The Influence of the Processes of Microbiogenic Deposition of Carbonates on the Surface of Iron-Aluminosilicate Marine Suspensions and the Transformation of the Resulting Bottom Sediments

A. V. Panko, I. G. Kovzun, V. A. Prokopenko, O. M. Nikipelova, and O. A. Tsyganovich

Abstract Mechanisms of microbiogenic deposition of nanoparticles and microparticles in fresh, salty, and marine suspensions of iron-aluminosilicates (clays) in the presence of carbonate admixtures, oxides of iron and manganese, and trace elements, as well as mechanisms of nanochemical biocolloidal transformation and separation of mineral components of suspensions and their enrichment were considered. It is shown that the study of these mechanisms is important for understanding the fundamental laws of complex physical, chemical, geomechanical, and biocolloidal transformation processes of the components of iron-aluminosilicate systems and materials, widely distributed in the Earth's crust and on its surface. From a practical point of view, it is important for the development of new highly efficient technologies for obtaining such materials, taking into account achievements of green chemistry. The importance of established regularities in the development of ideas about the biocolloidal formation of various ore deposits, primarily iron and iron-manganese nodules, is also shown taking into account the important role of periphyton in such processes in the presence of microorganisms and bacteria. General ideas concerning the basis for the creation of highly effective materials and eco-biotechnologies in the conditions of synergic

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action of periphyton complexes of microorganisms and bacteria under the influence of the laws of physicochemical geomechanics have been developed. Recommendations are provided for optimizing the methods of obtaining clay iron-aluminosilicate materials with improved properties under the influence of complex natural groups of bacteria and periphyton microorganisms, which allows, in some cases, to increase the efficiency of their use in technological processes by 6–12 times. Ways of applying the obtained results in various fields of human activity are outlined.

1 Introduction

It is known that the processes of precipitation of minerals from salty (i.e., marine), as well as fresh-water suspensions—mainly iron-aluminosilicate ones (IASS), are always accompanied, depending on the period of deposition, by the formation of bottom sediments [1–5]. Classical ideas about such processes are based on the fact that there is a huge number of groups of bacteria and microorganisms on the dispersed solid particles of suspensions, which in general belong to the periphyton [4], which includes bacteria and microorganisms—fungi, algae, protozoa, worms, mollusks, etc. that live on the border of solid and liquid phases [1, 3]. Thus, for example, it was established that in one cm^3 of suspension, only the number of heterotrophic bacteria reaches 16×10^6, and diatoms and other algae—3×10^6 cells with more than tens of thousands of their species [4]. The modern work [3] also shows that in fresh and salty sediments, there are thousands of species and tens of groups of specialized bacteria and microorganisms that take part in the formation of biogenic siderite, pyrite, magnetite, etc., and iron-manganese nodules.

A large number of different species and groups of bacteria, diatoms, animalcular microorganisms, and various iron-aluminosilicate fine particles in fresh, salty, and marine suspensions make them the site of many active biological, nanochemical, colloid-chemical, and mechanochemical interactions at the interface between water and mineral carbonates, and iron-aluminosilicates [3]. From the point of view of modern nanoscience, such interactions are characterized as nanobiocolloidal and are accompanied by the transformation of suspension components under the action of biochemogenic, biocolloidal, and physical–mechanical nanotransformations and inorganic reactions [3, 4, 6–11].

On the surface of solid particles of marine suspensions, a large number of various species and groups of bacteria and diatoms make them not only a place of complex biocolloidal transformations but of other processes too. Thus, causing changes in the environment, periphyton microorganisms of marine suspensions not only take part in the deposition of carbonates on microparticles of suspensions but also in releasing microelements from their inorganic mineral structures [11]. The latter processes are also accompanied by a chemical nanobiocolloidal transformation of minerals and their separation according to the laws of physicochemical geomechanics [3]. This is partly proved by the formation of iron ore deposits contaminated with iron-aluminosilicates aided by bacteria about two billion years ago [12], in recent millennia [11, 13, 14], and in present conditions [15–22].

Thus, a more detailed study of the effect of microbiogenic (biocolloidal) precipitation of carbonates on the surface of particles of iron-aluminosilicate marine suspensions on the nanochemical transformation of formed bottom sediments and their redistribution on the bottom of reservoirs according to the laws of physicochemical geomechanics and nanochemistry should be considered very relevant, and therefore, it is assigned in the basis of this study.

2 Materials and Methods

2.1 Materials

Study of the biocolloidal nanostructural geo- and mechanochemical dispersion processes and transformation of polymineral microdispersed iron-aluminosilicate systems (IASSs), and materials (IASMs) of natural and technogenic origin (iron ores, soils, pelitic sediments, natural and thermotreated clays, sands, etc.) have shown that as a result of changes in influencing factors in microdisperse (IASSs) and nanodisperse (NIASSs) systems, various very complex interactions can occur between their components [1, 3, 6, 8–16]. Such interactions include low- and high-temperature reduction or oxidation, dispersion or contact interparticle compaction, Ostwald ripening, change in the surface nanostructural phase composition, chemical leaching, adsorption, adhesion, cohesion, ion exchange, etc. Such interactions give new properties and change the chemical and mineralogical characteristics of dispersed IASSs and NIASSs. Similar changes occur in the Earth's crust, as well as on its surface, most often, as a result of the natural and technogenic processing of mineral rocks and their weathering. However, until now, the processes that occur in the studied systems were judged by their final parameters, but that does not explain the initial causes and mechanisms of the observed transformations. There is still no single, scientifically based approach to the explanation of the phenomena of polymineral IASSs transformation in conditions of their geomechanochemical and biocolloidal nanochemical dispersion. There are also no principal models of colloid-chemical interactions in similar systems that would provide an opportunity to justify the processes of controlling the behavior and characteristics of IASSs and NIASSs. Based on this, the selection of research objects was based on their general features, which are typical for most carbonate-iron-aluminosilicate systems and materials. Such materials should primarily include soils, clays, sedimentary iron ores of biocolloidal origin, pelitic sediments, and peloids. As iron-aluminosilicate materials, it was studied: various soils and clays; polymineral iron-aluminosilicate compositions formed from iron ores; pelagic shallow and deep-water sediments and peloids of the Black and Azov seas, Dashukovski bentonite and montmorillonite [1, 3, 6, 8–17].

Based on the given data (Figs. 1, 2 and 3 and Table 1), it was studied and analyzed the behavior of suspensions of the Azov and Black Seas and the transformation of iron ore (Fig. 3) of biocolloidal origin formed 15,000 years ago in the Azov–Black Sea region [17].

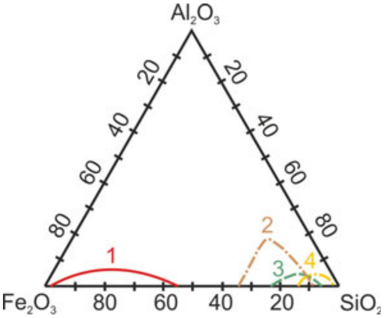


Fig. 1 Areas of the existence of various iron-aluminosilicate materials. 1—iron concentrates and ores; 2—clays, 3—peloids, oozes; 4—quartz and feldspar sands, (2–4)—soils

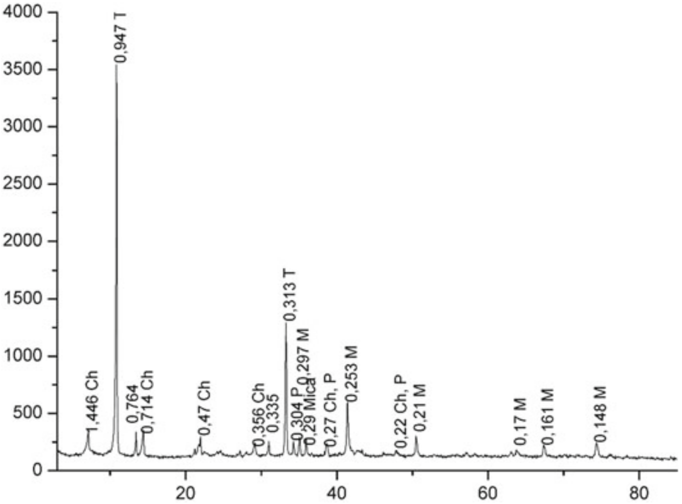


Fig. 2 XRD pattern of natural jaspilite microcrystalline ore. (Ch—chlorite, T—talc, P—pyrite, M—magnetite, Mica—mica)

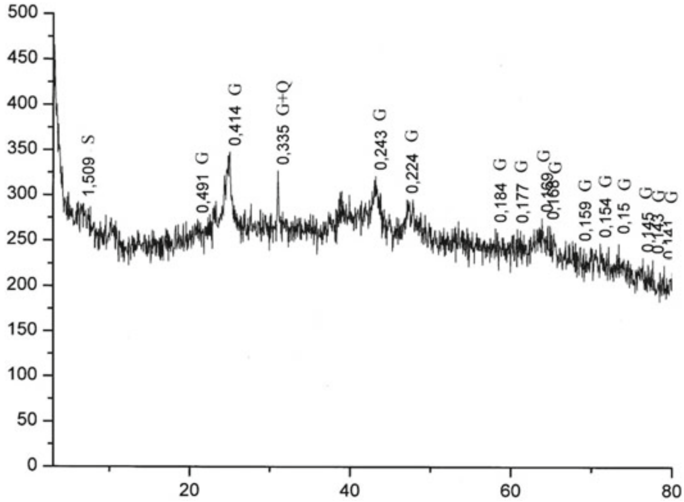


Fig. 3 XRD pattern of sedimentary nanostructured iron ore of biocolloidal origin (G—goethite, Q—quartz, S—saponite)

Table 1 Chemical composition of iron-aluminosilicate materials

Content of oxides, wt%	Polymineral iron-aluminosilicate compositions			Saponite-goethite clay	Black sea mud	River sand	Dashukovsky montmorillonite
SiO_2	18.34	18.31	19.46	46.73	54.57	98.83	49.52
Al_2O_3	2.09	1.76	1.93	5.12	11.35	0.06	21.06
Fe_2O_3	3.18	8.34	2.79	2.76	5.54	1.05	2.72
FeO	56.15	49.23	51.16	23.21	–	–	–
CaO	2.17	1.65	1.98	3.87	8.87	0.01	5.7
MgO	0.73	0.61	0.56	11.43	1.80	–	1.61
MnO	2.48	3.24	7.87	0.35	0.04	–	–
Na_2O	0.45	0.31	0.24	0.82	1.19	–	0.37
K_2O	0.33	0.25	0.26	0.36	1.86	–	0.28
LOI	14.21	16.26	13.67	8.57	13.03	–	17.98

LOI loss of ignition

2.2 Research Methods

Chemical, rheological, XRD, DTA, SEM, and adsorption methods of analysis, magnetic and gravitational separation, as well as medical and biological methods, were used in the research of IASSMs.

Chemical and X-ray fluorescence analyses used in the study of samples were carried out according to known methods of qualitative and quantitative methods of analysis of iron-aluminosilicate rocks.

XRD analysis of the samples was carried out on a Dron-UM-1 diffractometer with CoKα radiation and a nickel filter at room temperature. The diffractometer was connected to a computer for the automatic recording of diffractograms. The survey was carried out under the following conditions: surveying speed—1 degree/min. Registration of X-ray radiation was carried out on a BDS-6 scintillation counter. The determination of minerals was carried out according to the tables. Samples for research were prepared according to standard methods. The decoding of radiographs was carried out according to the data of the ASTM card file.

Electron microscopy (SEM) of the studied samples. SEM images were obtained with the help of an electronic microscope Selmi PEMU in the light field mode. The studied samples were prepared by the method of suspensions. TESLA BN, JEOL NeoScope JCM-5000, and JEOL JSM6490 LV scanning microscopes with INSA ENERGY-450 energy dispersive device (Oxford, Great Britain) were also used.

The rheological characteristics of the studied systems and materials were determined using a rotary viscometer with coaxial cylinders Rheotest-2 connected to a PC. The structural and mechanical properties of dispersions were studied on a Weiler-Rebinder device with automatic recording of strain–time curves. When performing rheological studies, the size distribution of particles was also determined.

Particle size distribution was determined using laser correlation spectrometry (MALVERN 3000 device).

3 Results and Discussion

Analogies in carbonate deposition in periphyton and on marine iron-aluminosilicate suspension, established by the analysis of literature data, simulation, and experimental studies, indicate that communities of various microorganisms are developing on solid particles of suspensions [1, 3, 13, 14]. This allows us to assume that along with the mechanism of microbiogenic (biocolloidal) precipitation of carbonates, the recently established features of the mechanism of nanobiocolloidal rearrangement of carbonates on the surface of dispersed iron-aluminosilicates [7–11] are applied to marine suspensions, depending on the mixing speed of the suspension. They are characterized by an increase in the number of carbonate nanoformations with an increase in the rate of turbulent mixing of the coastal suspension, for example, during storms and hurricanes, and in the conditions of laminar mixing of the suspension in metabolic processes—periphyton microorganisms deposit carbonate microparticles. For example, among microorganisms that deposit carbonates on the IASSs are diatoms, the number of species exceeds 12,000. Using the carbon dioxide of hydrocarbonates during intensive photosynthesis, they shift the carbonate balance in seawater in the direction of carbonate deposition [3, 4]:

$$Ca(HCO_3)_2 \rightarrow CO_2 + CaCO_3 \downarrow + H_2O \tag{1}$$

Precipitation of carbonates also occurs in the presence of heterotrophic bacteria:

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4 \tag{2}$$

$$Ca(HCO_3)_2 + 2NH_3 \rightarrow CaCO_3 \downarrow + (NH_4)_2CO_3 \tag{3}$$

$$2NH_3 + H_2O \rightarrow NH_4OH \tag{4}$$

$$Ca(HCO_3)_2 + NH_4OH \rightarrow CaCO_3 \downarrow + (NH_4)_2CO_3 + H_2O \tag{5}$$

or during denitrification:

$$Ca(NO_3)_2 + 3H_2 + C \rightarrow CaCO_3 \downarrow + H_2O + N_2 \tag{6}$$

or in the following way:

$$CaSO_4 + 2C \rightarrow CO_2 + CaS \text{ or } CaSO_4 + 4H_2 \rightarrow CaS + H_2O \tag{7}$$

and further:

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 \downarrow + H_2S \tag{8}$$

$$\begin{aligned} &2CH_3CH - OH - COONa + MgSO_4 \\ &\rightarrow MgCO_3 \downarrow + 2CH_3COONa + CO_2 + H_2S + H_2O \end{aligned} \tag{9}$$

$$\begin{aligned} &2CH_3CHOHCOONa + CaSO_4 \\ &\rightarrow CaCO_3 \downarrow + 2CH_3COONa + CO_2 + H_2O + H_2 \end{aligned} \tag{10}$$

$$\begin{aligned} &2KOOCCH_2CHOHCOOK + MgSO_4 \\ &\rightarrow MgCO_3 \downarrow + 4K_2CO_3 + 3CO_2 + H_2O + 3H_2S \end{aligned} \tag{11}$$

or when bacteria oxidize calci salts of organic acids:

$$Ca(HCOO)_2 + H_2O \xrightarrow[\text{}]{\substack{\text{bacteria} \\ \text{(periphyton)}}} CaCO_3 + CO_2 + H_2 \tag{12}$$

$$2Ca(HCOO)_2 \xrightarrow{\text{bacteria}} 2CaCO_3 + CO_2 + CH_4 \tag{13}$$

$$Ca(CH_3COO)_2 + H_2O \rightarrow CaCO_3 + CO_2 + 2CH_4 \tag{14}$$

$$Ca(CH_3CH_2CH_2COO)_2 + 3H_2O \rightarrow CaCO_3 + 2CO_2 + 5CH_4 \tag{15}$$

$$Ca(CH_3CH_2COO)_2 + 5H_2O \rightarrow CaCO_3 + 3CO_2 + 8CH_4 \tag{16}$$

$$Ca(CH_3CH_2COO)_2 + 7H_2O \rightarrow CaCO_3 + 4CO_2 + 11CH_4 \tag{17}$$

$$Ca(CH_3(CH_2)_8COO)_2 + 9H_2O \rightarrow CaCO_3 + 5CO_2 + 14CH_4 \tag{18}$$

$$Ca(CH_3COO)_2 + O_2 \rightarrow CaCO_3 + 3CO_2 + 3H_2O \tag{19}$$

The noted reactions (2)–(19) are presented in normal physiological processes of the metabolism of microorganisms: sulfate reduction, denitrification, use of salts of organic acids, or mineralization of the dead microorganism material. All conditions for reactions (2)–(19) exist in the slime of microorganisms on the surface of iron-aluminosilicate suspensions and in periphyton. In the marine environment, accordingly, there are conditions for additional allocation of microelements and nanochemical and mineralogical restructuring of iron-aluminosilicates in suspensions. In other words, in a such marine environment, there are all necessary substances and possibilities for bioflotation and enrichment of the forming ore deposits of jaspilites, iron-manganese nodules, iron ores of biocolloidal origin, peloids, sands, etc. [1, 3–14]. This is also confirmed by the fact that in 13 reactions out of 19 [reactions (6), (8)–(19)], carbonates are formed by microorganisms regardless of the content of hydrocarbonates, carbonate ions, and carbon dioxide in the surrounding water. Carbonate particles are also formed by reactions (1)–(5), (7). Their passage requires hydrocarbons, which are always present in seawater, or carbon dioxide, which is continuously produced by bacteria.

It is known that the amount of suspended ooze (suspension) in the World Ocean is approximately 13.7×10^9 tons [18–20]. The annual flow of rivers from land into the World Ocean according to the data of measurements in the Azov, Black, Mediterranean, and Red Seas, as well as in Antarctica, Indian, Pacific, and Atlantic Oceans gives an average value of carbonate content of about 7% in the suspension falling on the seabed. These carbonates are of microbiogenic (biocolloidal) origin [4].

As for iron-aluminosilicate sediments, their behavior within the framework of the developing scientific direction in recent years not only contributed to clarifying the mechanisms of ore-genesis in solid, sedimentary, and porous rocks and dispersed materials. It led to the development of new approaches to the relevant effective technologies of dispersion transformations, processing, and their use in large-scale production processes and also helped to develop ideas about the structural mechanisms of critical phenomena (creep, earthquakes, etc.) [1, 3].

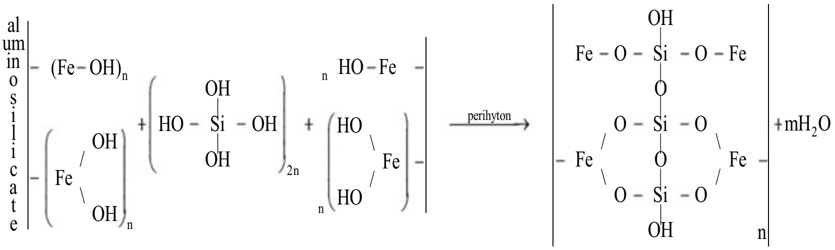
The research of biocolloidal, microbiological, and biochemical processes based on the use of the phenomenon of selective heterocoagulation of mineral substances with microorganisms, highlighted in works [3, 8], as well as in the processes of recrystallization of oceanic nodules [1, 3, 6, 21] had the maximum development in this direction. Further development of these areas made it possible to assess the interrelationship of microbiological, physicomechanical, and nanochemical features of self-dispersion processes for both dense and crushed or porous rocks [3]. But these results were obtained without assessing the impact of periphyton microorganisms on them.

Figure 4 shows the data confirming the total influence of microorganisms from various ecotrophic groups, including periphyton, on the properties of pelitic-turbiditic sediments of the Black Sea. These data indicate, on the one hand, the ability of marine sediments to restore their biomedical activity while an increasing number of colony-forming units (CFU). On the other hand, with an increase in the sediment exposure time, the values of the effective viscosity and the corresponding shear stress increase too. This increase correlates with the increase in the amount of divalent iron (II) in the sediment, formed as a result of the vital activity of iron-reducing bacteria, and also correlates with the increase in the number of nanoparticles and the decrease in the number of microparticles (Table 2). Such data indicate that the vital activity of microorganisms in the composition of biocolloidal periphyton aggregates leads to the activation of the synergetic effect on the dispersion of the mineral part of sediments [2, 3, 5]. This allows the well-known scheme [3] to be presented for the biocolloidal process in the presence of periphyton in the following form:

$$\begin{aligned} &Fe_2O_{3(\text{micro})} \xrightarrow[\text{periphyton}]{\text{bacteria and}} Fe(OH)_2 + Fe(OH)_3 \xrightarrow{CO_2} GR \cdot CO^{2-}_{3(\text{nano})} \\ &\rightarrow FeO_{(\text{nano})} + Fe_2O_{3(\text{nano})} + Fe_3O_4{}_{(\text{nano})} \end{aligned} \tag{20}$$

GR Green Rust.

Reactions of the transformation of iron-aluminosilicates are transformed in the following way:



(21)

n phase contact nanostructures.

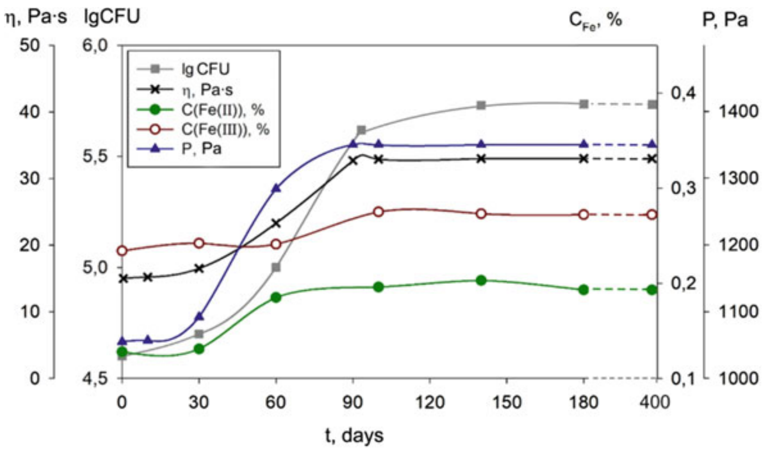


Fig. 4 Dependences of viscosity (η), shear stress (P), concentration (C, %) of Fe^{2+} (C(FeII)) and Fe^{3+}(C(FeIII)), and the number of colony-forming units (lgCFU) in the Black Sea nanostructured pelitic-turbiditic sediments taken from a depth of 2000 m, from the time of their exposure at a humidity of 46% in the presence of a natural complex of bacteria and microorganisms, including periphyton

Table 2 Physicochemical indicators of marine pelagic precipitations for water 46%

Index	Exposure, days				
	0	10	30	60	100
pH of liquid phase	7.0	7.1	7.3	7.4	7.4
Shear stress, Pa	1060	1070	1080	1290	1340
Viscosity, Pa·s	15	16	23	33	33
Concentration of particles < 250 μm, %	0.8	0.8	0.7	0.6	0.5
Concentration of nanoparticles, %	0.1	0.1	0.3	0.4	0.4
lgCFU	4.6	4.6	4.7	5.1	5.7

Such nanostructures, formed according to schemes (20) and (21), will most strongly bind aggregates of IASSMs, aluminosilicate, and silicate minerals in aqueous dispersions in the presence of complexes of various microorganisms, which is confirmed by the increasing values of viscosity and shear stress (Fig. 4; Table 2).

Therefore, along with physicochemical and nanochemical processes in dispersed iron-aluminosilicate sediments in the structure of pelites and peloids under the action of surface-active substances—metabolites of microorganisms and periphytons, biocolloidal interactions are activated. It affects the formation of nanodisperse-structured organic-clay-carbonate products that enrich bottom pelagic sediments and peloids with organic substances, clays, iron oxides, and carbonates, changing the chemical and mineralogical composition of the sediments.

4 Analysis of Nanostructural Phenomena in IASSs and NIASSs Associated with Rheological Processes in the Presence of Periphyton

It is known that clay minerals, especially montmorillonite, which is part of bentonite and polymineral clays, have the greatest influence on the rheological properties of nanostructured IASSs and NIASSs. They partially self-disperse in aqueous suspensions up to nanoparticles. The behavior of the latter does not correlate with the water content of the dispersions but has a significant dependence on the nanostructuring processes associated with the nanochemical properties and chemical structure of montmorillonite nanoparticles, as well as the properties of the biological products of bacteria and periphyton organisms. Thus, suspensions of calcium bentonite at a water content of 50% are characterized by the so-called hyperanomalous change in viscosity, but at a water content of 75%, the effect of hyperanomaly viscosity is no longer present. At the same time, after the nanochemical treatment of clay in the presence of periphyton organisms with the formation of sodium bentonite, the effect of hyperanomaly viscosity takes place again even when the humidity of the suspension reaches 90%. Its appearance is explained by an increase in the number of small nanoparticles of Na-montmorillonite and calcite in the composition of bentonite (Bt) due to the microbiogenic nanochemical process [3, 4, 14]:

$$\mathrm{Bt}^{2-} + \mathrm{Ca}^{2+} + \mathrm{Na_2CO_3} \xrightarrow[\text{peiphyton}]{\text{bacteria}} 2(\mathrm{Bt}^{-} \cdot \mathrm{Na}^{+})_n + (\mathrm{CaCO_3})_n \tag{22}$$

$$\begin{aligned} &\mathrm{Na_2CO_3} + 2\mathrm{H_2}O \rightleftarrows 2\mathrm{NaOH} + \mathrm{H_2CO_3};\\ &\mathrm{Bt}^{2-} \cdot \mathrm{Ca}^{2+} + 2\mathrm{NaOH} \rightleftarrows 2(\mathrm{Bt}^{-} \cdot \mathrm{Na}^{+}) + \mathrm{Ca(OH)_2};\\ &\mathrm{Ca(OH)_2} + \mathrm{H_2CO_3} \rightarrow (\mathrm{CaCO_3})_n + \mathrm{H_2O} \end{aligned} \tag{23}$$

n nanophase contact groups.

According to these schemes, calcite nanoparticles are deposited on the surface of sodium bentonite nanoparticles, which are covered with a slime layer under the action of bacteria and periphyton organisms—protozoa, fungi, microalgae, mollusks, etc. [2, 4, 14]. Slimes, which are composed of extracellular polysaccharides and polyuronides [14], isolate the formed nanophase contact groups from an external aggressive environment, such as CO_2, and give such groups stability. The main role of periphyton in such processes is traced.

But calcite is almost always present in natural bentonites and polymineral clays. Therefore, another process of formation of $CaCO_3$ nanoparticles is possible in parallel with Na-montmorillonite nanoparticles with the participation of CO_2 from the air [3, 4, 6]:

$$\xleftarrow{\text{increase of laminar flow (Ostwald ripening) – formation of microparticles}}$$

$$\mathrm{CaCO_{3(micro)} + CO_2 + H_2O \rightleftarrows Ca(HCO_3)_2 \rightleftarrows CaCO_{3(nano)} + H_2O} \tag{24}$$

$$\xrightarrow[\text{Increase of turbulent flow (nanochemical recondensation) – formation of nanoparticles}]{}$$

The direct reaction (24) of nanochemical recondensation occurs at high-rate turbulent mixing of clay suspensions (high shear rates in rheoviscosimeter), and the reverse at low mixing rates (laminar flow) [3]. However, the reverse reaction practically does not occur in the presence of slime produced microbiogenically thanks to periphyton.

Thus, the processes of nanostructuring of clay iron-aluminosilicate suspensions in the presence of periphyton, nanochemical processes of their transformation, including biocolloidal microbiogenic processes, as well as chemical and mineralogical restructuring of nanoparticles, have a significant impact on the rheological behavior of suspensions associated with the precipitation of solid components from them in bottom polymineral sediments and their separation by natural bioflotation into different compositions, for example, presented in Fig. 1.

Thus, the features of the formation of iron-aluminosilicates present in river and sea suspensions in the presence of bacteria, microorganisms, and periphyton [2–4, 21, 22], which, in addition to bacteria, includes protozoa, fungi, worms, crustaceans, mollusks, etc., which live on solid phases within a certain biotope. It was shown that redox processes in suspensions are accompanied by transitions of Fe(II) into $Fe(OH)_3$, FeOOH (goethite) and $FeCO_3$ (siderite), and Mn(II) into MnO_2 or Mn_3O_4. When such suspensions enter marine estuaries, from the point of view of modern nanoscience, they become the site of many active biological, nanochemical, and biocolloidal interactions at the interface between aqueous solution and solid carbonates, and iron-aluminosilicates. Such interactions are also accompanied by layer-by-layer separation of suspensions into three layers, which arise and form under the influence of periphyton and bacteria for up to 15 thousand years with the formation of ore deposits—iron ore, iron-manganese nodules, etc. of biocolloidal origin and have an amorphous structure (Figs. 3 and 4). At the same time, the lower enriched layer is composed of iron hydroxides doped with manganese and trace elements with admixtures of carbonates, sands, silts, soils, etc. (Fig. 1); the upper layer, accordingly, is enriched with iron hydroxides and depleted with admixtures of carbonates, manganese compounds, trace elements, sand, etc., which is partially confirmed also by known results [2–4, 15–22].

Based on the above considerations, the graphical data for load–unload curves of elastic–plastic materials, to which the authors of the work [3] include bentonite and other formations (Fig. 1), polymineral clay suspensions with bacteria and microorganisms in the conditions of hyperanomaly or ultraanomaly of viscosity effect presence [3] were obtained. Thus, the rheological indices can be shown in the coordinates of viscosity (η)–shear stress (P) in the form given in Fig. 5.

As can be seen from the given curves, the hyperanomaly of viscosity is more often characterized by curves 1 and 3, and the previously unknown effect of ultraanomaly of viscosity is more often by curve 2, and sometimes by curve 1. Both effects have been experimentally confirmed by numerous rheograms for different

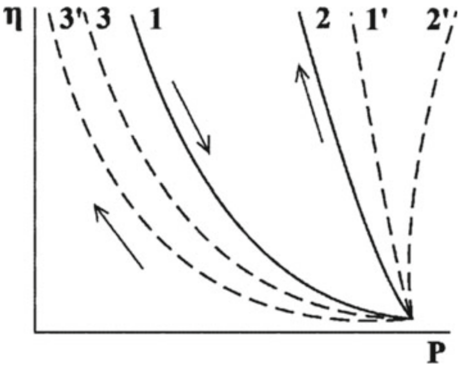


Fig. 5 Load–unload curves (1, 1′ and 2, 2′ respectively) in the conditions of plastic flow of elastic–plastic biocolloidal iron oxide silicate material; 3, 3′—load–unload curves under the conditions of the start of the hyperanomaly or ultraanomaly viscosity effect [3]

types of clays, pelitic sediments, and peloids given in [3], but the influence of periphyton on them. A preliminary conclusion should be drawn from these data that the effect of hyperanomaly viscosity more often is characteristic for less concentrated suspensions and with a lower content of iron compounds in them, and the effect of ultraanomaly viscosity is characteristic for more concentrated suspensions or at lower shear rates if the other previously mentioned factors remain stable [3]. At the same time, the water content of dispersions (W) changes as follows: $W_{1\text{-}3} < W_{1\text{-}2} < W_{1'\text{-}2'}$. These data and numerous data obtained for many sediments, soils, and sands indicate a significant role of rheological effects in the occurrence of critical processes in marine suspensions and oozes activated by bacteria that are the part of periphyton organisms (Fig. 4). But these results need an even deeper further comparative analysis and systematization.

The established regularities of nanostructural biocolloidal phenomena in dense and disperse materials of the Earth's crust also made it possible to develop and implement a number of methods of directional control of the structure of IASSs and NIASSs, based on the achievements of physicochemical geomechanics, biocolloidal chemistry and on the regularities of nanochemical contact interphase interactions [1, 3–5]. The conducted theoretical generalizations and experimental data made it possible to consider the kinetics and mechanisms of the transformation of dispersed IASSs as a result of their self-dispersion with the participation of nanochemical and microbiological processes in the presence of periphyton with the formation of new disperse structures with thermodynamically stable mineral phases; to develop the ideas of the mechanisms of elastic–plastic creep under similar conditions of IASSs suspensions; to outline further ways of development of the specified fundamental problems with the application of the obtained laws in geological sciences, colloid and biocolloidal chemistry with the aim of creating modern technological processes for application in eco-biotechnologies of environmental protection, ore mining, metallurgy, oil and gas production, ceramic, construction, and other industries, in agriculture, and in medicine for the development of new methods of rehabilitation and spa treatment of patients, prophylaxis of hemophilia, creation of wound-healing, burn-treatment, and medical-cosmetic products, etc. (Fig. 6).

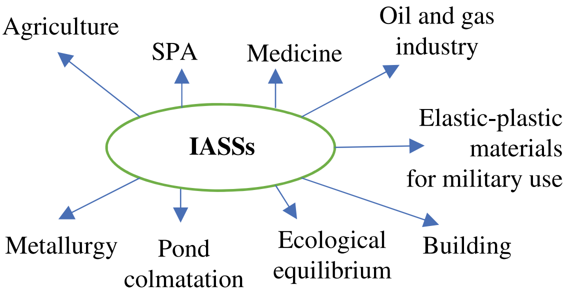


Fig. 6 Fields of application of iron-aluminosilicate materials activated by bacteria and periphyton organisms

The data shown in Fig. 6 are explained on a standalone example for a storage pond of salty mine waters, which are formed during the extraction of deep iron-aluminosilicate ore deposits in the Kryvyi Rih Basin (Fig. 7).

The data in Fig. 7a show that the bottom sediment was washed out through the karst pores of the rocks underlying the bottom of the pond during the 25 years of operation of the pond. After filling the bottom of the pond in 2012 with a suspension of coastal polymineral clay with alkaline admixtures, the subsidence of the bottom of the pond decreased six times, and the calculated stability of the dam increased up to six years (Fig. 7b). After adding biocolloidal nanostructural clay colmatants with bacteria and periphyton to the sediment, the durability of the dam increased up to 10–12 years or more (Fig. 7c).

5 Conclusions

Thus, the obtained results indicate that in the processes of precipitation in fresh, salty, and marine suspensions based on iron-aluminosilicates, along with processes with carbonates, the important ones are those that take place with the participation of microbiogenic reduction of Fe^{3+}—the fourth most common element of the Earth's crust. Under reductive conditions, the process of microbial biocolloidal iron reduction is accompanied by the formation of new minerals [3, 6, 17, 21] such as siderite, pyrite, magnetite, and iron-manganese nodules. Those are formed in lakes and estuaries due to the vital activity of organisms such as Metallogenium personatum, Caulococeus manganifer, etc. In anaerobic conditions of iron reduction, in the microbial combination, the activity of organisms with a respiratory type of metabolism, which performs the decomposition of cellulose, hydrocarbons, ammonification, nitrification, and oxidation of iron is inhibited. On the contrary, anaerobic fermenters, iron reducers, sulfate reducers, and actinomycetes increase their activity along with the activity of periphyton.

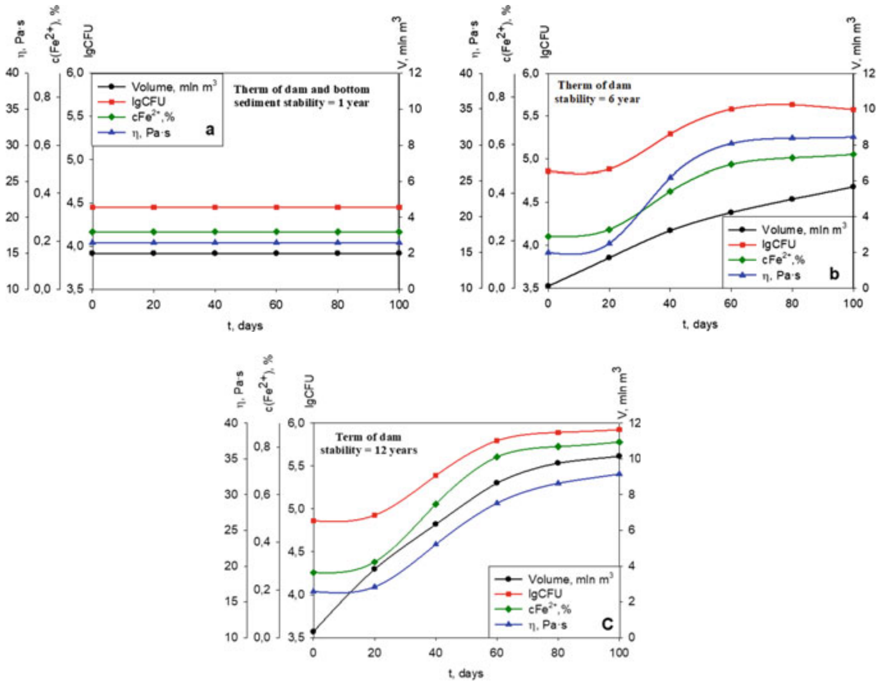


Fig. 7 Dependence of the ooze properties of the storage pond of mine iron ore waters from the conditions in it: **a** before the implementation of the technology (term of stability of the bottom and dam was 1–2 years); **b** after treatment with alkaline nanostructured inorganic clay colmatants (the term of stability of the bottom and dam was increased to six years); **c** after the implementation of biocolloidal nanostructural clay colmatants with bacteria and periphytons (the term of stability of the bottom and dam is increased to 10–12 years)

Generalized ideas have been developed for the creation of new highly effective materials and eco-biotechnologies concerning the conditions of synergetic action of complexes of periphyton organisms according to the laws of physicochemical geomechanics. Additionally, the understanding of processes with polymineral carbonate-iron-aluminosilicate particles leading to the formation of new mineral structures and their enrichment, has been expanded. Recommendations are provided for optimizing the methods of obtaining new materials and controlling eco-bio-geo-technological processes in the presence of complex natural communities of microorganisms and periphyton.

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