-made objects note to a number of factors of their negative impact on the environment [8-10]: air pollution from "dusting ment" and the emission of sulphur-containing gases; pollution of the soils, rivers, drinking water sources, snow cover with heavy non-ferrous metals; reduce the germination ability of seeds of wild plants; deterioration of health of the population of nearby settlements; the withdrawal of land, reduction of reproduction of green mass and, accordingly, oxygen content in the air, which contributes to the formation of hypoxidized regime in the region.

Far Eastern scientists are fully aware of the consequences of the negative impact of mineral waste storage facilities on the environment and the need to eliminate this influence. Render smth harmless of a huge amount of waste dispersed throughout the region requires an economically, environmentally and technologically optimized systematic approach [2, 7, 10-12] in developing a programme of



necessary activities. For the development of such a program requires a comprehensive study of the properties of wastes.

This is necessary to choose the most efficient and effective methods of waste rendering harmless: to use as secondary raw material; -to use in other technologies; to reclaim for agricultural purposes; treating for the purpose of rendering harmless of polluting components; isolate from the environment.

Physico-chemical state of man-made objects, tendencies of change of this state in time and space, processes occurring in waste, are characterized by a number of indicators. Almost always the acid-base and redox indicators pH-Eh, the mineral composition of groundwater, the formation of new mineral forms [12, 13] are estimated. Surface-active properties of high dispersed solid waste provide a significant contribution to the complex properties inherent to this object. Properties such as adhesion, wettability, physical and chemical adsorption are related to surface phenomena and processes [16-18]. For highly dispersed solid phases, surface processes determine the phenomena of coagulation, sedimentation, and foam quenching пены [21]. As a rule, adsorption processes are accompanied by heat release. The amount of heat released depends on many factors: the state of the surface, the adsorption mechanism, competing processes, wettability and others. Chemical adsorption can lead to significant changes in the state of the waste [14-16, 19, 20]. It may be due to the occurrence of insoluble films of chemical reaction products on the surface. By chemical nature, it can be oxides and hydroxides of metals, salt and the complex compounds, both soluble and formed by the type of soil-absorbing complex [Tarasov]. Surface processes can reduce the "dusting ment" of waste during changes of the physical- chemical nature of the surface.

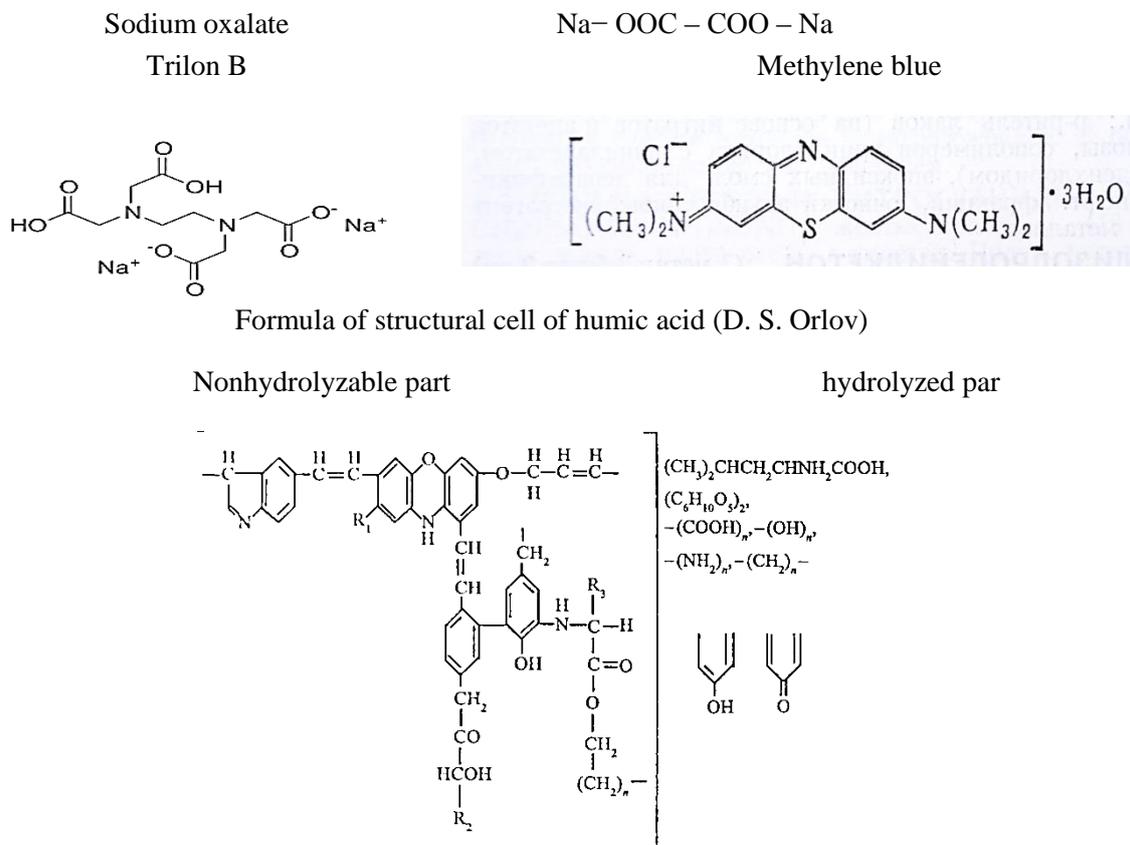
The surface changed in a certain way can promote fixing of humus connections on it that will promote soil formation in the course of recultivation. The presence of complexing agents can have a dual effect on the waste. The formation of soluble complexes with ligands of small size and large stability constants will facilitate the transition of metals out of immobile mineral forms to mobile, which will contaminate the hydrosphere. The complexing agents of this type are organic acids of plants, such as oxalic acid. On the other hand, polydentate organic complexing agent of chelate type with a large molar mass can give due to chemisorption the organo-mineral layers that prevent the migration of waste components into the environment.

From the above it follows the relevance of the study of surface-active properties of tin ore processing wastes in connection with their influence on the state and processes in these technogenic formations.

## 2. Experimental part

The object of the research rendering services the waste of processing tin ores of the former mining and processing plant "Solnechny" of the Khabarovsk territory. As ligands were chosen organic substances, differing molar masses and the polydentate possibilities: sodium oxalate 0,05 n, trilon B of 0,05 n, the dye methylene blue of 0,01% , sodium humate 0,01%. In order to study the influence of pH on the surface activity of the waste in the aquatic environment and the environments of 0,01 n. and 0,1 n. H<sub>2</sub>SO<sub>4</sub> and 0,01 n NaOH was performed 30-minute contact 1 g. of waste with solutions of ligands. The structure of ligand molecules is shown in figure 1.

For research chemical methods were used: direct and inverse titrimetry. Colored solutions of ligands (methylene blue and sodium humate) from the burette were gradually adding to the titration flask, containing 1 g of waste in the appropriate medium (aqueous, acidic or alkaline) until the appearance of a stable non-vanishing color of the ligand. Colorless ligands (sodium oxalate and trilon B 0,05 n) were weighed in precisely measured quantities with 1g of waste in a glass, added the appropriate medium and kept in contact for 30 minutes with stirring. Then the solid phase were separated on the filter "red tape", after which the filtrate were titrated with reagents: sodium oxalate - by KMnO<sub>4</sub> solution 0,05 n in acidic medium; trilon B - by MgSO<sub>4</sub> solution in ammonia medium with indicator eriochrome black T. According to the results of titration calculated absorbed by 1 kg of waste the number of ligands ( table 1.)



**Figure1.** The structure of the ligands molecules.

**Table 1.** Results of determination of the number of millimole (mg) the ligands in reaction on surface after of contact with 1 kg of waste of processing tin ores.

Ligand	M.m. g/mol	The number of the absorbed ligands, mmol (mg) per 1 kg of waste			
		H <sub>2</sub> O	0,01 n H <sub>2</sub> SO <sub>4</sub>	0,1 n H <sub>2</sub> SO <sub>4</sub>	0,01 n NaOH
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	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	более 5-6 тыс.	-	(795)	(490)	(320)

For of explain the behavior of sodium oxalate were donated further studies. For of reveal the fact and nature of the interaction of sodium oxalate with waste, we used its restorative and complexing functions. Titration with KMnO<sub>4</sub> established that after contact with the waste, almost the entire sodium oxalate passed into the filtrate and non fixed on the surface of the waste. Titration with trilon B found an increase in the concentration of metal cations in the aqueous-oxalate extract (568 mmol/kg) in comparison with the aqueous (2,5 mmol /kg). This fact allows to the conclusion that oxalate ion forms soluble complexes with metal cations of waste and then extracts them into the aqueous phase.

The analysis of the data obtained shows the following:

1) the molar mass of the ligand is important only if it reflects the sizes of the molecule, the more complex the molecule is and the more donor centers it has, the less molecules will be placed on the waste surface;

2) low-molecular ligands of small size may not be fixed on the surface of the waste, but more likely 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;

3) the most favorable for the formation of surface complex compounds are neutral and weakly acidic environments. The increase in acidity contributes to the process of surface sorption probably due to the dissolution of the oxide-hydroxide and carbonate forms and the formation of surface complexes in their place.

Alkalinization of the medium reduces the amount of sorbed molecules, probably due to the formation of insoluble bases on the surface. To verify the assumption that the active centers of complexation are cations that are part of the minerals, studies have been conducted to establish their anionic or cationic nature by quenching the foam formed by anionic and non ionogenic surfactants. As an anionic surfactant was selected Stearox (4%), and non ionogenic surfactant – Prevocel (4%). Preliminary tests have shown that tailings waste has the ability to extinguish foam, formed by surfactants.

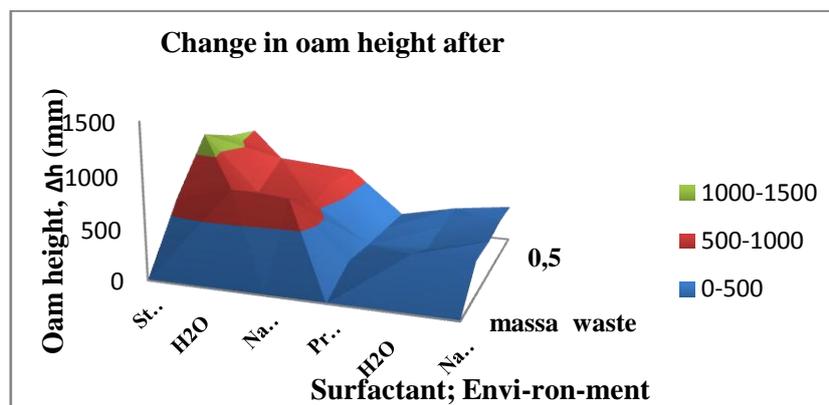
During the experiment, different masses of waste were used and the change in the height of the foam column in the cylinder in time was measured. The results of these measurements are presented in table 2, 3, figure 2.

**Table 2.** The datas of measuring the foam height  $h$  (mm) at the initial moment of its formation by the action of Stearox and Prevocel in different environments, and then after 400 seconds after bringing of different masses (g) of waste.

Mass of waste (g)	Environment	Stearox			Prevocel		
		$h(0)$	$h(400)$	$\Delta h$	$h(0)$	$h(400)$	$\Delta h$
0,0	H <sub>2</sub> O	1100	320	780	670	340	330
	H <sub>2</sub> SO <sub>4</sub>	1600	950	650	420	220	200
	NaOH	1580	840	740	705	370	335
0,1	H <sub>2</sub> O	780	170	610	510	310	200
	H <sub>2</sub> SO <sub>4</sub>	1400	230	1170	430	250	180
	NaOH	1600	1050	550	720	390	330
0,5	H <sub>2</sub> O	970	130	840	580	330	250
	H <sub>2</sub> SO <sub>4</sub>	1250	200	1050	450	270	180
	NaOH	1710	1080	630	770	400	370
1,0	H <sub>2</sub> O	500	70	430	640	350	290
	H <sub>2</sub> SO <sub>4</sub>	1200	200	1000	460	290	170
	NaOH	1730	1100	630	800	440	360

**Table 3.** Change in foam height after 400 seconds ( $\Delta h$ ) mm after adding different waste masses in environments with different acidity.

Surfactant	Environment	0,0	0,1 g. waste	0,5 g. waste	1,0 g. waste
Stearox	H <sub>2</sub> O	780	610	840	430
	H <sub>2</sub> SO <sub>4</sub>	650	1170	1050	1000
	NaOH	740	550	630	630
Prevocel	H <sub>2</sub> O	330	200	250	290
	H <sub>2</sub> SO <sub>4</sub>	200	180	180	170
	NaOH	335	330	370	360



**Figure2.** Change in foam height after 400 seconds ( $\Delta h$ ) mm after adding different waste masses in environments with different acidity.

Analys of the datas of tables 2 and 3, figure 2 is allows us to draw the following conclusions:

1) Tailings waste mass has almost no effect on foam quenching for both surfactants, which may indicate that the surface-active properties are mainly manifested by the highly dispersed phase of the waste.

This assumption obliges that the dispersion composition of tailings waste should be investigated and taken into account.

2) In respect of the investigated surfactants the waste shows the ability to extinguish the foam, and for the anionic Stearox the effect is more significant than for non ionogenic Prevoceol.

3) Acidic medium enhances the effect of foam quenching in the case of Stearox, which can be explained by the dissolution of the oxide-hydroxide and carbonate forms, resulting in an increase in the number of cationic centers on the surface of the waste.

Alkaline medium slightly reduces the effect of foam quenching, which may be a consequence of blocking the cationic centers as a result of the formation of insoluble metal hydroxides.

4) For the non-ionogenic surfactant (Prevoceol) is observed an inverse relationship: alkaline medium slightly enhances the effect of extinguishing the foam, and the acid medium - on the contrary it reduces.

Apparently this is due to the ionization of phenolic groups Prevotella, of a surfactant based on oxyethylated alkylphenols of the type of OP-10 [Sachet].

5) Greater impact of tin ore processing waste on the stability of the foam formed by anionic Stearox indicates the prevalence of cationic active centers on the waste surface.

6) The adhesion properties of the waste with respect to plant materials were studied on smooth white writing paper (cellulose) and their manifestation was established qualitatively by comparing the color of the paper surface after the waste layer was on it for 5 minutes. The surface acquires a yellowish color, characteristic of highly dispersed sulfur (sulfuric color), which is not washed away by a stream of water. There was no detailed study of the adhesion process, but a preliminary qualitative study also involves consideration of the share of adhesion in the processes of pollution of vegetation.

On the basis of the identified facts, it can be concluded that the study of surface-active properties of waste processing of tin ores of the far Eastern region should be continued, taken into account and should be use their ability to retain on its surface complex organic substances in the development and implementation of measures for reclamation and compensation of environmental damage accumulated during the industrial period. Surface-active properties of waste can contribute to improvement of the population of nearby settlements, in the case of using modern biotechnologies ,for example, with the use of the drug "Polisorb" [22].

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