The Study of the Dynamics of Flotation Agent Decomposition in a Tailings Dump

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Abstract. Recently, waste from flotation enrichment of ferruginous quartzites has been widely used to produce building materials for various purposes. A special feature of using this type of waste is the modifying effect of the adsorbed flotation agent. As a rule, flotation reagents based on amino- and diaminoesters have insignificant desorption, which practically excludes their accumulation in the water of the tailings dump. However, with prolonged presence of aminoesters in water, not only the formation of organic bases, but also their hydrolytic cleavage is possible. This may lead to a weakening of the modifying effect of the flotation agent on the properties of the binding compositions. For 1.1-aminoesters, the hydrolysis process is very fast. Hydrolysis of 1.3-aminoesters, which include isodecyloxypropylamine (the main component of the flotation agent for additional enrichment of ferruginous quartzites) has not been studied. In this paper, changes in the chemical composition of the adsorption products of a flotation agent based on isodecyloxypropylamine (PA-14) on tailings during long-term storage in dumps are studied. To study the dynamics of decomposition of the flotation agent in the tailings dump, we used waste of flotation of ferruginous quartzites taken from the tailings dumps of the Mikhailovsky mining and processing plant. According to the results of research, it was found that the processes of chemical decomposition of isodecyloxypropylamine in industrial water are very slow. During long-term storage in a tailings dump, amino- and diaminoesters are partially hydrolyzed to form higher alcohols, amino alcohols, amines, and diamines.

Keywords: Flotation reagents · Flotation waste · Mining and processing plant · Flotation · Adsorption · The dynamics

1 Introduction

A significant reduction in the cost of construction is achieved through the use of local industrial waste in the production of construction materials [1–4].

Recently, studies of mining waste from the Kursk magnetic anomaly (KMA) deposits as filler for construction materials are very relevant [1–4]. Such research opens up the possibility of expanding the raw material base of various mineral additives and obtaining high-quality materials for construction on their basis. In particular, the possibility of using waste from flotation enrichment of ferruginous quartzites to produce low-water-demand binders (LWDB), fine-ground multicomponent cements (FGMC) and concretes

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based on them is investigated; dry building mixes for various purposes (self-leveling floors, plaster solutions, repair compositions) and low-roasted loam-belite binder of hydrothermal hardening [5–11]. One of the important features of using waste from flotation enrichment of ferruginous quartzites is the modifying effect of the flotation agent adsorbed on their surface on the properties of binding compositions [12, 13]. However, the degradation of adsorbed flotation reagents is possible in the tailing dump, which depends on their structure [14–16]. This may lead to a weakening of the modifying effect of the flotation agent on the properties of the binding compositions.

In this paper, changes in the chemical composition of the adsorption products of a flotation agent based on isodecyloxypropylamine (PA-14) on tailings during long-term storage in a tailings storage facility are studied.

2 Materials and Methods

2.1 Materials

To study the dynamics of decomposition of the flotation agent in the tailings dump, we used waste flotation of ferruginous quartzites taken from the tailings dumps of the Mikhailovsky mining and processing plant (MMPP). Waste samples at MMPP were collected from beach areas of tailings dumps. Laboratory samples were taken from the average sample for research by quartering.

The bulk and true densities of flotation waste are 1.46 g/cm^3 and 2.53 g/cm^3, respectively.

The chemical composition of ferrous quartzite flotation waste is shown in Table 1.

The object of research is the flotation agent PA-14 (TOMAH PRODUCTS ING, USA), which is currently used for flotation of hematite and magnetite concentrate. The chemical composition of the flotation agent consists of an aminoester (ethyroamine), 3-(isodecyloxy)propylamine-1. Physical properties: light yellow liquid with a characteristic ammonia smell for amines, density ~0.851 g/cm^3, insoluble in water. To increase the solubility, PA-14 was partially neutralized with acetic acid. The mass fraction of isodecyloxypropylamine acetate in the neutralized product is 25–30%.

2.2 Methods

To study the hydrolysis of isodecyloxypropylamine in process water in the presence of tailings, the following was added to the test tube: 50 ml of process water, 1 g of waste from flotation re-enrichment of ferruginous quartzites, and 1.0 g of PA-14 flotation agent. The mixture was actively mixed for 5 h. We used the Fourier-IR method on a vertex 70 spectrometer manufactured by Bruker Optics. The survey was performed in the mid-infrared range from 370 to 4000 cm^{-1} using the OPUS software.

Table 1. Chemical composition of flotation waste.

Material ID	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	CO_2	ect
%	65–70	0.1–0.5	16–20	2.5–3.5	0.9–1.5	0.3–0.5	1–2.5	0.1–0.2	0.1–0.2	0.2

3 Results

According to the literature, it is known that water interacts with aliphatic amines, and consequently with amino- and diaminoesters to form organic bases. The interaction of aminoesters with water leads to the creation of an alkaline environment. The longer the hydrocarbon radical, the greater the electron density is forced on the nitrogen. As a result, the interaction of isodecyloxypropylamine creates a high alkalinity of the medium.

$$(CH_3)_2CH(CH_2)_7{-}O{-}CH_2CH_2CH_2{-}NH_2 + HOH \rightarrow R{-}O{-}CH_2\\ CH_2CH_2{-}NH_3^{+}OH$$

The reaction of aminoesters with water does not lead to degradation of the aminoester, as its structure is preserved.

If aminoesters are found in water for a long time, not only the formation of organic bases, but also their hydrolytic cleavage is possible. For 1.1-aminoesters, the hydrolysis process is very fast. Hydrolysis of 1.3-aminoesters, which include isodecyloxypropylamine, has not been studied. Theoretically hydrolysis should take place and be described by the reaction equation:

$$(CH_3)_2CH(CH_2)_7{-}O{-}CH_2CH_2CH_2{-}NH_2 + HOH \rightarrow (CH_3)_2CH(CH_2)_7\\ {-}OH + HO{-}CH_2CH_2CH_2NH_2$$

The reaction products are the highest limit alcohol (isodecyl) and the lowest amino alcohol (aminopropanol).

Visual changes in the flotation agent PA-14 as a result of long-term storage (for 3 years) in water at a temperature of 18–25 °C showed the following: the volume of the solution decreased, flotation waste was located at the bottom of the test tube, the liquid above the waste was divided into three layers: the upper orange-yellow color, the middle light yellow color, and the lower colorless (slight turbidity). On the basis of the coloring layers (the flotation reagent PA-14 in the beginning of the experiment had a bright yellow color) we made assumption that the upper layer is a solution of water in the flotation reagent, PA-14, the middle layer is the solution of a flotation reagent in water and the lower layer is also the solution of a flotation reagent in water, but with much lower concentrations. Isodecyloxypropylamine was partially oxidized, which explains the orange-yellow color of the upper layer.

A weak amine smell was preserved (less expressed than in the case of the initial flotation agent), the pH of the upper layer was 8.0, and the pH of the initial flotation agent was 10. The refractive index of the upper layer is 1.4510, the refractive index of the initial flotation agent is 1.4644. The refractive index decreased, which indicates the possible presence of water, as water has a refractive index of 1.3330.

IR spectra of the initial flotation agent PA-14 (aliphatic aminoester) and all three layers were taken. For comparison, the spectrum of individual primary aliphatic aminadeutbutylamine (Fig. 1a) was removed, as it contains a branched radical, as well as the radical of the aminoester - the main component of the PA-14 flotation reagent. The spectrum of an individual primary amine should show strong, medium-strength, weak, narrow and wide bands of valence and strain vibrations. Valence vibrations **N-H**: 3347 cm^{-1}, asymmetric $\mathbf{NH_2}$; 3285 cm^{-1}, symmetrical $\mathbf{NH_2}$ (overlap). Valence vibrations **C-H**: 3000–2850 cm^{-1} $\mathbf{CH_3}$**,** $\mathbf{CH_2}$. Deformation vibrations **N-H**: 1590 cm^{-1}, $\mathbf{NH_2}$ (shear). Deformation vibrations **C-H**: 1457 cm^{-1} $\mathbf{CH_3}$ (shear); 1375–1348 cm^{-1}, $\mathbf{CH_3CH_2}$. **Nitrogen**: 1200–800 cm^{-1}, valence **C-N** and rolling **N-H** (for a pure sample), mostly rolling **N-H**.

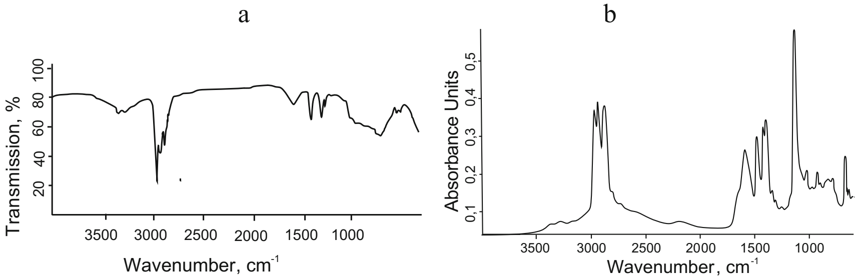

Fig. 1. IR-spectrum of a) Deut-butylamine and b) PA-14.

The formula of the aminoester is $(CH_3)_2CH(CH_2)_7O(CH_2)_3NH_2$. The deut-butylamine radical is smaller than the isodecyl radical, so some band shift is expected. In addition, the aminoester molecule has an oxygen bridge, which is typical for a simple ether bond. The presence of an ether bond should also be reflected by the appearance of bands in the infrared spectrum of the aminoester.

Shown in Fig. 1b, the range of flotation reagent PA-14 is largely the same spectrum of deut-butyl (should only note that in Fig. 1a the transmission spectrum of deut-butylamine is given, and in Fig. 1b the absorption spectrum of a flotation reagent PA-14). It is enough to compare the area of 3500–3000 cm^{-1}, where two bands correspond to the valence vibrations of N-H, and the area of 3000–2850 cm^{-1} (the bands correspond to the valence vibrations of C-H). Further, up to the frequencies of 1590 cm^{-1}, there are no absorption (transmission) bands. Then the absorption bands of the PA-14 flotation agent are slightly shifted relative to the bands observed in the spectrum of deut-butylamine.

The infrared spectrum in the 1200–800 cm^{-1} area of deut-butylamine differs significantly from the infrared spectrum of the PA-14 flotation reagent. A narrow very strong band 1110.36 cm^{-1} appears - the characteristic frequency of CH_2-O-CH_2. This is how a simple ether bond can manifest itself, which is present in the aminoester of the flotation agent PA-14, but is naturally absent in deut-butylamine. The C-N valence vibrations and the N-H rolling vibrations are weak and are shielded by a very strong absorption band characteristic of simple ethers.

Thus, the aminoester of the flotation agent PA-14 has all the absorption bands characteristic of primary aliphatic amines and the absorption band characteristic of simple esters (1150–1060 cm^{-1}, p. s.).

Comparing the infrared spectrum of the upper layer of the emulsion (Fig. 2a) with the IR spectrum of PA-14, we can note the following: the nature of both spectra in the 3000–1000 cm^{-1} area is identical. The spectra are characterized by the same set of absorption bands (transmittance) at equal frequencies (a slight shift in the absorption bands can be ignored). The bands corresponding to the valence vibrations C-H: 3000–2850 cm^{-1} **CH_3**, **CH_2** and the deformation vibrations **N-H**: 1590 cm^{-1}, **NH_2** (shear) were preserved. There are bands of deformation vibrations **C-H**: 1457 cm^{-1} CH_3 (shear); 1375–1348 cm^{-1}, **CH_3 CH_2**.

There are also major differences. Thus, the upper layer has a significant decrease in the height of the absorption band characteristic of CH_2-O-CH_2 esters. This may indicate hydrolysis of the aminoester. Valence vibrations **N-H**: 3347 cm^{-1}, asymmetric **NH_2**; 3285 cm^{-1}, symmetrical **NH_2** is absent from the upper layer spectrum.

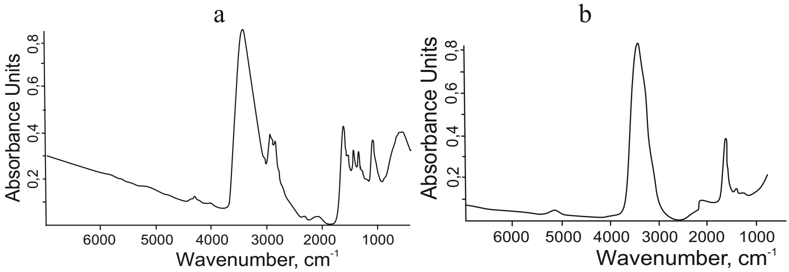

Fig. 2. IR-spectrum of a) the top layer of the emulsion PA-14 and b) the middle layer of the emulsion PA-14.

But this can be explained not by the absence of an amino group, but by the valence vibrations of the OH group of water and the isodecyl alcohol $(CH_3)_2CH(CH_2)_7OH$ formed as a result of hydrolysis of the aminoester. It should be noted that the process of hydrolysis of an aminoester at room temperature is a long process, so the initial aminoester is present simultaneously with the hydrolysis products, but its amount should decrease over time. The concentration of aminoester in the upper layer is quite understandable, as its density is less than that of water.

The aminoester is concentrated at the air-water interface. The hydrophobic radical is oriented to the air, while the NH_2 polar group is directed to water and dissolved in it. As a result, the water surface is covered with a kind of "stockade" of aminoester molecules, forming a layer 0.1 nm or more thick. The surface tension of the water decreases. The number of aminoester molecules located at the air-water interface is determined by the size of the aminoester molecules and the area of the interface. Those aminoester molecules that could not concentrate at the air-water interface are freely distributed in the volume of water. Thus, the upper layer contains the maximum amount of aminoester that was not adsorbed on the tailings, water, and products of partial hydrolysis and oxidation of the aminoester. This self-organization of aminoester molecules leads to less active evaporation of water over time than in the initial period.

The infrared spectra of the middle and lower layers are identical, so only the IR spectrum of the middle layer is shown (Fig. 2b). They differ significantly from the infrared spectrum of the upper layer. The bands corresponding to the valence vibrations **C-H**: 3000–2850 cm^{-1} $\mathbf{CH_3}$, $\mathbf{CH_2}$, and the deformation vibrations **N-H**: 1590 cm^{-1}, $\mathbf{NH_2}$ (shear) disappeared. The relative intensity of the absorption band of deformation vibrations **C-H**: 1457 cm^{-1} $\mathbf{CH_3}$ (shear) can be characterized as weak; the absorption bands 1375–1348 cm^{-1}, $\mathbf{CH_3CH_2}$ as very weak.

Stretching vibrations of **N-H**: 3347cm^{-1}, asymmetric $\mathbf{NH_2}$; 3285 cm^{-1}, symmetric $\mathbf{NH_2}$ on the spectrum of the middle and lower layers are absent. This can be explained either by the complete absence of aminoester in the middle and lower layers, or by its very low concentration. Therefore, these bands are shielded by bands of valence vibrations of the OH group of water and the isodecyl alcohol $\mathbf{(CH_3)_2CH(CH_2)_7OH}$ formed as a result of hydrolysis of the aminoester.

If the upper layer is characterized by a decrease in the intensity of the absorption band 1100 cm^{-1}, then in the case of the middle and lower layers, the relative intensity of the absorption band 1100 cm^{-1} can be characterized as very weak, which indicates an extremely low concentration of aminoester. The absorption band of 1600–1700 cm^{-1} is due to the presence of water in the middle and lower layers in greater quantities than in the upper layer.

It should be noted that over time, the appearance of the test tubes practically did not change, which indicates a small influence of flotation enrichment tailings on the processes occurring in process water with the PA-14 flotation agent during long-term storage.

4 Conclusion

According to the conducted research, the processes of chemical decomposition of isodecyloxypropylamine in industrial water are very slow. During long-term storage in a tailings dump, amino and diaminoesters are partially hydrolyzed to form higher alcohols, amino alcohols, amines, and diamines. The higher alcohols formed because of hydrolysis (decyl, isodecyl, etc.) are safer than aminoesters. They have low volatility and, being surfactants, are concentrated at the water-air interface.

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