

The use of chemical and instrumental methods in the study of the forms of occurrence of sulfides in bottom sediments

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Abstract. On the example of the estuary of the Mius River - the mouth of the Mius River, the Mius estuary, the Taganrog Bay of the Azov Sea, a complex of chemical and instrumental methods was applied, including those developed by the authors. This made it possible to study the physicochemical parameters, the content of total hydrogen sulphide, the form of occurrence of sulfides, the total content of iron and their behavior in the bottom sediments of early diagenesis. Bottom sediments were formed at negative Eh values. Sulfides in bottom sediments are mainly in the form of molecular hydrogen sulfide and acid-soluble iron sulfides. The content of total hydrogen sulfide varied within wide limits, reaching 3.2 mg/g of wet weight, and of gross iron - from 25.4 to 45.1 mg/g dry weight. A significant relationship was found between the content of sulfide sulfur and gross iron. The presence of hydrotroilite was identified by the typical smell of hydrogen sulfide, black color, oily sludge, lack of magnetic properties and by visual study of its formations using electron microscopy. Under a microscope, images of coacervates (colloidal accumulations) of hydrotroilite of a round-ellipsoidal shape (lenticular), from gray to black, mercury-like, were obtained in a wet preparation. It was established for the first time that hydrotroilite exists in the natural environment as a gel-like substance capable of moving in the bottom of sediments. Upon collision, small formations coalesced into larger globules. The important role of hydrotroilite as a mercury accumulator in the early diagenesis of bottom sediments is shown.

1 Introduction

Hydrogen sulfide, which is formed in the bottom sediments of salty, brackish and fresh water bodies of the Earth, mainly by biogenic means, is a gas that can have a toxic effect on aquatic organisms and may lead to their death. In works [1-3], on the example of a number of water bodies in Russia, the regularities of the distribution of total hydrogen sulfide in water and bottom sediments were studied. However, these works did not focus on the study of the forms of occurrence of sulfide minerals and, first of all hydrosulfides. Meanwhile,

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the knowledge of their formation, migration and transformation in low-temperature conditions is of great scientific and practical interest [4, 5]. As an experimental testing ground for a comprehensive study of the forms of hydrogen sulfide and hydrosulfides in bottom sediments, we have chosen the Azov Sea proper, its bay and estuary. It should be noted that the choice of the body of water was not accidental, since at the moments of stagnation of water masses, it often becomes a "freezing" water body. This is due to the consumption of oxygen for the oxidation of reduced gases (hydrogen sulfide, methane, ammonia) and organic substances [1, 6, 7]. In the bottom sediments of the water streams and bodies, black and black-gray oily to the touch layers with the smell of hydrogen sulfide are formed, which are represented by iron hydrosulfide - presumably hydrotroilite. Despite the toxic effect of the gaseous hydrogen sulfide on aquatic organisms, in contrast to it, the iron sulfides formed in bottom sediments can play a positive role. The iron sulfides show a tendency to accumulate mercury, contributing to the removal of the element from water and its self-purification [2].

In this regard, taking into account the relevance and scientific significance, for the first time a complex of chemical and instrumental methods, including original ones, were used, which made it possible to study the physicochemical parameters, the content of total hydrogen sulfide, the form of finding of iron hydrosulfides, its gross content and behavior under various conditions.

2 Materials and methods

Along the profile of the estuary of the Mius River - the mouth of the Mius River, the Mius estuary, the Taganrog Bay of the Azov Sea, water and bottom samples were taken in accordance with the map (Fig. 1) [8].



Fig. 1. Schematic map of the study area of the Mius River, the Miusky estuary (the Miusky reservoir) and the Taganrog Bay.

Sampling of bottom sediments was carried out in accordance with the requirements of GOST 17.1.5.01-80. Bottom sediments were sampled using a 1 m long soil pipe of the GOIN design, and if it was impossible to use it (in the case of sandy and shell deposits), using a bottom grab "Ocean-0.025" [9]. For the purpose of subsequent analysis, the bottom sediments were separated in layers, every 2.0-5.0 cm. Samples weighing about 50 g were placed in plastic bags and kept in a refrigerator until analysis. In the coastal zone of water bodies, samples of bottom sediments were taken by pressing a specially designed plastic sampler into them [10]. A visual description of the lithological composition of bottom sediments was made, and their granulometric composition was determined at individual stations. To determine the oxidation-reduction potential and hydrogen index, licensed ionomers of the company "Ecotest-2000" were used. In the section of bottom sediments of the Mius River, the Mius estuary and the Taganrog Bay, we carried out synchronous determinations of the total hydrogen sulfide content, Eh values, density and humidity. Bottom sediments were described and electronic images were taken. Determination of the content of gross iron was carried out according to the method [11].

Measurements of the mass fraction of sulfide sulfur ($\Sigma\text{H}_2\text{S}$) are based on the conversion of bottom sediment sulfides into hydrogen sulfide by the action of hydrochloric acid, followed by the stripping of hydrogen sulfide with nitrogen of special purity into a sodium hydroxide solution and the determination of sulfide ions by a photometric method with N, N-dimethyl-p-phenylenediamine. Total hydrogen sulfide ($\Sigma\text{H}_2\text{S}$) was determined by the method [12] in bottom sediments in a natural state, which included both molecular hydrogen sulfide and obtained by acid decomposition of X-ray amorphous colloidal iron sulfides. Simultaneously with sampling in pre-weighed and numbered weighing bottles, a weighed portion of bottom sediments was taken to determine the mass fraction of dry sediment and its moisture content. When preparing preparations for the isolation of sulfide minerals, the material was washed with distilled water from readily soluble salts and then the particles were separated by size in accordance with Stokes' law. When preparing the preparations, acid treatment was not carried out. The clay fraction less than 0.001 mm was separated by elutriation in distilled water by being settled at room temperature for 24 hours, then draining the upper 7 cm of the colloid column and further settling or centrifuging. Then the preparation was stirred up and left again defended for another 24 hours. This procedure was carried out until the complete selection of the clay fraction. After washing from readily soluble salts and selection of the clay fraction, wet and dry preparations were prepared for the study. Due to the fact that the studied iron sulfide was a hydrated mineral, further microscopic studies were carried out in a wet preparation with a column of 5 mm water and using a USB microscope MiViewCap with magnification from 10 to 200 times, displaying the image on a computer screen and photographing for further processing. Then the resulting preparation was dried at room temperature and further examined in a dry state using an electron microscope. Note that a separate sample of bottom sediments to determine hydrosulfides in them was treated with HCl. The magnetic properties of the sediments were also investigated.

3 Results and discussion

In the Mius estuary, bottom sediments are represented by black plastic clayey silt in places with the smell of hydrogen sulfide, passing with depth into silt with a sandy fraction of a denser consistency. They changed as we moved towards its confluence with the Taganrog Bay from dark gray to brownish silts with different contents of sandy and shell rock material and the smell of hydrogen sulfide. In Taganrog Bay, bottom sediments were represented by silts containing sandy shell material (Fig. 2). When sampling, we felt the smell of hydrogen sulfide.



Fig. 2. Column of bottom sediments of the Taganrog Bay, represented by shells with sand and silt.

The sampling depth of the investigated bottom sediments did not exceed 25 cm. The density varied in the range of 1.33-2.97 g/cm³, and the natural moisture content was 19.6-63.5%. The bottom sediments were characterized by negative values of the redox potential - from -245.0 to -5.0 mV, which contributed to the active formation of reduced gases in the presence of labile organic matter. The content of total hydrogen sulfide ($\sum\text{H}_2\text{S}$) varied from 0.005 to 3.2 mg/g w.w. (wet weight). The contents of $\sum\text{H}_2\text{S}$ in bottom sediments in a wet state were converted to dry weight. The contents of $\sum\text{H}_2\text{S}$ in dry weight of bottom sediments varied from <0.005 to 5.28 mg/g d.w. (dry weight). There was no clear pattern in the change in the H₂S content with the immersion of bottom sediments, which is explained by the small interval of sampling depths. At the same time, earlier in [1] in the Azov Sea, a tendency towards a decrease in the content of total hydrogen sulfide in bottom sediments to a depth of 1.0 m was revealed. Increased concentrations of $\sum\text{H}_2\text{S}$ prevailed in black-gray silts with the smell of hydrogen sulfide.

It was important to find out the amount of gross iron in bottom sediments and how closely it is related to the $\sum\text{H}_2\text{S}$ content. It turned out that the content of gross iron was in an amount from 25.4 to 45.1 mg/g dry weight. A tendency towards an increase in its content from the upper to the lower layers of bottom sediments were noted. Knowing the sedimentation rate in the Azov Sea [13], it is assumed that such a distribution is explained by the inflow of mine waste water into the Mius River and further on the Mius estuary, discharged in the last century from Ukrainian part of Donbass. To clarify the tightness of the relationship between total hydrogen sulfide and that of gross iron, regression equations were calculated (Fig. 3). It turned out that a significant relationship ($R = 0.67$) was found between the content of sulfide sulfur and gross iron, which is agrees with our results presented below, obtained from a microscopic study of bottom sediments. It draws attention to the fact that the tightness of this connection is not high. This indicates that iron is also present in bottom sediments in the form of minerals, in which it is represented by its oxides and hydroxides. Visually, in the bottom sediments of the Azov Sea and the Mius estuary, smears of brown iron hydroxide were observed [1, 8], and under a microscope, iron oxides (hematite), which were characterized by magnetic properties.

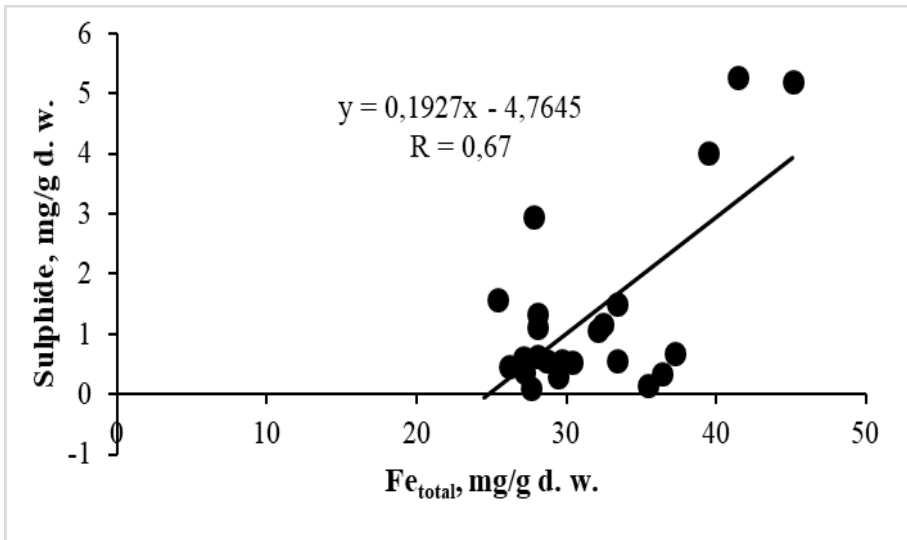
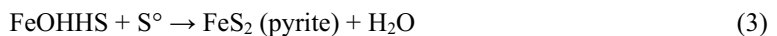


Fig. 3. Regression model of the relationship between the content of sulfide sulfur and gross iron.

If the question of the forms of occurrence of iron oxides was not particularly acute, then the question of which authigenic mineral formations are iron sulfides is still controversial. Most researchers recognized the possibility of the formation of both acid-soluble forms (mainly hydrotroilite) and pyrite under conditions of early diagenesis [4, 5]. The presence of hydrotroilite was identified mainly by the typical smell of hydrogen sulfide, black color and oily sludge.

According to I.I. Volkov. [5], in modern sediments the main amount of acid-soluble iron sulfides is represented by X-ray amorphous colloidal black iron monosulfide. Its composition and formula have not been confidently diagnosed until now. At present, various scientists describe it as a hydrate of iron monosulfide (FeSnH_2O) or hydrosulfide (FeSH_2S). I.I. Volkov came to the conclusion that X-ray amorphous colloidal iron monosulfide is either a sulfide with no constant composition, or is a mixture of sulfides in variable proportions (melnikovite, mackinovite, greigite). In this case, hydrotroilite is easily oxidized by oxygen, transforming into colorless iron sulfate (FeSO_4). According to [4, 5], the following iron sulfides are found in sea bottom sediments by X-ray diffraction analysis: amorphous iron sulfide - hydrotroilite (FeSnH_2O), crystalline differences - pyrite (FeS_2), marcasite (FeS_2), melnikovite and its analog greigite (Fe_3S_4), also mackinovite (FeS). According to these researchers, with an excess of molecular hydrogen sulfide, hydrotroilite transforms into pyrite (FeS_2).

V.V. Fadeev [14] experimentally studied the mechanism of pyrite formation during the interaction of Fe (III) with hydrogen sulfide in the low-temperature region (up to 300 °C) and showed that it has a three-stage nature, corresponding to schemes (1-3):



It is important that in X-ray amorphous iron monosulfide, along with adsorbed water, the presence of structural protons localized in the OH- and HS- groups was established. This allowed V.V. Fadeev to describe it by the formula $\text{FeOHHS} \cdot n\text{H}_2\text{O}$.

Under a microscope, we obtained images of coacervates (colloidal accumulations) of hydrotroilite in a wet preparation of a round-elliptical shape (lenticular), from gray to black, mercury-like, moving in the field of the microscope. For the first time, we observed that upon collision, they coalesced into larger globules (from 0.1 to 0.3 mm). Thus, it was shown that hydrotroilite exists in the natural environment as a gel-like substance capable of moving in bottom sediments. Note that the preparation had a pronounced odor of hydrogen sulfide, which intensified when exposed to HCl. In a dry preparation, hydrotroilite globules looked like black concretions, shiny and resinous. Thus, it has been shown that the transformation of hydrotroilite from a gel-like state into semisolid clots is associated with the loss of water molecules. Despite the fact that hydrotroilite in its composition contains a magnetic element iron, attempts to isolate by using a strong magnet, both from a wet and dry preparation, did not give a positive effect. It turned out, as previously assumed, it is not magnetic and X-ray amorphous. The foregoing, in our opinion, confirms its presence in bottom sediments in the form of coacervates capable of coalescence to form larger globules. The gel-like state in natural conditions of hydrotroilite is facilitated by the presence of adsorbed water. The loss of water contributes to its transition into FeOHHS aggregates, which under an electron microscope look like shiny black resin-like concretions.

We've noted a tendency [2] for the accumulation of mercury in bottom sediments of early diagenesis in layers containing increased concentrations of iron sulfides. According to the information taken from [15], we constructed a regression relationship between the total mercury content and the percentage of pyrite in the coals of the Eastern Donbass. As seen from Fig. 4 there is a close relationship ($R = 0.897$) between these elements. It was concluded that the gross of mercury was accumulated in sulfides at the stage of peat accumulation, i.e. during sedimentogenesis and subsequent diagenesis of bottom sediments.

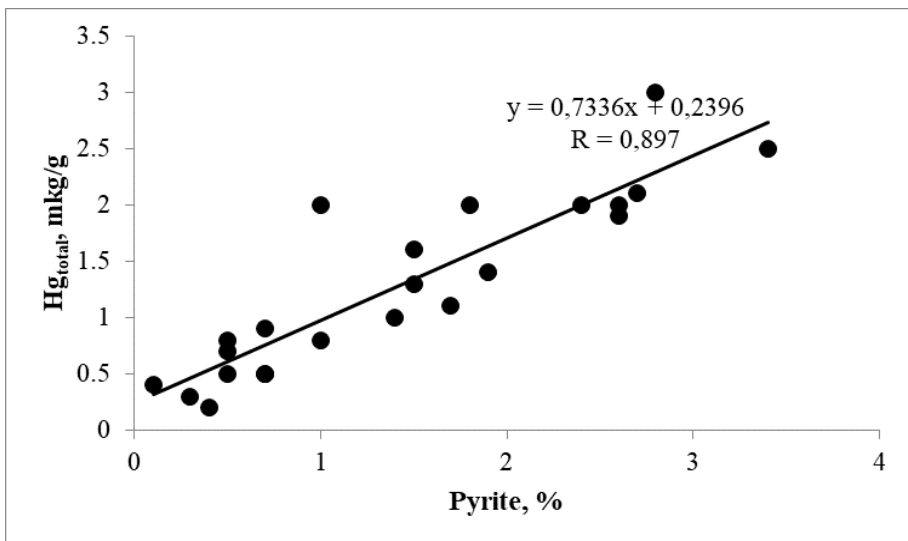


Fig. 4. Dependence between the gross mercury content and the percentage of pyrite in the coals of the Eastern Donbass.

The mercury content is preserved in pyrite formed from iron sulfide monohydrate during subsequent diagenetic and epigenetic transformations. Gross iron is contained in an amount from 25.4 to 45.1 mg/g dry weight. A tendency towards an increase in its content from the upper to the lower layers of bottom sediments was noted. Knowing the rate of sedimentation in the Azov Sea, it is assumed that such a distribution is explained by the

inflow of mine waste water into the Mius River and further on the Mius estuary, discharged in the last century from the territory of the Ukrainian part of Donbass. To clarify the closeness of the relationship between total hydrogen sulfide and that of gross iron, regression equations were calculated. It turned out that a significant relationship ($R = 0.67$) was found between the content of sulfide sulfur and gross iron, which is in agreement with the presented results obtained by microscopic study of bottom sediments. It draws attention to the fact that the tightness of this connection is not high. This indicates that iron is also present in bottom sediments in the form of minerals, in which it is represented by its oxides and hydroxides. Visually, smears of brown iron hydroxide were observed in the bottom sediments of the Sea of Azov and the Mius estuary, and iron oxides (hematite), which were characterized by magnetic properties, were observed under a microscope.

4 Conclusion

Using an electron microscope, images of coacervates (colloidal accumulations) of hydrotroilite were obtained in a wet preparation in a round-elliptical shape (lenticular), from gray to black, mercury-like, moving in the field of the microscope. On collision, they coalesced into larger globules. It is shown that hydrotroilite exists in the natural environment as a gel-like substance capable of moving in bottom sediments. Note that the preparation had a pronounced odor of hydrogen sulfide, which intensified when exposed to HCl. In a dry preparation, hydrotroilite globules looked like black concretions, shiny and resinous. It was found that the transformation of hydrotroilite from a gel-like state into semisolid clots is associated with the loss of water molecules. Despite the fact that hydrotroilite in its composition contains a magnetic element iron, attempts to isolate it using a strong magnet, both from a wet and dry preparation, did not give a positive effect. It turned out, as previously assumed, to be X-ray amorphous and non-magnetic. The gross of mercury accumulates in sulfides even during sedimentogenesis and subsequent diagenesis of bottom sediments. The mercury content is preserved in pyrite formed from iron sulfide monohydrate during subsequent diagenetic and epigenetic transformations.

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